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organic germanium, tin
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Nahum

and

Zeev
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Foreword


The book covers two types of chapters. The majority are new chapters on topics which were not covered in the previous volume. These include chapters on reaction mechanisms involving the title organic derivatives, on reactive intermediates derived from them, like cations and carbene analogs, on NMR spectra, and on gas phase and mass spectrometry of organic germanium, tin and lead derivatives. There are chapters on their alkaline and alkaline earth metal compounds, on highly reactive multiply-bonded derivatives involving the title elements and on their hypervalent compounds, their synthetic applications, biological activities, polymers, cage compounds, unsaturated three membered ring derivatives and a new germanium superacid.

The second group of chapters are updates or extensions of material included in previous chapters. These include chapters on theory, on comparison of the derivatives of the three metals, on new advances in structural and photochemistry and in substituent effects and acidity, basicity and complex formation.

The volume opens with a new historical chapter on the genesis and evolution of organic compounds of the three elements, written by one of the pioneers in the field. We hope that such a historical background adds perspectives to those working both in the field and outside it.

The contributing authors to the book come from nine countries including some from Russia and Latvia who contributed several chapters. Part of the work in the field in these countries was covered by articles in Russian which were frequently not easily available to non-Russian readers. We now have many references including *Chemical Abstract* citations which will facilitate access to these articles.

The literature coverage in the book is mostly up to mid- or late-2001.

One originally planned chapter on radical reactions was not delivered, but part of the material can be found in another, more mechanistically oriented chapter.

This and the preceding volume should be regarded as part of a larger collection of books which appeared in recent years in ‘The Chemistry of Functional Groups’ series and deal with the chemistry of organic derivatives of the group 14 elements (excluding carbon). These also include four parts on the chemistry of organic silicon compounds (Z. Rappoport and Y. Apeloig, Eds., Vol. 2, parts 1–3, 1998 and Vol. 3, 2001) which follow two earlier volumes (S. Patai and Z. Rappoport, Eds., 1989) and an update volume, *The Silicon-Heteroatom Bond* (1991). The 136 chapters in the ten volumes cover extensively the main aspects of the chemistry of this group in the periodic table. Some comparisons of the derivatives of these groups appear both in the present and in earlier volumes.

This book was planned to be coedited by Prof. Y. Apeloig from the Technion in Haifa, Israel, but he was elected to the presidency of his institute and was unable to proceed.
with the editing beyond its early stage. I want to thank him for the effort that he invested and for his generous advice. I also want to thank the authors for their contributions.

I will be grateful to readers who draw my attention to mistakes in the present volume, or mention omissions and new topics which deserve to be included in a future volume on the chemistry of germanium, tin and lead compounds.

Jerusalem  
April 2002  

ZVI RAPPORTE
The Chemistry of Functional Groups
Preface to the series

The series ‘The Chemistry of Functional Groups’ was originally planned to cover in each volume all aspects of the chemistry of one of the important functional groups in organic chemistry. The emphasis is laid on the preparation, properties and reactions of the functional group treated and on the effects which it exerts both in the immediate vicinity of the group in question and in the whole molecule.

A voluntary restriction on the treatment of the various functional groups in these volumes is that material included in easily and generally available secondary or tertiary sources, such as Chemical Reviews, Quarterly Reviews, Organic Reactions, various ‘Advances’ and ‘Progress’ series and in textbooks (i.e. in books which are usually found in the chemical libraries of most universities and research institutes), should not, as a rule, be repeated in detail, unless it is necessary for the balanced treatment of the topic. Therefore each of the authors is asked not to give an encyclopaedic coverage of his subject, but to concentrate on the most important recent developments and mainly on material that has not been adequately covered by reviews or other secondary sources by the time of writing of the chapter, and to address himself to a reader who is assumed to be at a fairly advanced postgraduate level.

It is realized that no plan can be devised for a volume that would give a complete coverage of the field with no overlap between chapters, while at the same time preserving the readability of the text. The Editors set themselves the goal of attaining reasonable coverage with moderate overlap, with a minimum of cross-references between the chapters. In this manner, sufficient freedom is given to the authors to produce readable quasi-monographic chapters.

The general plan of each volume includes the following main sections:

(a) An introductory chapter deals with the general and theoretical aspects of the group.
(b) Chapters discuss the characterization and characteristics of the functional groups, i.e. qualitative and quantitative methods of determination including chemical and physical methods, MS, UV, IR, NMR, ESR and PES — as well as activating and directive effects exerted by the group, and its basicity, acidity and complex-forming ability.
(c) One or more chapters deal with the formation of the functional group in question, either from other groups already present in the molecule or by introducing the new group directly or indirectly. This is usually followed by a description of the synthetic uses of the group, including its reactions, transformations and rearrangements.
(d) Additional chapters deal with special topics such as electrochemistry, photochemistry, radiation chemistry, thermochemistry, syntheses and uses of isotopically labelled compounds, as well as with biochemistry, pharmacology and toxicology. Whenever applicable, unique chapters relevant only to single functional groups are also included (e.g. ‘Polyethers’, ‘Tetraaminoethylenes’ or ‘Siloxanes’).
This plan entails that the breadth, depth and thought-provoking nature of each chapter will differ with the views and inclinations of the authors and the presentation will necessarily be somewhat uneven. Moreover, a serious problem is caused by authors who deliver their manuscript late or not at all. In order to overcome this problem at least to some extent, some volumes may be published without giving consideration to the originally planned logical order of the chapters.

Since the beginning of the Series in 1964, two main developments have occurred. The first of these is the publication of supplementary volumes which contain material relating to several kindred functional groups (Supplements A, B, C, D, E, F and S). The second ramification is the publication of a series of ‘Updates’, which contain in each volume selected and related chapters, reprinted in the original form in which they were published, together with an extensive updating of the subjects, if possible, by the authors of the original chapters. A complete list of all above mentioned volumes published to date will be found on the page opposite the inner title page of this book. Unfortunately, the publication of the ‘Updates’ has been discontinued for economic reasons.

Advice or criticism regarding the plan and execution of this series will be welcomed by the Editors.

The publication of this series would never have been started, let alone continued, without the support of many persons in Israel and overseas, including colleagues, friends and family. The efficient and patient co-operation of staff-members of the publisher also rendered us invaluable aid. Our sincere thanks are due to all of them.

The Hebrew University
Jerusalem, Israel

SAUL PATAI

ZVI RAPPOPORT

Sadly, Saul Patai who founded ‘The Chemistry of Functional Groups’ series died in 1998, just after we started to work on the 100th volume of the series. As a long-term collaborator and co-editor of many volumes of the series, I undertook the editorship and I plan to continue editing the series along the same lines that served for the preceding volumes. I hope that the continuing series will be a living memorial to its founder.

The Hebrew University
Jerusalem, Israel

June 2002
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List of abbreviations used

Ac    acetyl (MeCO)
acac  acetylacetone
Ad    adamantyl
AIBN  azoisobutyronitrile
Alk   alkyl
All   allyl
An    anisyl
Ar    aryl

Bn    benzyl
Bz    benzoyl (C₆H₅CO)
Bu    butyl (also t-Bu or Bu')

CD    circular dichroism
Cl    chemical ionization
CIDNP chemically induced dynamic nuclear polarization
CNDO  complete neglect of differential overlap
Cp    η⁵-cyclopentadienyl
Cp*   η⁵-pentamethylycyclopentadienyl

DABCO 1,4-diazabicyclo[2.2.2]octane
DBN  1,5-diazabicyclo[4.3.0]non-5-ene
DBU  1,8-diazabicyclo[5.4.0]undec-7-ene
DIBAH diisobutylaluminium hydride
DME  1,2-dimethoxyethane
DMF  N,N-dimethylformamide
DMSO dimethyl sulfoxide

ee    enantiomeric excess
EI    electron impact
ESCA  electron spectroscopy for chemical analysis
ESR  electron spin resonance
Et    ethyl
eV    electron volt
List of abbreviations used

Fc  ferrocenyl
FD  field desorption
FI  field ionization
FT  Fourier transform
Fu  furyl(OC₄H₃)

GLC  gas liquid chromatography

Hex  hexyl(C₆H₁₃)
c-Hex  cyclohexyl(c-C₆H₁₁)
HMPA  hexamethylphosphortriamide
HOMO  highest occupied molecular orbital
HPLC  high performance liquid chromatography

i-  iso
Ip  ionization potential
IR  infrared
ICR  ion cyclotron resonance

LAH  lithium aluminium hydride
LCAO  linear combination of atomic orbitals
LDA  lithium diisopropylamide
LUMO  lowest unoccupied molecular orbital

M  metal
M  parent molecule
MCPBA  m-chloroperbenzoic acid
Me  methyl
MNDO  modified neglect of diatomic overlap
MS  mass spectrum

n  normal
Naph  naphthyl
NBS  N-bromosuccinimide
NCS  N-chlorosuccinimide
NMR  nuclear magnetic resonance

Pc  phthalocyanine
Pen  pentyly(C₅H₁₁)
Pip  piperidyl(C₅H₁₀N)
Ph  phenyl
ppm  parts per million
Pr  propyl (also i-Pr or Prᵢ)
PTC  phase transfer catalysis or phase transfer conditions
Py, Pyr  pyridyl (C₅H₄N)
List of abbreviations used

R  any radical
RT room temperature

s-  secondary
SET single electron transfer
SOMO singly occupied molecular orbital

T  tertiary
TCNE tetracyanoethylene
TFA trifluoroacetic acid
THF tetrahydrofuran
Thi thieryl(SC₄H₃)
TLC thin layer chromatography
TMEDA tetramethylethylene diamine
TMS trimethylsilyl or tetramethylsilane
Tol tolyl(MeC₆H₄)
Tos or Ts tosyl(p-toluenesulphonyl)
Trityl triphenylmethyl(Ph₃C)

Xyl xylyl(Me₂C₆H₃)

# CHAPTER 1

## Genesis and evolution in the chemistry of organogermanium, organotin and organolead compounds

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*The task of science is to induce the future from the past*

Heinrich Herz

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Germanium, tin and lead are members of one family, called the silicon subgroup. Sometimes these elements are called mesoids as well, due both to their central position in the short version of Mendeleev’s Periodic Table and to their valence shells, which occupy an intermediate place among the I–VII Group elements. They can also be called the heavy elements of Group 14 of the Periodic Table.

The history of the silicon prototype of this family and its organic derivatives is elucidated in detail in the literature. In contrast, we could not find any special accounts dealing with the history of organic germanium, tin and lead compounds. The only exception is a very brief sketch on the early history of the chemistry of organotin compounds. Some scattered information on the organic compounds of germanium, tin and lead can be found in some monographs and surveys. In this chapter we try to fill the gaps in this field.

Humanity first encountered the heavy elements of Group 14 at different times; with germanium, it happened quite unusually in the middle of the 19th century. As with the discovery of the planet Neptune, which was first predicted by astronomers and almost immediately discovered, Mendeleev, who predicted the existence of three hitherto unknown elements, reported at the Russian Chemical Society session on December 10, 1870 on the discovery of one of these elements as follows: ‘...to my mind, the most interesting among undoubtedly missing metals will be one that belongs to Group IV and the third row of the Periodic Table, an analog of carbon. It will be a metal, following silicon, and we call it ‘eca-silicon’. Moreover, Mendeleev even predicted the physical and chemical properties of the virtual element. Having no conclusive proof of the existence of eca-silicon, Mendeleev himself began experimental investigations aimed at finding it in different minerals. It is noteworthy that as early as 1864 Newlands and Meyer suggested the possible existence of an element like eca-silicon and predicted its atomic weight. However, Mendeleev was the first to predict properties of the element in detail.

Fifteen years later the German chemist Winkler, working at the Freiberg Academy of Mines, was able to isolate during the investigation of a recently discovered mineral argirodit (Ag₆GeS₅) a new element in its free state. Initially, Winkler wanted to
name the new element neptunium, after the newly discovered planet Neptune. However, this name seemed to be given for another falsely discovered element, so he called the new element germanium in honor of his motherland\textsuperscript{18--21}. At the time several scientists sharply objected to this name. For example, one of them indicated that the name sounded like that of the flower Geranium while another proposed for fun to call the new element Angularium, i.e. angular (causing debates). Nevertheless, in a letter to Winkler, Mendeleev encouraged the use of the name germanium. It took same time until the identity of \textit{eca}-silicon and germanium was established\textsuperscript{18--22}. Polemics, as to which element germanium is analogous flared up ardently. At first, Winkler thought that the newly discovered element filled the gap between antimony and bismuth. Having learned about Winkler’s discovery, almost simultaneously in 1886 Richter (on February 25, 1886) and Meyer (on February 27, 1886) wrote him that the discovered element appeared to be \textit{eca}-silicon. Mendeleev first suggested that germanium is \textit{eca}-cadmium, the analog of cadmium. He was surprised by the origin of the new element, since he thought that \textit{eca}-silicon would be found in titanium–zirconium ores. However, very soon, he rejected his own suggestion and on March 2, 1886, he wired Winkler about the identity of germanium and \textit{eca}-silicon. Apparently, this information raised doubts in Winkler’s mind about the position of germanium in the Periodic Table. In his reply to Mendeleev’s congratulation he wrote: ‘...at first I was of the opinion that the element had to fill up the gap between antimony and bismuth and coincide with \textit{eca}-stibium in accordance with your wonderful, perfectly developed Periodic Table. Nevertheless, everything showed us we dealt with a perfectly well developed Periodic Table. But everything implied that we are dealing with \textit{eca}-silicon\textsuperscript{23}. The letter was read at the Russian Physical and Chemical Society section on March 7. Winkler reported that the properties of the element and its common derivatives corresponded closely to those predicted for \textit{eca}-silicon. A second letter by Winkler was read in a Chemical Section meeting of the Russian Physical and Chemical Society on May 1, 1886. Winkler reported that the properties of germanium and its simpler derivatives were surprisingly very similar to those predicted for \textit{eca}-silicon\textsuperscript{22,24}. This is reported in Winkler’s paper in the Journal of the Russian Physical and Chemical Society entitled ‘New metalloid Germanium’, translated into Russian at the author’s request\textsuperscript{25,26}.

An inspection of Table 1 impresses one by the precise way in which Mendeleev predicted the properties of germanium and its elementary derivatives.

In 1966, Rochow\textsuperscript{27} somewhat criticized the accuracy of Mendeleev’s predictions of the properties of \textit{eca}-silicon (germanium). He stated: ‘Mendeleev predicted that \textit{eca}-silicon would decompose steam with difficulty, whereas germanium does not decompose it at

<table>
<thead>
<tr>
<th>Properties</th>
<th>( M = \text{Es} )</th>
<th>( M = \text{Ge} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic weight</td>
<td>72.0</td>
<td>72.3</td>
</tr>
<tr>
<td>Specific weight</td>
<td>5.5</td>
<td>5.469</td>
</tr>
<tr>
<td>Atomic volume</td>
<td>13.0</td>
<td>13.2</td>
</tr>
<tr>
<td>Specific weight of ( \text{MO}_2 )</td>
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<td>4.703</td>
</tr>
<tr>
<td>B.p. of ( \text{MCl}_4 )</td>
<td>\textit{ca} 90°</td>
<td>88°</td>
</tr>
<tr>
<td>Specific weight of ( \text{MCl}_4 )</td>
<td>1.9</td>
<td>1.887</td>
</tr>
<tr>
<td>B.p. of ( \text{M(C}_2\text{H}_5)_4 )</td>
<td>\textit{ca} 160°</td>
<td>160°</td>
</tr>
<tr>
<td>Specific weight of ( \text{M(C}_2\text{H}_5)_4 )</td>
<td>0.96</td>
<td>1.0</td>
</tr>
</tbody>
</table>
all. This is to say that germanium is less metallic than was predicted. Mendeleev also said that acids would have a slight action on the element, but they have none; again it is a more negative element than was predicted. There are many more chemical facts which point in the same direction: germanium is more electronegative than was expected by interpolation, and it actually behaves a great deal like arsenic’. Rochow was right to some extent. It is known that in accordance with Mendeleev’s predictions germanium has more metallic characteristics than silicon; in a thin layer or under high temperatures germanium reacts with steam, and it reacts very slowly with concentrated $\text{H}_2\text{SO}_4$, $\text{HNO}_3$, HF and Aqua Regia. In relation to the Allred and Rochow electronegativity scale the electronegativity of germanium is higher than that of silicon. However, according to other scales and to Chapter 2 of this book, the electronegativity of germanium is lower or approximately the same as that for silicon. As illustrated in Table 1 Mendeleev predicted not only the possibility of existence, but also the properties of the simple organogermanium derivative $\text{Et}_4\text{Ge}$.

It is noteworthy that Winkler synthesized $\text{Et}_4\text{Ge}$ in 1887. Its properties were consistent with those predicted by Mendeleev. Organogermanium chemistry was born at this time.

In contrast to germanium the exposure of mankind to tin and lead was much earlier and not so dramatic. Up to the seventeenth century, tin and lead were often confused, as is witnessed by their Latin names, i.e. Plumbum album, Plumbum candidum (Sn) and Plumbum nigrum (Pb). Tin was known in countries of the Near East at least from the middle of the third millennium BC. Lead became known to the Egyptians at the same time as iron and silver, and very probably earlier than tin.

Many of Mendeleev’s predecessors (Pettenkofer, Dumas, Cooke, Graham and others) assumed that tin and lead cannot belong to the same group as silicon and Mendeleev was the first to include them in the same group of his Periodic Table with silicon and $\text{eca}$-silicon. He made this courageous prediction based on the assumption that the unknown element $\text{eca}$-silicon should have properties intermediate between metals and nonmetals and that all these elements, including carbon, should belong to one group.

The forefather of the chemistry of organic compounds of tin and lead was the Swiss chemist Carl Löwig. In the middle of the nineteenth century in the Zurich University laboratory (which was not set up to handle toxic compounds), he developed for the first time several methods for the synthesis of common organic derivatives of these two elements and described their properties.

Following Edward Frankland, who paid attention to organotin compounds as early as 1853, Löwig became one of the founders of organometallic chemistry but, unfortunately, historians of chemistry have forgotten this. In spite of his work with rather toxic organotin and organolead compounds during a period of several years in the absence of safety precautions, Löwig lived a long life and died only in 1890 due to an accident.

It is necessary to outline the nomenclature that we use before starting to develop the genesis and evolution of the chemistry of organic derivatives of heavy elements of Group 14. From the moment of their appearance and to some extent up to now, the names of organic derivatives of tin and lead were based on the name of the corresponding metals. It should be mentioned that tin and lead are called quite differently in English, German, French and Russian — Tin, Zinn, Etein, Олово, and Lead, Blei, Plomb, Свинец, respectively. In addition, archaic names of these compounds (such as trimethyltin oxide and alkylgermanium acid) are incompatible with the modern nomenclature of organosilicon compounds, which are the prototypes of this mesoid group. In this chapter we use the nomenclature of organic compounds of germanium, tin and lead approved by IUPAC in analogy with the nomenclature of organosilicon compounds, based on their Latin names (Germanium,
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Stannum, Plumbum). It is not the central metallic atom that is named, but only its hydride $\text{MH}_4$ (germane, stannane, plumbane) and the substituents which replace hydrogen atoms in the hydride molecule. Compounds in which the metal atom valence is either higher or lower than 4 are named in analogy to the nomenclature of organosilicon compounds.

In this chapter, we have tried to gain some insight into the genesis and development of the chemistry of organic germanium, tin and lead compounds up to the end of the 20th century. We have also paid attention to the work of the early researchers which was sometimes forgotten in spite of their tedious work under more difficult conditions than in the present time, which laid the fundamental laws of the chemistry of organic germanium tin and lead compounds. The organic chemistry of the heavy elements (Ge, Sn, Pb) of the silicon sub-group has been previously reviewed extensively either in reviews devoted to organic derivatives of all these elements or in separate reviews on organogermanium, organotin, and organolead compounds. Valuable information can also be found in chapters devoted to organometallic compounds and in many surveys. Excellent bibliographical information on reviews devoted to organogermanium (369 references), organotin (709 references) and organolead compounds have been published in Russia. Unfortunately, all the literature cited did not review the historical aspect, so our attempt to extract from that vast body of information the chronological order of the genesis and development of the organic chemistry of germanium tin, and lead compounds was not an easy task. It forces us to re-study numerous original publications, in particular those published in the 19th century. Nevertheless, the references presented in chronological order still do not shed light on the evolution of this chemistry, but they have important bibliographic value.

II. ORGANOGERMANIUM COMPOUNDS

A. Re-flowering after Half a Century of Oblivion

Up to the middle of the 20th century organogermanium derivatives were the least understood among the analogous compounds of the silicon subgroup elements. As mentioned above, the first organogermanium compound, i.e. tetraethylgermane, was synthesized for the first time by Winkler in 1887 by the reaction of tetrachlorogermande with diethylzinc, i.e. a quarter century later than the first organic compounds of silicon, tin and lead were obtained.

The synthesis of $\text{Et}_4\text{Ge}$ proved unequivocally that the germanium discovered by Winkler belong to Group IV of the Periodic Table and that it was identical to Mendeleev’s eca-silicon. Consequently, Winkler was the forefather of both the new germanium element and also the chemistry of its organic derivatives, whereas Mendeleev was their Nostradamus.

During the period between 1887 and 1925 no new organogermanium compound was reported. The forty years of the dry season resulted mainly from the scarcity and high prices of germanium and its simplest inorganic derivatives. This reflected the low natural reserves of argirodit, the only mineral source of germanium known at that time. The picture changed dramatically when in 1922 new sources of germanium were discovered. In particular, 0.1–0.2% of Ge were found in a residue of American zinc ore after zinc removal. Dennis developed a method for the isolation of tetrachlorogermande from the ore. In 1924, 5.1% of Ge was found in germanite, a mineral from southwestern Africa. Rhenierite, a mineral from the Belgian Congo, containing 6–8% of Ge, became another source of germanium. In 1930–1940, processing wastes of coal ashes and sulfide ores became the main sources of germanium. These developments allowed American, English and German chemists to start in 1925 to carry
out fundamental investigations of organogermanium compounds, in spite of the fact that germanium was still very expensive.\textsuperscript{145–150}

Thus, the chemistry of organogermanium compounds actually started to develop in the second quarter of the twentieth century. Its founders were L. M. Dennis, C. A. Kraus, R. Schwartz and H. Bayer, whose results were published in 1925–1936. A period of low activity then followed in this field and was resumed only in the middle of the century by leaders such as E. Rochow, H. Gilman, H. H. Anderson, O. H. Johnson, R. West and D. Seyferth. Organogermanium chemistry started to flourish in the sixties when many new investigators joined the field. These included the French chemists M. Lesbre, J. Satge and P. Mazerolles, the German chemists M. Schmidt, H. Schmidbaur, M. Wieber, H. Schumann and J. Ruidisch, the English chemists F. Glockling and C. Eaborn, the Russian chemists V. F. Mironov, T. K. Gar, A. D. Petrov, V. A. Ponomarenko, O. M. Nefedov, S. P. Kolesnikov, G. A. Razuvaev, M. G. Voronkov and N. S. Vyazankin, the Dutch chemist F. Rijkens the American chemist J. S. Thayer and others.

Activity was stimulated by the intensive development of the chemistry of organometallic compounds, particularly of the silicon and tin derivatives. The chemistry of organogermanes was significantly developed as well due to the essential role of germanium itself and its organic derivatives in electronics,\textsuperscript{151,152} together with the discovery of their biological activities (including anticancer, hypotensive, immunomodulating and other kinds of physiological action).\textsuperscript{80,81,86,153} In addition, a progressive decrease in the prices of elemental germanium and its derivatives expanded their production and helped their growth. The rapid expansion of organogermanium chemistry is clearly evident due to the increase in the number of publications in this field.

From 1888 till 1924 there were no publications and prior to 1934 just 26 publications were devoted to organogermenes.\textsuperscript{154} Only 25 references on organogermanium compounds were listed in an excellent monograph by Krause and Grosse published in 1937;\textsuperscript{155} 60 publications appeared before 1947, 99 before 1950 and 237 during the period 1950–1960.\textsuperscript{48,78} By 1967 the number of publications was over 1800 and by 1971 it exceeded 3000.\textsuperscript{36,37} By 1970 about 100 publications had appeared annually and by this time 370 reviews dealing with organogermanium compounds had appeared.\textsuperscript{79}

In 1951 already 230 organogermanium compounds were known,\textsuperscript{157} in 1961 there were 260\textsuperscript{158} and in 1963 there were more than 700.\textsuperscript{159} As the chemistry of organogermanium compounds is three-quarters of a century younger than the organic chemistry of tin and lead, it is reasonable to consider in this chapter the most important references published before 1967, when two classical monographs were published.\textsuperscript{36,37,78} Due to space limitation we will avoid, where possible, citing reaction equations in the hope that they will be clear to the readers.

### B. Organometallic Approaches to a C−Ge and Ge−Ge Bond

Thirty-eight years after Winkler developed the organozinc method for the synthesis of tetraethylgermane, Dennis and Hance\textsuperscript{160} reproduced it, but this method for synthesis of aliphatic germanium derivative was not used later. However, in the years 1927–1935 arylzinc halides were used for the synthesis of tetraarylgemanes.\textsuperscript{23,161–165}

Application of Grignard reagents in organometallic synthesis led to the synthesis of common aliphatic, aromatic and alicyclic germanium derivatives during the years 1925–1932. Dennis and Hance\textsuperscript{160} were the first to produce in 1925 tetraalkylgermanes $R_4Ge$ ($R = Me, Et, Pr, Bu, Am$)\textsuperscript{145,160,166–169} from Grignard reagents. Kraus and Flood\textsuperscript{148} used organomagnesium reagents for the synthesis of tetraalkylgermanes. In 1925 Morgan and Drew\textsuperscript{149}, and later Kraus and Foster\textsuperscript{161} synthesized tetraphenylgermane, the
1. Genesis and evolution in the organic chemistry of Ge, Sn, and Pb compounds

first compound having a Ph—Ge bond, from GeCl₄ and PhMgBr. The maximum (70–75%) yield was reached at a GeCl₄ : PhMgBr ratio of 1 : 5. In 1934 Bauer and Burschkies showed for the first time that a reaction of GeCl₄ and Grignard reagents results in hexaorganyldigermanes R₃GeGeR₃ (R = 4-MeC₆H₄ and PhCH₂). In 1950, Johnson and Harris noted the formation of hexaphenyldigermane Ph₃GeGePh₃ was produced in a higher yield along with Ph₄Ge. Seyferth and Glockling and Hooton concluded that the intermediate product in the reaction of GeCl₄ and ArMgBr leading to Ar₃GeGeAr₃ was Ar₃GeMgBr.

In line with this assumption Gilman and Zeuech found in 1961 that Ph₃GeH reacted with several Grignard reagents (such as CH₂CHCH₂MgX or ArMgBr) to give Ph₃GeMgX (X = Cl, Br). The latter has cleaved THF, since a product of the reaction followed by hydrolysis seemed to be Ph₃Ge(CH₂)₄OH. Mendelsohn and coworkers indicated the possibility of the formation of R₃GeMgX in the reaction of GeCl₄ and Grignard reagents.

In the period 1931–1950 the organomagnesium syntheses became the laboratory practice for preparing tetraorganylgermanes. Tetraalkyl- and tetraarylgermanes containing bulky organic substituents could be synthesized only with difficulty, if at all, using Grignard reagents. In this case the reaction resulted in triorganyhalogermane R₄nGeXₙ (n = 1–3) were prepared for the first time in 1925 by Morgan and Drew, who isolated phenylbromogermanes Ph₄nGeBrₙ (n = 1, 3) together with tetraphenylgermane from the reaction of GeBr₄ and PhMgBr. However, the organomagnesium synthesis of organylhalogermanes has not found much use due to the simultaneous production of other compounds and the difficulty of separating them. The only exceptions were R₃GeX products having bulky R substituents.

In the reaction of HGeCl₃ and MeMgBr, Nefedov and Kolesnikov obtained a mixture of both liquid and solid permethyloligogermanes Me₃MeₙMe. In 1932, Krause and Renwanz synthesized the first heterocyclic organogermanium compound, tetra-2-thienylgermane, from the corresponding Grignard reagent. In the same year Schwarz and Reinhardt synthesized by the same method the first germacycloalkanes (1,1-dichloro- and 1,1-diethyl-1-germacyclohexanes). They also synthesized tetra-N-pyrrrolylgermane by the reaction of GeCl₄ and potassium pyrrole.

Since 1926 the organomagnesium synthesis was also used for preparing more complex tetraorganylgermanes such as R₃GeR₀₂ and R₂GeR₀₂R₀₂. The first unsaturated organogermanium compounds having α,β- or β,γ-alkynyl groups at the Ge atom were synthesized in 1956–1957 by Petrov, Mironov and Dolgy using Grignard or Norman reagents.

In 1925, the Dennis group used along with the organozinc and organomagnesium synthesis of tetraorganylgermanes, also the Wurtz–Fittig reaction (i.e. the reaction of aryl halides with sodium metal and tetrahalogermanes). The Wurtz–Fittig reaction was extensively employed for the synthesis of organogermanium compounds having Ge—Ge bonds such as R₃GeGeR₃. The first representative of the Ph₃GeGePh₃ series was synthesized in 1925 by Morgan and Drew, and subsequently by Kraus and coworkers, using the reaction of triphenylbromogermane and sodium metal in boiling xylene. Analogously, Bauer and Burschkies produced in 1934 R₃GeGeR₃, R = 4-MeC₆H₄ and PhCH₂. In addition, they found that the reaction of GeCl₄, Na and RBr (R = 4-MeC₆H₄) led to R₃GeGeR₃ in good yield together with R₄Ge.
Kraus and Flood\textsuperscript{148} found that hexaethylgermane was not formed in the reaction of triethylbromogermane and sodium metal in boiling xylene. However, they produced hexaethylgermane by heating Et$_3$GeBr and Na in a sealed tube at 210–270°C without solvent or by the reaction of Et$_3$GeBr and Na in liquid ammonia.

The possibility of producing diphenylgermylene alkali metal derivatives like Ph$_2$GeM$_2$ (M = Li, Na) was shown in 1952 by Smyth and Kraus\textsuperscript{197} when they obtained Ph$_2$GeNa$_2$ by cleavage of Ph$_4$Ge with concentrated solution of sodium in liquid ammonia. In 1930, Kraus and Brown\textsuperscript{198} produced a mixture of perphenyloligocyclogermances (Ph$_2$Ge)$_n$ by the reaction of sodium metal with diphenyldichlorogermane in boiling xylene. However, only in 1963 did Neumann and Kühlein\textsuperscript{199} show that the main crystalline product of the reaction is octaphenylcyclooligogermane (Ph$_2$Ge)$_4$. Cleavage of (Ph$_2$Ge)$_n$ with sodium in liquid ammonia resulted in Ph$_2$GeNa$_2$. Reaction of (PhGe)$_4$ with iodine which resulted in cleavage of the Ge–Ge bond, allowed the authors\textsuperscript{199} to synthesize the first organo-tetragermanes involving three Ge–Ge bonds X[Ph$_2$Ge]$_4$X (X = I, Me, Ph). By the reaction of diphenyldichlorogermane and lithium (or sodium naphthalene) Neumann and Kühlein\textsuperscript{175,199,200} isolated higher perphenylcyclogermances with \(n = 5\) (37\%) and \(n = 6\) (17\%). It is particularly remarkable that, unlike their homologs with \(n = 4\), these compounds could not be cleaved with iodine.

In 1962–1965 Nefedov, Kolesnikov and coworkers\textsuperscript{201–205} investigated the reaction of Me$_2$GeCl$_2$ with lithium metal in THF. The main products were (Me$_2$Ge)$_6$ (80\% yield) at 20–45°C and the polymer (Me$_2$Ge)$_n$ (50\% yield) at 0°C.

In 1966 Shorygin, Nefedov, Kolesnikov and coworkers\textsuperscript{206} were the first to investigate and interpret the UV spectra of permethyloligogermances Me(Me$_2$Ge)$_n$Me (\(n = 1–5\)). The reaction of Et$_2$GeCl$_2$ with Li in THF led mostly to polydiethylgermane (Et$_2$Ge)$_n$\textsuperscript{207}. At the same time Mironov and coworkers\textsuperscript{208,209} obtained dodecamethylcyclohexasgermane (Me$_2$Ge)$_6$ by the same procedure.

In 1969, Bulten and Noltes\textsuperscript{210} synthesized the perethyloligogermances Et(Et$_2$Ge)$_n$Et (\(n = 2–6\)) by the organolithium method. The oligomer with \(n = 6\) was thermally stable and heating at 250°C for 8 hours resulted in only 20\% decomposition.

By a reaction of Li amalgam with Ph$_2$GeBr$_2$, Metlesics and Zeiss\textsuperscript{211} produced 1,2-dibromotetraphenyldigermane instead of the cyclic oligomers obtained previously in a similar reaction with Li metal. A reaction of Li amalgam with PhGeBr$_3$ gave PhBr$_2$GeGeBr$_2$Ph, the thermolysis of which resulted in PhGeBr$_3$.

Curiously, the reaction of phenyltrichlorogermane with sodium or potassium produced a compound (PhGe)$_n$, which Schwarz and Lewinson\textsuperscript{187} mistook for hexaphenylhexagermanebenzene Ph$_6$Ge$_6$. Five years later Schwartz and Schmeisser\textsuperscript{212} found that the action of potassium metal on PhGeCl$_3$ yielded a product, which in turn was to be a linear hexamer having terminal Ge(III) atoms i.e. a biradical of a structure *(PhGe=GePh)*. They thought that this structure could be confirmed by addition reactions with bromine, iodine and oxygen, which indeed took place. However, HI and HBr were not involved in the addition reactions.

Two dozen years later Metlesics and Zeiss\textsuperscript{213} obtained the same product by the reaction of PhGeCl$_3$ with Li amalgam. They found that the product was a polymer consisting of (PhGe)$_n$, (Ph$_2$Ge)$_n$ and (PhGeO)$_n$ chains.

In 1950–1960 it was found that triarylgermyl derivatives of alkali metals could be obtained by cleavage of Ge–H\textsuperscript{214,215}, C–Ge\textsuperscript{174,195,216,217}, Ge–Ge\textsuperscript{218–221} and Ge–Hal\textsuperscript{222} bonds by Li, Na or K in the appropriate solvents.

In 1950, Glarum and Kraus\textsuperscript{214} investigated the reaction of alkylgermanes R$_4$–$_n$GeH$_n$ (\(n = 1–3\)) and sodium metal in liquid ammonia. They found that alkylgermanes RGeH$_3$ reacted with Na to give RGeH$_2$Na.
As early as in 1927, Kraus and Foster produced for the first time triphenylgermylsodium as its ammonia complex Ph₃Ge(NH₃)₃Na. They also found that the reaction of Ph₃GeNa with H₂O or NH₄Br in liquid ammonia led quantitatively to Ph₃GeH. The reaction of Ph₃GeNa and Ph₃GeF in liquid ammonia resulted in Ph₃GeGePh₃.

In 1957–1959, Gilman and coworkers found that Ph₃GeGePh₃ was cleaved by sodium in THF solution in the presence of PhBr and Ph₄Ge to give Ph₃GeNa. In 1932 it was found that the reaction of Ph₃GeNa with organic halides RX gave Ph₃GeR, whereas when R = Ph, Ph₃GeGePh₃ was isolated. The reaction of Ph₃GeNa with oxygen led to Ph₃GeONa. In the years 1950–1952, Kraus and coworkers further developed this chemistry by studying the reactions of Ph₃GeNa with organic mono- and dihalides of different structure, such as HCCl₃, CCl₄, BCl₃, or HSiCl₃. The product of the latter reaction was (Ph₃Ge)₃SiH.

In 1930, Kraus and Brown prepared octaphenyltrigermane by the reaction of Ph₃GeNa and Ph₂GeCl₂. It was the first organogermanium compound with more than one Ge–Ge bond. The two Ge–Ge bonds could readily be cleaved by bromine. Kraus and Scherman synthesized in 1933 the first unsymmetrical hexaorganyldigermane Ph₃GeGeEt₃ by the reaction of Ph₃GeNa and Et₃GeBr.

In 1932, Kraus and Flood prepared the first compound having a Ge–Sn bond (Ph₃GeSnMe₃) by the reaction of Ph₃GeNa and Me₃SnBr. In 1934, Kraus and Nelson synthesized Ph₃GeSiEt₃ by the reaction of Ph₃GeNa and Et₃SiBr.

The reaction of hexaethyldigermane and potassium in ethylamine solution led Kraus and Flood to the first synthesis of triethylgermylpotassium. Its reaction with ethyl bromide resulted in Et₄Ge. However, attempts to cleave hexamethyldigermane either by potassium or by its alloy with sodium were unsuccessful.

The action of potassium metal with Me₃GeBr without solvent resulted in Me₃GeGeMe₃. Gilman and coworkers synthesized Ph₃GeK by cleavage of Ph₃GeGePh₃ with a sodium and potassium alloy in THF in the presence of an initiator (PhBr or Ph₄Ge). Triphenylgermylpotassium was produced in a 26% yield during a slow cleavage of Ph₃CGePh₃ by the same alloy. The development of a method for the synthesis of Ph₃GeK opened a route to carry out its addition to double bonds, such as 1,1-diphenylethylene, which resulted in Ph₂CH₂CH₂GePh₃, or to activated conjugated bonds.

Lithium metal has been used for organogermanium synthesis since 1932, but organolithium compounds were used only since 1949. Lithium and its organic derivatives were used in three approaches: (1) reactions of lithium and organogermanium compounds; (2) reactions of organolithium compounds with organic and inorganic germanium compounds; (3) synthesis based on compounds having a Ge–Li bond.

Although fundamental research in this field was undertaken in Gilman’s laboratory, Kraus and Flood were the pioneers in using lithium for the synthesis of organogermanium compounds. In 1932, they discovered that the reaction of Et₃GeX (X = Cl, Br) and lithium in ethylamine resulted in Et₃GeGeEt₃. With excess lithium, the Ge–Ge bond of hexaethylgermane was cleaved to give Et₃GeLi. When the latter was treated with NH₃ or NH₄Br in an ethylamine solution, Et₃GeH was formed.

In 1950, Glarum and Kraus developed a very convenient method for the synthesis of alkylgermyllithium compounds (RGeH₂Li) by the reaction of RGeH₃ with lithium in ethylamine solution. An analogous reaction of R₂GeH₂ and lithium led to R₂GeHLi. Later, Vyzazkin, Razuvaev and coworkers synthesized Et₃GeLi in >90% yield by the reaction of lithium and (Et₃Ge)₂Hg or (Et₃Ge)₂TI.

Gilman and coworkers obtained Ph₃GeLi by a simpler method. The reaction of Ph₃GeBr with Li in THF gave the compound, although in a lower (52%) yield. In 1956,
Gilman and Gerow\textsuperscript{229,235} synthesized \( \text{Ph}_3\text{GeLi} \) in 70\% yield by the cleavage of \( \text{Ph}_4\text{Ge} \) with lithium metal in a diglyme solution. They later showed that aryl groups were cleaved from the Ge atom in the same solvent much more easily than alkyl or phenyl groups.

Tamborski and coworkers\textsuperscript{236} found that the reaction of \( \text{Ph}_3\text{GeCl} \) and lithium metal in THF involved the intermediate formation of \( \text{Ph}_3\text{GeGePh}_3 \) and resulted in \( \text{Ph}_3\text{GeLi} \).

Gross and Glockling\textsuperscript{237} developed in 1964 a very effective method for the synthesis of \( \text{(Ph}_2\text{CH}_2)_3\text{GeLi} \) based on the cleavage of \( \text{(PhCH}_2)_4\text{Ge} \) by lithium in diglyme. Gross and Glockling\textsuperscript{237,238} found that, when tetrabenzylgermane is treated with lithium, two \( \text{PhCH}_2 \) groups were cleaved, and \( \text{(PhCH}_2)_2\text{GeLi}_2 \) was probably formed.

The organolithium synthesis proved to be the simplest and most convenient route to organogeramic compounds, including those carrying bulky substitutes on the Ge atom. The method was first used in 1930 by Kraus and Brown\textsuperscript{198} and found many applications shortly after.

In 1949, Johnson and Nebergall\textsuperscript{230} showed that the use of \( \text{RLi} \) for \( \text{R}_4\text{Ge} \) production resulted in higher yields than that for \( \text{RMgX} \). Ten years later Gilman and coworkers\textsuperscript{174} found that the reaction of \( \text{GeBr}_4 \) and \( \text{EtLi} \) led to \( \text{Et}_4\text{Ge} \) and \( \text{Et}_3\text{GeGeEt}_3 \). In 1953, Summers\textsuperscript{239} discovered that reaction of \( \text{PhLi} \) with \( \text{GeI}_2 \) gave a polymer \( (\text{PhGe})_n \). In contrast, the reaction of \( \text{GeI}_2 \) with \( \text{Bu}_2\text{Hg} \) produced 1,2-diiodotetrahydrogermane\textsuperscript{240}.

Developed by Nefedov, Kolesnikov and coworkers\textsuperscript{185,203}, the reaction of \( \text{RLi} \) with H\text{GeCl}_3 resulted in linear and cyclic oligomers and polymers consisting of alternate Ge–Ge bonds.

The Ge–H bonds in triarylgermanes were cleaved as well by organolithium compounds to form \( \text{Ar}_3\text{GeLi} \). Together with the latter \( \text{Ar}_3\text{GeR} \) and \( \text{Ar}_3\text{GeGeAr}_3 \) were also formed\textsuperscript{173,235}. Johnson and Harris\textsuperscript{173} investigated the reaction of \( \text{PhLi} \) and \( \text{Ph}_3\text{GeH} \) and found that, depending on the mixing sequence of the reagents, the product could be either \( \text{Ph}_4\text{Ge} \) or \( \text{Ph}_3\text{GeGePh}_3 \). Trialkygermanes reacted less readily than triarylgermanes with \( \text{RLi} \) (\( \text{R} = \text{Bu}, \text{Ph} \)).

In 1956, Gilman and Gerow\textsuperscript{229,235} and then Brook and Peddle\textsuperscript{242} developed an effective, nearly quantitative method for the synthesis of \( \text{Ph}_3\text{GeLi} \) by the reaction of \( \text{Ph}_3\text{GeH} \) and BuLi.

Gilman and coworkers\textsuperscript{220,229,235,243} found that \( \text{Ph}_3\text{GeLi} \) could be added to 1,1-diphenylethylene, 1-octadecene and benzalacetophenone (but not to 1-octene, cyclohexene and E-stilbene). The reaction of \( \text{Ph}_3\text{GeLi} \) with enolizable ketones followed equation 1\textsuperscript{244}.

\[
\text{Ph}_3\text{GeLi} + \text{CH}_3\text{COPh} \rightarrow \text{Ph}_3\text{GeH} + \text{LiCH}_2\text{COPh} \quad (1)
\]

On the other hand, addition of \( \text{Ph}_3\text{GeLi} \) to benzophenone gave \( \text{Ph}_2(\text{Ph}_3\text{Ge})\text{COH} \). An analogous addition of \( \text{Ph}_3\text{GeLi} \) to formaldehyde and benzaldehyde led to \( \text{Ph}_3\text{GeCH}_2\text{OH} \) and \( \text{Ph}(\text{Ph}_3\text{Ge})\text{CHOH} \), respectively. Triphenylgermyllithium adds to 1,4-benzalacetone (equation 2)\textsuperscript{218} and reacts as a metal-active reagent with CH acids such as fluorene\textsuperscript{195,246}.

\[
\text{Ph}_3\text{GeLi} + \text{PhCH} = \text{CHCOPh} \rightarrow \text{Ph}(\text{Ph}_3\text{Ge})\text{CHCH}_2\text{COPh} \quad (2)
\]

Chalcogens \( \text{E} (\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}) \) readily insert into the Ge–Li bond. For example, reaction of \( \text{E} \) with \( \text{PhGeLi} \) yields \( \text{Ph}_2\text{GeEli} \) (\( \text{E} = \text{O}, \text{S}, \text{Se}, \text{Te} \)). Brook and Gilman found that triphenylgermyllithium was oxidized to \( \text{Ph}_3\text{GeOLi} \), and carbon dioxide could easily be inserted into the molecule to give \( \text{Ph}_3\text{GeCOOLi} \). Thermal decomposition of \( \text{Ph}_3\text{GeCOOH} \) led to \( \text{Ph}_3\text{GeOH} \). Triphenylgermyllithium cleaved the oxirane ring with ring opening to give \( \text{Ph}_3\text{GeCH}_2\text{CH}_2\text{OLi} \).
The reactions of GeI$_2$ with organic lithium, manganese, aluminum and mercury derivatives were widely investigated as a possible route for producing diorganylgermylene R$_2$Ge. However, the reaction proceeds in a complex manner and has no preparative application. However, Glocking and Hooton discovered later that the reactions of GeI$_2$ and phenyllithium or mesitylmagnesium bromide led to the corresponding products Ar$_3$GeLi or Ar$_3$GeMgBr whose hydrolysis resulted in Ar$_3$GeH. The first bulky oligogermylene, i.e. (Ph$_3$Ge)$_3$GeH, was obtained in 1963 by this reaction. A year later Vyaazankin and coworkers synthesized methyl-tris(triphenylgermyl)germane (Ph$_3$Ge)$_3$GeMe.

C. Nonorganometallic Approaches to a C–Ge Bond

E. G. Rochow, whose name became famous due to his discovery of the direct synthesis of organohalosilanes from elementary silicon, tried to develop an analogous method for the synthesis of organohalogermanes. In 1947 he showed that the methylhalogermanes MeGeX$_3$ and Me$_2$GeX$_2$ were formed in the reaction of methyl chloride or methyl bromide and elementary germanium in the presence of copper or silver metals at 300–400°C. Later, he added EtCl, PrCl and PhCl to the reaction. Generally, a mixture of alkylhalogermanes R$_4$GeX$_n$ ($n = 2, 3$) was obtained in the process. The product ratios were dependent on the temperature and the catalyst structure. When MeCl and EtCl were used a mixture of R$_2$GeCl$_2$ and RGeCl$_3$, R = Me, Et, was formed in a ratio very close to 2:1. The yields of methyltrichlorogermane were increased on increasing the temperature and were dependent on the copper content in the contact mass, as well as on the addition of Sb, As and ZnCl$_2$ to the reaction mixture.

In 1956–1958, this direct organylhalogermanes synthesis was thoroughly investigated at the Petrov, Mironov and Ponomarenko laboratory. A variety of halides, such as allyl and methallyl chloride, allyl bromide and CH$_2$Cl$_2$ (but, not vinyl chloride), were found to react. With the latter, MeGeCl$_3$ (27%), Cl$_3$GeCH$_2$GeCl$_3$ (23%) and (CH$_2$GeCl$_2$)$_3$ (19%) were produced. Alkyltribromogermanes RGeBr$_3$ (R = Pr, Bu) were synthesized by the reaction of the corresponding alkyl bromides with sponged germanium at 300–340°C.

Alkyliodogermanes were produced by direct synthesis only in 1963–1966. It is noteworthy that no compounds having Ge–H bonds (such as RGeHCl$_2$ or R$_2$GeHCl) were formed during the direct synthesis of alkylchlorogermanes, in contrast with the direct synthesis of alkylchlorosilanes.

A hydrogermylation reaction (the term was first introduced by Lukevics and Voronkov, i.e. the addition of organic and inorganic germanium derivatives having Ge–H bonds to unsaturated compounds) was first performed by Fischer, West and Rochow in 1954. They isolated hexyltrichlorogermane (in 22% yield) after refluxing for 35 hours a mixture of trichlorogermane and 1-hexene in the presence of a benzoyl peroxide initiator. Two years later, the reaction of HGeCl$_3$ and other alkenes in the presence of the same initiator was carried out at 70–85°C to give the appropriate alkyltrichlorogermanes in low yields (9–24%) as well. In 1957, Gilman and coworkers added HGeCl$_3$ to 1-octene, 1-octadecene, cyclohexene, allyltriphenylsilane and -germane in the presence of benzoyl peroxide or under UV radiation.

In 1958 Ponomarenko and coworkers found that HGeCl$_3$ was exothermally added to ethylene at 40 atm pressure in the presence of H$_2$PtCl$_6$ to give EtGeCl$_3$ in 25% yield. In the same year Mironov and Dzhurinskaya in Petrov’s laboratory unexpectedly discovered that the reaction of HGeCl$_3$ and diverse unsaturated compounds proceeded exothermally at room temperature and without either catalyst or initiator. On the
contrary, the presence of either a catalyst or an initiator actually decreased the yield of the hydrogermylation products 270–272.

A noncatalytic hydrogermylation reaction was carried out at 85 °C in a sealed tube in 1956. Furthermore, HGeBr3 273, HGeI3 274, R2GeHCl (at 100–150 °C) 275, R2GeHBr (at 150 °C) 275, R2GeH2 (at 140–150 °C) 276, and R3GeH (at 50–200 °C) 276–278 were reacted in the noncatalytic hydrogermylation process. However, addition of R3GeH to unsaturated compounds proceeded more easily in the presence of H2PtCl6 52,53.

In 1962, Satge and Lesbre 279,280 carried out for the first time hydrogemylation of the carbonyl group of aldehydes and ketones.

The best method for the synthesis of aryltrihalogermanes based on the reaction of aryl iodides and GeX4 (X = Cl, Br) in the presence of copper powder was discovered by Mironov and Fedotov 281,282 in 1964. Bauer and Burschkies 283 discovered in 1932 an unusual way of Ge–C bond formation by condensation of GeCl4 and aromatic amines according to equation 3. The reaction products were isolated as the corresponding substituted phenylgermsesquioxanes.

\[
\text{R}_2\text{NC}_6\text{H}_5 + \text{GeCl}_4 \rightarrow \text{Cl}_3\text{GeC}_6\text{H}_4\text{NR}_2 \cdot \text{HCl} \rightarrow \frac{1}{n}(\text{R}_2\text{NC}_6\text{H}_4\text{GeO}_{1.5})_n
\] (3)

In 1955, Seyferth and Rochow 283 developed a nontrivial method of Ge–Ge bond formation based on the insertion of a carbene (H2C: formed from diazomethane) into a Ge–Cl bond of GeCl4 to form CIC2GeCl3. Later, Seyferth and coworkers 284,285 extended this approach to the formation of the GeCH2X (X = Cl, Br) group by the reaction of dihalocarbenes (generated from PhHgCX2Br) with Ge–H bonds.

Kramer and Wright 286,287 and Satge and Rivière 288 demonstrated the possibility of carbene (formed from diazomethane) insertion into the Ge–H bond to give a Ge–CH3 moiety. However, this reaction is of no practical application. It was more interesting to insert substituted carbenes (generated from diazo derivatives such as ethyl diazoacetate, diazoacetone and diazoacetophenone) into Ge–H bonds in the presence of copper powder. In this case a Ge–CH2X group was formed, where X was the corresponding functional group 276,277,289.

In 1958, Nesmeyanov and coworkers 290 found that decomposition of aryldiazonium tetrafluoroborates with zinc dust in the presence of GeCl4 resulted in formation of aryltrichlorogermanes in <30% yield, isolated as the corresponding arylgermsesquioxanes.

In 1960, Volpin, Kursanov and coworkers 291–293 showed that dihalogermanenes add to multiple bonds by reacting GeI2 with tolan (PhC≡CPh) at 220–230 °C 292. The main product of the reaction was assigned to 1,1-diiodo-2,3-diphenyl-1-germa-2-cyclopropene, which the authors considered to be a new three-membered heterocyclic aromatic system 291,292,294. When this substance was allowed to react with RMgX (R = Me, Et), the iodine atoms were replaced by alkyl substituents, whereas upon the action of NaOH they were substituted by OH groups. The OH groups of the hydroxy derivative obtained were replaced by halogen 291 on reaction with HCl or HBr. However, it was established later that the isolated adduct was actually 1,1,4,4-tetraiodo-2,3,5,6-tetraphenyl-1,4-digerma-2,5-cyclohexadiene 295–298.

Reaction of GeI2 and acetylene at 130–140 °C and 10 atm 299 gave 44% yield of an adduct whose structure was assigned to 1,1-diiodo-1-germa-2-cyclopropene (i.e. 1,1-diiododigermymyrene) 299. Its iodine atoms were replaced by OH and Cl atoms 299 and by Me groups using known reactions. However, X-ray analysis established the structure of the isolated chlorinated compound as 1,1,4,4-tetracloro-1,4-digerma-2,5-cyclohexadiene. Hydrogenation of 1,1,4,4-tetramethyl derivative synthesized from the latter afforded the 1,1,4,4-tetramethyl-1,4-digermacyclopentane, whereas its bromination...
led to \( \text{Me}_2\text{Ge(\text{CH} = \text{CHBr})Br} \). Simultaneously, a polymer \((-\text{I}_2\text{Ge}-\text{CH} = \text{CH} - \text{I})_n\) with average molecular weight of 4300 (after removal of lower molecular weight fractions) was formed in a 56% yield. Probably the low molecular weight polymer fractions had macrocyclic structures resembling their silicon analog \((-\text{R}_2\text{SiCH} = \text{CH} - \text{R})_n\). The reaction of acetylene with \( \text{GeBr}_2 \) leads to analogous polymers.

In 1960, Russian chemists found that \( \text{GeI}_2 \) acts easily with diarylmercuranes \( \text{Ar}_2\text{Hg} \) to give \( \text{Ar}_4\text{GeI}_n \) in good yield, together with \( \text{ArHgI} \) and \( \text{Hg} \). In contrast, dialkyl mercury derivatives reduced \( \text{GeI}_2 \) to \( \text{Ge} \) metal, but did not form dialkyldiiodoger-
manes (one of the products was \( \text{I}_2\text{RGeGeRI}_2 \)).

In 1963, Mironov and Gar showed that \( \text{GeCl}_2 \) and \( \text{GeBr}_2 \) (generated from \( \text{HGeX}_3 \)) add to 1,3-butadiene to give the corresponding 1,1-dihalo-1-germa-3-cyclopentene. Analogously, \( \text{GeI}_2 \) adds to 2-methyl- and 2,3-dimethylbutadiene.

Another approach to the formation of a C–Ge bond resulting in organyltrihaloger-
manes was based on the reaction of dihalogermylenes (\( \text{GeX}_2 \)) with organic halides. For this purpose, the more stable and easily available \( \text{GeI}_2 \) was usually used. In 1933, Flood and coworkers discovered that the reaction of \( \text{GeI}_2 \) with alkyl iodides proceeds smoothly to give alkyltrio-germanes. Pope and Pfeiffer and their coworkers performed analogous synthesis of \( \text{RSnI}_3 \) from \( \text{SnI}_2 \) as early as 1903. This reaction can be regarded as an insertion of diiodogermylene into the C–I bond. \( \text{F}_3\text{GeGeI}_3 \), \( \text{ICH}_2\text{GeI}_3 \), \( \text{PhGeI}_3 \), \( \text{MeOCH}_2\text{GeI}_3 \), and \( \text{EtOCH}_2\text{GeI}_3 \) were also similarly synthesized at 110–290°C in sealed ampoules.

In 1965, Mironov and Gar found that allyl bromide adds easily to \( \text{GeBr}_2 \) to form allyltetra-tribromoger-
mane in a 65% yield. In 1935, Tchakirian and Lewinsohn used a complex of \( \text{GeCl}_2 \) and \( \text{CsCl} \), i.e. cesium trichloroger-
mane \( (\text{CsGeCl}_3) \), to synthesize \( \text{RGeCl}_3 \). Heating \( \text{CsGeCl}_3 \) with \( \text{PhI} \) at 250°C afforded phenyltrichloroger-
mane in 80% yield. Alkyl iodides also reacted similarly under similar conditions. However, this method did not find any application.

D. C—Ge Bond Cleavage. Organylhalogermanes

The C–Ge bond is less stable toward heterolytic and homolytic cleavage reactions than the C–Si bond, but it is more stable than the C–Sn and C–Pb bonds. This is consistent with the bond energies of these bonds (see Chapter 2).

The first example of heterolytic cleavage of the C–Ge bond was the cleavage of tetraorganogermanes (and later of organylhalogermanes) by halogens or hydrogen halides (mainly \( \text{Br}_2 \) and \( \text{HBr} \)). A synthetic method of organylhalogermanes \( (\text{R}_4\text{nGeX}_n, n = 1–3) \) based on this reaction has been widely used. It was first used in 1927 in the laboratories of Kraus and Dennis and afterwords by many chemists.

In 1927, Kraus and Foster showed that refluxing tetraphenylgermane with a bromine solution in \( \text{CCl}_4 \) for 7 hours gave triphenylbromogermane. In the same year, Omdorff, Tabern and Dennis discovered that by using 1,2-dibromoethane as a solvent, the reaction was completed within a few minutes. The second phenyl group could be also cleaved, but with difficulty. However, with excess bromine, or by adding \( \text{AlBr}_3 \) catalyst, more \( \text{Ar}_2\text{GeBr}_2 \) was obtained in satisfactory yields. In 1931, Schwarz and Lewinsohn cleaved the Ar–Ge bond in many tetraarylgermanes by bromine.

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In 1932, Kraus and Flood obtained \( \text{Et}_3\text{GeBr} \) in 82% yield during bromination of tetraethylgermanium in an \( \text{EtBr} \) media. \( \text{R}_3\text{GeBr} \) derivatives \( (\text{R} = \text{Pr}^{15}, \text{Bu}^{314,316}) \) were then synthesized by the same method. The feasibility of cleavage of substituents attached to the Ge atom by reaction with bromine decreases in the following order: \( \text{4-PhC}_6\text{H}_4 > \text{Ph} > \text{CH}_2\text{=CHCH}_2 > \text{Bu} > \text{i-Pr} > \text{Pr} > \text{Et} > \text{Me}^{77} \).
In the early 1950s Anderson used bromine, or bromine and iodine halides in the presence of iron powder (i.e. $\text{FeX}_3$ formed in situ) to cleave the C–Ge bond. In a number of cases, cleavage of $\text{R}_4\text{Ge}$ with bromine gave mixtures of $\text{R}_{4-n}\text{GeBr}_n$ ($n = 1–3$) which were difficult to separate. Fuchs and Gilman suggested separating such mixtures by hydrolysis to the corresponding oxygen derivatives followed by their retransformation to halides. Organoylidogermanes were obtained by C–Ge bond cleavage with iodine and $\text{Al}_3$ catalyst. $\text{EtGeI}_3$ was obtained from $\text{Et}_2\text{GeI}_2$ by this method.

Organoylidogermanes and organyfluorogermanes were prepared by the reaction of isostructural organylhalogermanes (chlorides and bromides) with $\text{NaI}$ in acetone or with $\text{SbF}_3$, respectively.

In 1930, Dennis and Patnode used HBr for the first time to cleave the C–Ge bond. In each case, the reaction did not continue beyond the stage of forming $\text{R}_3\text{GeBr}$, $\text{R}_4\text{Ge}$ reacted with $\text{HCl}$ or $\text{HI}$ only in the presence of aluminum halides.

It is noteworthy that under the action of sulfuric acid the C–Ge bond of $(\text{PhCH}_2)_4\text{Ge}$ was not cleaved, and $(\text{HSO}_3\text{C}_6\text{H}_4\text{CH}_2)_4\text{Ge}$ was formed. In the early 1960s it was shown that the C–Ge bond could be cleaved by $\text{AlCl}_3$ and particularly easily by $\text{GaCl}_3$ and $\text{InCl}_3$.

In 1963 Razuvaev, Vyazankin and coworkers found that alkyl halides in the presence of $\text{AlCl}_3$ cleaved the C–Ge bond in tetraalkylgermanes to give trialkylhalogermanes in good yield. This reaction was later used by other investigators.

In 1931, Schwarz and Lewinsohn first obtained $\text{PhGeCl}_3$ in 75% yield by the cleavage of $\text{Ph}_4\text{Ge}$ with tetrachlorogermane in an autoclave at 350°C during 36 hours. The cleavage reactions of the Ge–halogen bond leading to the formation of germium–pnicogen and germanium–chalcogen bonds are considered in Sections II.F and II.C, respectively. Hence, we only indicate that in 1955 Rochow and Allred found that $\text{Me}_2\text{GeCl}_2$ dissociates to $\text{Me}_2\text{Ge}^{2+}$ and $2\text{Cl}^-$ ions in dilute aqueous solutions.

E. Compounds having a Ge–H Bond

The first representative of organogermanium hydrides $\text{R}_{4-n}\text{GeH}_n$ ($n = 1–3$) was triphenylgermane. Kraus and Foster obtained it in 1927 by reaction of $\text{NH}_4\text{Br}$ and triphenylgermylsodium in liquid ammonia. Five years later Kraus and Flood similarly synthesized triethylgermane.

In 1950 the first alkyl germanes $\text{RGeH}_3$ (R = Me, Et, Pr, i-Am) were obtained by Kraus and coworkers by the reaction of $\text{NaGeH}_3$ and alkyl bromides or chlorides (the same method was also used later). They also synthesized the first dialkylgermane $\text{i-AmEtGeH}_2$ from $\text{i-AmBr}$ and $\text{EtGeH}_2\text{Li}$ in an ethylamine media. Analogously, the reaction of $\text{i-AmEtGeHLi}$ and $\text{EtI}$ led to $\text{i-AmEt}_2\text{GeH}_2$.

It is remarkable that according to Kraus the reaction of $\text{NaGeH}_3$ and $\text{PhBr}$ in liquid ammonia gave benzene and the monomeric germylene $\text{GeH}_2$. Onyszchuk added $\text{H}_3\text{GeBr}$, $\text{Me}_3\text{GeBr}$, $\text{Me}_3\text{SiCl}$, $\text{Me}_2\text{SiCl}_2$ and $\text{MeI}$ to $\text{NaGeH}_3$ and obtained the corresponding substituted compounds containing Ge–Ge and Ge–Si bonds.

In 1953, West succeeded in obtaining $\text{Ph}_3\text{GeH}$ and $\text{Me}_2\text{GeH}_2$ by reducing $\text{Ph}_3\text{GeBr}$ and $(\text{Me}_2\text{GeS})_n$ with zinc amalgam and hydrochloric acid. However, $\text{MeGeCl}_3$ was not reduced by this method.
1. Genesis and evolution in the organic chemistry of Ge, Sn, and Pb compounds

The most accessible synthesis of organohydrogermanes was based on the reduction of the corresponding organohalogermanes (R₄⁻ₙGeXₙ, n = 1–3) with complex hydrides such as LiAlH₄, NaBH₄, and LiAlH(OBu-t)₃. The less reactive lithium hydride and deuteride have been also recommended for this reduction, and sodium hydride in the presence of boron or aluminum derivatives was also used.

The Ge–Cl bonds in (c-C₆H₁₁)₃GeX (X = Cl, Br) were first reduced to the Ge–H bonds with LiAlH₄ in 1947 by Finholt and coworkers. Two years later this method of organohydrogermane synthesis was implemented by Johnson and Nebergall. Johnson and Harris obtained in this way the first diarylgermane Ph₂GeH₂. Johnson and Nebergall succeeded in reducing the Ge–O bond of (c-C₆H₁₁)₃GeOH and Ph₃GeOGePh₃ by LiAlH₄ to (c-C₆H₁₁)₃GeH and Ph₃GeH, respectively.

Lesbre and Satge obtained trialkylgermanes by reducing trialkylalkoxygermanes, trialkyl(alkylthio)germanes, and triethyl(diphenylphosphinyl)germane with LiAlH₄.

In 1963, the reduction of the corresponding halides with LiAlH₄ gave the optically active organogermanes RPh(1-C₁₀H₇)GeH (R = Me, Et), which were resolved to the optically active enantiomers.

Triorganylgermanes were also formed by the reaction of GeCl₄ and organylmagnesium halides having bulky substituents such as i-Pr, 2-MeC₆H₄ and c-C₆H₁₁. The intermediates of this reaction seem to be triorganylgermylmagnesium halides R₃GeMgX, whose hydrolysis gave R₃GeH. Triethylgermane was formed by cleavage of the Ge–M bonds of Et₃GeM (M = Li, Cd, Hg, Bi) with water, alcohols or acetic acid.

In 1961, Satge and Lesbre used trialkylgermanes in the presence of AlX₃ for partial reduction of R₂GeX₂ (X = Cl, Br) to R₂GeHX. An analogous reaction was performed four years earlier in organosilicon chemistry.

The same authors also synthesized dialkylhalogermanes R₂GeHX (X = Br, I) by the reaction of R₂GeH₂ and haloalkanes in the presence of AlX₃. Again, the analogous organosilicon reaction was reported four years earlier.

Mironov and Kravchenko suggested an original synthesis of alkyldichlorogermanes RGeHCl₂ based on alkylation of the Et₂O-D₃GeCl₃ complex with tetraalkylstannanes and tetraalkyl-plumbanes. The reaction with Me₄Sn resulted in 80% yield of Me₄GeHCl₂. The reaction with higher tetraalkylstannanes was complicated with by-processes.

In 1950, Johnson and Harris found that thermal decomposition of Ph₃GeH gave Ph₂GeH₂ and Ph₄Ge. The diphenylidgermane product was also unstable and decomposed slowly even at room temperature, forming tetraphenylermane as one of the products. Phenylgermane decomposed to Ph₂GeH₂ and GeH₄ at 200°C. The reaction proceeded instantly in the presence of AlCl₃ even at room temperature. In contrast, the alkylgermanes R₄⁻ₙGeHₙ were more stable and their stability toward thermolysis increased on decreasing the value of n. At 400–450°C tricyclohexylgermane decomposed to elementary germanium, cyclohexene and hydrogen, and at ca 360°C cyclohexane, benzene and polycondensed compounds having c-C₆H₁₁ groups were formed. In contrast, the thermal decomposition of (c-C₆H₁₁)₃SiH proceeded at 600–650°C. Since 1949, it was established that the first products of Ge–H bond oxidation, e.g. of R₃GeH, were triorganylgermanoles R₃GeOH, which then condensed to give digermoxanes R₃GeOGeR₃.

Kraus, Flood and Foster, and much later other research chemists, discovered that organic germanium hydrides R₄⁻ₙGeHₙ (n = 1–3) reacted extremely readily with halogens to form corresponding halides R₄⁻ₙGeXₙ (X = Cl, Br, I).

Even in 1927, Kraus and Foster showed that triphenylgermane reacted with HCl to give the triphenylchlorogermane. Thirty years later Anderson conducted an analogous
reaction of trialkylgermane, e.g. triethylgermane and hydrochloric acid. HCl and HBr reacted with RGeH₃ and R₂GeH₂ only in the presence of AlCl₃ or AlBr₃. In 1953, Anderson found that the reaction of concentrated H₂SO₄ with trialkylgermanes gave hydrogen and bis(trialkylgermyl) sulfates (R₃GeO)₂SO₂. According to Satge, the reaction of Et₃GeH and benzenesulfonic acid leads similarly to Et₃GeOSO₂Ph.

(ETO₃GeO)₃B was obtained by the reaction of Et₃GeH and H₂BO₃ in the presence of copper powder. An analogous reaction of Et₃SiH and H₂BO₃ in the presence of colloidal nickel was reported four years earlier. Bu₃GeH reacts quantitatively with acetic acid in the presence of copper. Perfluoroalkanecarboxylic acids reacted smoothly with Et₃GeH without any catalyst to form triethyl/perfluoroacyloxygermanes. In contrast, Cl₃CCOOH, Br₃CCOOH and ICH₂COOH were reduced to CH₃COOH by Et₃GeH. Anderson also conducted the reaction of R₂GeH₂ with H₂SO₄.

In 1953, Anderson found that the reaction of concentrated H₂SO₄ with trialkylgermanes gave hydrogen and bis(trialkylgermyl) sulfates (R₃GeO)₂SO₂. According to Satge, the reaction of Et₃GeH and benzenesulfonic acid leads similarly to Et₃GeOSO₂Ph.

In 1962, Lesbre and Satge found that R₃GeH condensed with water or with alcohols, glycols and phenols (R’OH) in the presence of copper powder to form hydrogen and R₃GeOH or R₃GeOR, respectively. The reaction of Bu₂GeH₂ and 1,4-butanediol led to 2,2-dibutyl-1,3-dioxo-2-germacyclopentane. Unlike Si–H and especially Sn–H bonds, the Ge–H bond is rather stable to alkaline hydrolysis or alcoholysis. For example, R₄-nGeHₙ (R = alkyl; n = 1–3) did not react with a 20% NaOH solution. According to Fuchs and Gilman, trihexylgermane did not react with aqueous-alcoholic KOH solution, whereas Ph₃GeH reacted easily with a similar solution, and HexGeH₃ and R₂GeH₂ reacted very slowly at 80°C.

Organogermainium hydrides are very good reducing agents. In 1957, Anderson showed that Et₃GeH reduced transition metal salts to their lower valence state (Cu II to Cu I, TiIV to TiIII or TiII, VIV to VIII, CrIV to CrIII) or to the free metals (Au, Hg, Pd, Pt).

In 1961, Satge found out that Et₃GeH reduced GeCl₄ first to GeCl₂ and then to GeO. Nametkin and coworkers used an analogous reaction to reduce TiCl₄ to TiCl₂. In ether, the reaction gave a 2Et₂O · HGeCl₃ complex.

In 1961, it was found that organogermainium hydrides R₄-nGeHₙ reduced organic halogen derivatives in the absence of catalysts to the corresponding hydrocarbons. The reaction is easier the higher the value of n and the atomic number of the halogen.

Bu₂GeH₂ reduces iodobenzene with greater difficulty than it reduces aliphatic monohalides. At 220°C, Bu₃GeH reduces CCl₄ to HCCl₃ almost quantitatively. Triorganylgermanes readily reduce acyl chlorides and chloromethyl ether, preferably in the presence of traces of AlCl₃. In 1964, it was found that organogermainium hydrides also readily reduced N-halosuccinimides.

In 1966, Vyazankin and Bochkarev found that, depending on the reaction conditions, heating of triethylgermane and elementary sulfur, selenium and tellurium gave the respective triethylgermylchalcogenols Et₃GeEH (E=S, Se) or bis(triethylgermyl)chalcogenides (Et₃Ge)₂E (E=S, Se, Te). The latter were also formed when diethylselenide and diethyltelluride were used instead of Se and Te. The reaction of Et₃GeH and Et₃SnH afforded unsymmetrical chalcogenides Et₃GeESnEt₃ (E=S, Se). Vyazankin and coworkers determined that the M–H bond reactivity with chalcogens increased considerably in the following order for M: Si < Ge < Sn.
F. Organogermanium Chalcogen Derivatives

Organogermanium compounds in which the Ge is bonded to a Group 16 element (chalcogen) were first encountered in 1925.

The first compounds having germoxane Ge—O bonds were Ph₃GeOH, Ph₃GeOGePh₃ and (Ph₂GeO)₄. In 1925, Morgan and Drew synthesized hexaphenyldigermoxane in quantitative yield by the reaction of aqueous-alcoholic AgNO₃ with Ph₃GeBr. The germoxane quantitatively generated Ph₃GeBr by reaction with concentrated HBr. In 1930, Kraus and Wooster obtained Ph₃GeOGePh₃ by hydrolysis of Ph₃GeNH₂. They discovered that the digermoxane was cleaved to Ph₃GeONa and Ph₃GeNa by Na in liquid ammonia.

In 1933, Simons and coworkers showed that hexaaryldigermoxanes Ar₃GeOGeAr₃ (Ar = 3-MeC₆H₄, 4-MeC₆H₄) were formed not only by the reaction of aqueous-alcoholic AgNO₃ with Ar₃GeBr, but also by a 0.5N NaOH solution. (2-MeC₆H₄)₃GeCl and aqueous-alcoholic AgNO₃ gave (2-MeC₆H₄)₃GeOH. In 1934, Bauer and Burschkies obtained (PhCH₂)₃GeOGe(Ph₂Ph)₃ by the same method. When concentrated HHal was added to the latter, the corresponding tribenzylhalogermanes were isolated.

In 1930, Dennis and Patnode first reported that self-condensation of trimethylgermanol Me₃GeOH under anhydrous conditions led to Me₃GeOGeMe₃ which, however, was neither characterized nor examined. In 1961, Schmidt and Ruidisch, Griffiths and Onyszchuk and others in 1966 simultaneously synthesized hexamethyldigermoxane by the reaction of Me₂GeX (X = Cl, Br) and Ag₂CO₃. In 1932, Kraus and Flood obtained hexaethyldigermoxane Et₃GeOGeEt₃ nearly quantitatively by hydrolysis of Et₃GeBr with aqueous KOH or NaOH solutions. It was transformed to the corresponding triethylhalogermanes by reaction with concentrated HCl or HBr. The reaction of Et₃GeOGeEt₃ and Li gave an equimolar mixture of Et₃GeOLi and Et₃GeLi.

In 1951, Anderson obtained hexaethyldigermoxane by reacting Et₃GeBr with Ag₂CO₃ and studied its cleavage by HNCS. Later, he obtained R₃GeOGeR₃ with R = Pr, Bu, i-Pr, and investigated their cleavage by organic and inorganic acids. Me₃GeOGeMe₃ was even cleaved with such an exotic reagent as Me(PO)F₂. Hexaorganyldigermoxanes carrying bulky substituents could not generally be obtained by hydrolysis of the corresponding triorganylhalogermanes. However, they were produced by other methods. For example, in 1953, Anderson synthesized R₃GeOGeR₃, R = i-Pr by the reaction of i-Pr₃GeBr and Ag₂CO₃. The cleavage of hexaisopropyldigermoxanes with inorganic acids HX resulted in i-Pr₃GeX (X = F, Cl, Br, I, NCS).

Triphenylgermanol was the first organogermanium compound containing the Ge—OH group. Contrary to expectations, attempts by Morgan and Drew, Kraus and Foster to obtain Ph₃GeOH by hydrolysis of Ph₃GeBr had failed and Ph₃GeOGePh₃ was always the only reaction product. Nevertheless, in 1954, Brook and Gilman obtained high yield of Ph₃GeOH by the reaction of Ph₃GeBr in aqueous-alcoholic KOH. However, Kraus and Foster synthesized triphenylgermanol for the first time in 1927 by hydrolysis of Ph₃GeONa or by treating the latter with NH₄Br in liquid ammonia. The Ph₃GeONa was prepared by oxidation of Ph₃GeNa in the same solvent. In 1966, the synthesis of Ph₃GeOH by a slow hydrolysis of Ph₃GeH₃ was reported.

Dennis and Patnode assumed the existence of trimethylgermanol, but neither they nor Schmidt and Ruidisch succeeded in isolating it. Schmidt and Ruidisch used titrimetric and cryoscopic methods to show that Me₃GeCl was hydrolyzed by water to Me₃GeOH,
but its attempted isolation from the aqueous solution failed and only Me₃GeOGeMe₃ was isolated. However, lithium trimethylgermanolate Me₃GeOLi was obtained by cleavage of Me₃GeOGeMe₃ with methylthiium. Et₃GeBr hydrolysis had not resulted in triethylgermanol and hexaethyldigermoxane was always formed instead.

It was not possible to isolate trialkylgermanols R₃GeOH with R = Me, Et, Pr, Bu until 1970, since they turned out to be considerably less stable than the isostructural trialkylsilanols and trialkylstannanols. Nevertheless, when the germanium atom was bonded to bulky substituents such as i-Pr, c-C₆H₁₁, 2-MeC₆H₄ and 1-C₁₀H₇, the corresponding rather stable triorganylgermanoles were isolated. Thus, in 1932, Bauer and Burschkies synthesized tricyclohexylgermanol by the reaction of (c-C₆H₁₁)₃GeBr with aqueous-alcoholic AgNO₃. Johnson and Nebergall repeated this reaction after 17 years. Simons and coworkers similarly obtained (2-MeC₆H₄)₃GeOH from the appropriate chloride.

In 1952, West successfully used for the first time the reaction of R₃GeX for the synthesis of (1-C₁₀H₇)₃GeOH. The latter was so stable that it was transformed slowly and partially to the corresponding digermoxane only at 175°C during 24 hours.

Triisopropylgermanol was first synthesized by Anderson in 1954 by hydrolysis of i-Pr₃GeBr in aqueous 6N NaOH solution. Later, he used i-Pr₃GeCl for obtaining the same product which he obtained by alkali hydrolysis of the reaction products of GeBr₄ with excess i-PrMgBr (i.e. i-Pr₃GeBr). The i-Pr₃GeOH was then converted to i-Pr₃GeX by reaction with HX (X = F, Cl, I).

Compounds with R = Ph were the first representatives of perorganylcyclogermoxanes (R₂GeO)ₙ and the corresponding linear polymers HO(R₂GeO)ₙH. In 1925, Morgan and Drew isolated two products from hydrolysis of Ph₂GeBr₂ which were described as HO(Ph₂GeO)₄ and (Ph₂GeO)₄ and named according to Kipping’s nomenclature ‘trianhydrotetrakis(diphenylgermanediol)’ and ‘tetraanhydrotetrakis(diphenylgermanediol)’, respectively.

Five years later Kraus and Brown found out that the solid products of hydrolysis of Ph₂GeBr₂ with concentrated aqueous ammonia have the (Ph₂GeO)₂ structure.

In 1960, Metlesics and Zeiss investigated the thermal decomposition of (Ph₂GeO)₄ and (Ph₂GeO)₂ in vacuum, which resulted in (Ph₂GeO)₃. In the same year Brown and Rochow similarly obtained (Me₂GeO)₃ from thermolysis of the products of the hydrolysis of Me₂GeCl₂.

In 1932, Flood isolated two products with a composition of Et₂GeO from the aqueous NaOH hydrolysis of Et₂GeBr₂. A liquid was identified as hexaethylcyclotrigermoxane (Et₂GeO)₃, where the other, an insoluble solid, was ascribed to the dimer. In 1950, Anderson reproduced the experiment, and suggested that the latter was octaethylcyclotetragermoxane (Et₂GeO)₄.

In 1948, Rochow discovered that the hydrolysis product of Me₂GeCl₂ was easily dissolved in water in contrast to the hydrolysis product of Me₂SiCl₂. The solution was evaporated without leaving any residue, indicating the formation of volatile hydrolysis products. This was also observed in the reaction of Me₂GeCl₂ with aqueous ammonia. This led Rochow to the conclusion that the hydrolysis reaction of Me₂GeCl₂ was reversible.

In 1948, Trautman and Ambrose patented a method for producing (Et₂GeO)₃. In 1953, Anderson synthesized (i-Pr₂GeO)₃, the first cyclogermoxane having rather bulky substituents at the Ge atom, by hydrolysis of the reaction products of GeBr₄ and i-PrMgBr with aqueous NaOH. Hexaisopropylcyclotrigermoxane cleavage by appropriate acids gave i-Pr₂GeX₂ (X = F, Cl, Br, I).
According to Mazerolles\textsuperscript{385}, the oxidation of germacycloalkanes \((\text{CH}_2)_n\text{GeH}_2\), \(n = 4\) gave the corresponding cyclotrigermoxane \([\text{(CH}_2\text{)}_4\text{GeO}]_3\) but, when \(n = 5\), a mixture of \([\text{(CH}_2\text{)}_5\text{GeO}]_4\) and \([\text{(CH}_2\text{)}_5\text{Ge(H)}\text{OH}]\) was formed.

The pioneers of organogermanium chemistry, Morgan and Drew\textsuperscript{149}, were the first to synthesize polyorganylgermoxanol and polyorganylgermsesquioxane, which for a long time were termed organyl germanoic acid and its anhydride, respectively. The amorphous polymer soluble in alkalis, obtained by hydrolysis of \(\text{PhGeBr}_3\), had a composition varying from \(\text{PhGeO}_2\text{H}\) to \(\text{PhGeO}_1\text{.5}\), depending on the reaction conditions. The authors were sure that the product had a structure intermediate between those of phenylgermanoic acid \(\text{PhGeOOH}\) and its anhydride \((\text{PhGeO})_2\text{O}\).

In 1927, Orndorff, Tabern and Dennis\textsuperscript{145} synthesized the aforementioned anhydride, i.e. polyphenylgermsesquioxane \((\text{PhGeO}_1\text{.5})_n\), by treatment of \(\text{PhGeCl}_3\) with a dilute aqueous ammonia solution. The anhydride had high solubility in alkalis and could be re-precipitated from the alkali solution by carbon dioxide. Other polyorganylgermsesquioxanes \((\text{RGeO}_1\text{.5})_n\) with \(\text{R} = \text{PhCH}_2, 4\text{-MeC}_6\text{H}_4\) and \(\text{Me}_2\text{NC}_6\text{H}_4\) were produced analogously. Five years later Bauer and Burschkies\textsuperscript{181} described a few more polyorganylgermsesquioxanes.

The first polyalkylgermsesquioxane \((\text{EtGeO}_1\text{.5})_n\) was obtained by Flood\textsuperscript{188} as a by-product of a reaction that he investigated. A year later he synthesized it by the reaction of \(\text{EtGeI}_3\) and \(\text{Ag}_2\text{O}\) or by hydrolysis of \((\text{EtGeN})_n\), the product of ammonolysis of \(\text{EtGeI}_3\)\textsuperscript{306}. In 1939, Tchakirian\textsuperscript{386} obtained ‘alkylgermanium acids’ \(\text{RGeOOH}\) (\(\text{R} = \text{Me, Et}\)) by hydrolysis of \(\text{RGeCl}_3\). Analogously, ‘germanomalonic acid’ \(\text{CH}_2\text{(GeOOH)}_2\) was synthesized from \(\text{CH}_2\text{(GeCl)}_3\).

Organoxy and acyloxy derivatives having \(\text{Ge}--\text{OR}\) and \(\text{Ge}--\text{OOCR}\) groups as well as a heterogermoxane \(\text{Ge}--\text{OM}\) group (\(\text{M} = \text{a metal or a nonmetal atom}\)) belong to organogermanium compounds with germoxane bonds. In 1949, Anderson\textsuperscript{387} reported the formation of alkylalkoxygermanes \(\text{Et}_4\text{–}_n\text{Ge(OR)}_n\) (\(\text{R} = \text{Me, Et, Bu}; \text{n} = 1, 2\)) during the reaction of \(\text{EtGeI}_3\) and the appropriate alcohols; he did not isolate or characterize the compounds. In 1954, West and coworkers\textsuperscript{388} described the synthesis of all the methylmethoxygermanes by the reaction of \(\text{Me}_2\text{GeI}_2\) and \(\text{MeGeCl}_3\) with sodium methoxide. In 1956, Anderson\textsuperscript{389} also synthesized the first trialkylaryloxygermanes \(\text{Et}_3\text{GeOC}_6\text{H}_4\text{R} (\text{R} = 3\text{-Me, 2-NH}_2)\textsuperscript{389}\). As early as in 1962, Lesbre and Satge\textsuperscript{360} produced the \(\text{Et}_3\text{GeOPh}\), the simplest representative of this series. \(\text{Et}_3\text{GeOCH}_2\text{Ph}\)\textsuperscript{280} was synthesized at the same time\textsuperscript{280}. In 1961, Griffiths and Onyszchuk\textsuperscript{373} similarly obtained \(\text{Me}_3\text{GeOMe}\). In 1954, Brook and Gilman\textsuperscript{195} pointed out that one of the first arylalkoxygermanes \(\text{Ph}_3\text{GeOMe}\) was the thermal decomposition product of \(\text{Ph}_3\text{GeCOOMe}\) at 250\textdegree C with CO elimination. For comparison, triphenylmethoxygermane was synthesized from \(\text{Ph}_3\text{GeBr}\) and \(\text{MeONa}\). In 1968, Peddle and Ward\textsuperscript{390} discovered the rearrangement of \(\text{Ph}_3\text{GeH}_2\text{OMe}\) to \(\text{Ph}_3\text{GeOMe}\).

In 1961, Griffiths and Onyszchuk\textsuperscript{373} found that the reaction of \(\text{MeGeH}_2\text{Br}\) and \(\text{MeONa}\) at \(-80\textdegree C\) gave \(\text{MeGeH}_2\text{OMe}\), which slowly decomposed to form the polymer \((\text{MeGeH})_n\) and \(\text{MeOH}\).

In 1962, two new approaches to trialkylalkoxygermane were introduced at the Satge laboratory\textsuperscript{36}. The first was based on the dehydrocondensation of trialkylgermanes and alcohols or glycols. Using \(\text{R}_2\text{GeH}_2\) led not only to \(\text{R}_2\text{GeOR}_2\), but also to \(\text{R}_2\text{GeHOR}'\). Dehydrocondensation of \(\text{Bu}_2\text{GeH}_2\) with \(\text{HO(CH}_2\text{)}_4\text{OH}\) resulted in 2,2-dibutyl-1,3-dioxo-2-germacycloheptane. A year later Wieber and Schmidt\textsuperscript{391} synthesized one of the simplest heterocyclic systems, 2,2-dimethyl-1,3-dioxo-2-germacyclopentane, by the reaction of \(\text{Me}_2\text{GeCl}_2\) and ethylene glycol in the presence of \(\text{Et}_3\text{N}\). They also produced the benzyl
derivatives of 2,2-dimethyl-1,3-dioxa-2-germacyclopentane and 2,2-dimethyl-1,4-dioxa-2-
-germacyclohexane. The second approach to compounds \( \text{R}_3\text{GeOR} \) was the addition reaction of \( \text{R}_2\text{GeH} \) to carbonyl compounds in the presence of copper powder.

In 1964, Satge used a re-alkoxylation reaction, with alcohols having boiling points higher than those of \( \text{MeOH} \) or \( \text{EtOH} \), to replace the alkoxy group in \( \text{R}_3\text{GeOR} \) by another alkoxy group. This method was used later by other investigators.

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not occur with acetic acid. In the reaction with $\text{Et}_3\text{GeH}$ the $\text{RCOOH}$ ($\text{R} = \text{Cl}_3\text{C}$, $\text{Br}_3\text{C}$, $\text{ICH}_2$) behaved in a quite different manner and were reduced to $\text{CH}_3\text{COOH}$.

In the period of 1951 till 1957, Anderson enriched the acyloxygermane chemistry by sixty-six compounds $\text{R}_4-n\text{Ge(OOCR)}_n$ with $\text{R} = \text{Et, Pr, i-Pr, Bu, c-C}_6\text{H}_{11}$; $\text{R}' = \text{H, Alk, Ar, haloalkyl}$; $n = 1–3$.

In 1962, Lesbre and Satge discovered that the dehydrocondensation reaction of trialkylgermane and carboxylic acids could be catalyzed by copper powder. For instance, the reaction of $\text{Bu}_3\text{GeH}$ and $\text{MeCOOH}$ gave $\text{Bu}_3\text{GeOOCMe}$ in 60% yield.

In 1954, Brook and Gilman synthesized $\text{Ph}_3\text{GeOOCCGePh}_3$ by the reaction of $\text{Ph}_3\text{GeBr}$ and $\text{Ph}_3\text{GeCOONa}$.

A year later Brook discovered that under short heating to 200°C triphenylgermanecarboxylic acid $\text{Ph}_3\text{GeCOOH}$ eliminated $\text{CO}$ and $\text{H}_2\text{O}$ and transformed to $\text{Ph}_3\text{GeOOCGePh}_3$. Further heating of the latter afforded $\text{Ph}_3\text{GeOGePh}_3$. Evidently, $\text{Ph}_3\text{GeOH}$ was an intermediate product in the initial stage of the thermolysis.

The first organogermanium compounds having a metal-germoxane $\text{Ge}/\text{M}$ group were alkali metal triorganylgermanolates $\text{R}_3\text{GeOM}$ produced in 1925–1932 by Morgan and Drew, as well as by Kraus and coworkers. Later, they and many other investigators obtained and used Li and Na germanolates and $\text{R}_3\text{GeOMgX}$ for synthetic purposes.

Among heterogermoxanes in which the germanium atom was bonded via oxygen to a nonmetal (metalloid) atom, bis(trialkylgermyl)sulfates ($\text{R}_3\text{GeO})_2\text{SO}_2$ with $\text{R} = \text{Et, Pr, i-Pr}$ and cyclic dialkylgermylene sulfates ($\text{R}_2\text{GeO})_2\text{SO}_2$ with $\text{R} = \text{Me, Et, Pr, i-Pr}$ were the first to be synthesized by Anderson in 1950–1956. For the synthesis of compounds with $\text{R} = \text{Et}$, the reactions of $\text{H}_2\text{SO}_4$ with $\text{Et}_3\text{GeOGeEt}_3$ and ($\text{Et}_2\text{GeO})_4$ were first used. Later, ($\text{R}_3\text{GeO})_2\text{SO}_2$ and ($\text{R}_2\text{GeO})_2\text{SO}_2$ with $\text{R} = \text{Me, Et, Pr, i-Pr}$ were obtained by the reaction of $\text{H}_2\text{SO}_4$ with $\text{R}_3\text{GeOOCMe}$, $\text{i-Pr}_3\text{GeOH}$ and $\text{R}_2\text{Ge(OOCMe)}_2$. Anderson used the reactions of $\text{Et}_3\text{GeH}$ and $\text{H}_2\text{SO}_4$ or $\text{HgSO}_4$ for synthesis of bis(triethylgermyl) compounds. In 1951, he also produced the first organogermanium compound having a $\text{GeO}N$ group, i.e. $\text{Et}_3\text{GeONO}_2$ by the reaction of $\text{Et}_3\text{GeBr}$ and $\text{AgNO}_3$. In 1955, Rochow and Allred obtained $\text{Me}_2\text{GeCrO}_4$, isostructural to ($\text{R}_2\text{GeSO}_4)_2$ by the reaction of $\text{Me}_2\text{GeCl}_2$ and $\text{K}_2\text{CrO}_4$ in aqueous media.

In 1961, Satge carried out the dehydrocondensation of $\text{Et}_3\text{GeH}$ and $\text{PhSO}_3\text{H}$, which resulted in $\text{Et}_3\text{GeOSO}_2\text{Ph}$.

In 1950–1967 Schmidt, Schmidbaur and Ruidisch synthesized a large series of heterogermoxanes having $\text{GeO}M$ groups with $\text{M} = \text{B, Al}_4$, $\text{Ga}_4$, $\text{In}_4$, $\text{Si}_4$, $\text{N}_4$, $\text{P}_4$, $\text{As}_4$, $\text{S}_4$, $\text{Se}_4$, $\text{Cl}_4$, $\text{V}_4$, $\text{Cr}_4$ and $\text{Re}_4$. Those were mostly the trimethylgermyl esters of the corresponding inorganic acids such as ($\text{Me}_3\text{GeO})_n\text{Y}$ with $\text{Y} = \text{NO}_2$, $\text{ClO}_3$, $\text{ReO}_3$ ($n = 1$); $\text{SO}_2$, $\text{SeO}_2$, $\text{CrO}_2$ ($n = 2$); $\text{B, PO, AsO, VO}$ ($n = 3$). They were produced by hexamethyldigermoxane cleavage with anhydrides of inorganic acids: $\text{P}_2\text{O}_5$, $\text{As}_2\text{O}_5$, $\text{SO}_3$, $\text{SeO}_3$, $\text{V}_2\text{O}_5$, $\text{CrO}_3$, $\text{Re}_2\text{O}_7$. The same types of compounds were synthesized by reaction of $\text{Me}_3\text{GeCl}$ with the silver salts of the corresponding acids. Similarly, Srivastava and Tandon prepared ($\text{Ph}_3\text{GeO})_2\text{Y}$ with $\text{Y} = \text{SO}_2$ and $\text{SeO}_2$.

In 1961–1964 Schmidbaur, Schmidt and coworkers synthesized a series of compounds $\text{R}_4-n\text{Ge(OSiMe)}_n$ with $\text{R} = \text{Me, Et, i-Pr}$; $n = 1–3$. For example, trimethyl(trimethylsiloxyl)germane $\text{Me}_3\text{GeOSiMe}_3$ and dimethylbis(trimethylsiloxyl)germane $\text{Me}_2\text{Ge(OSiMe)}_2$ were obtained by the reaction of alkali metal trimethylsilanolates $\text{Me}_2\text{SiOM}$ and $\text{Me}_3\text{GeCl}$ or $\text{Me}_2\text{GeCl}_2$. Schmidbaur and Schmidt studied the cleavage of trimethyl(trimethylsiloxyl)germane with sulfuric and chromic anhydrides ($\text{SO}_3$ and $\text{CrO}_3$), which gave $\text{Me}_2\text{GeOSO}_2\text{OSiMe}_3$ and $\text{Me}_3\text{GeOCrO}_2\text{OSiMe}_3$, respectively.
Me₃GeOSiMe₃ reacts with AlCl₃ and POCl₃, only the Si—O bond cleaves, thus leading to Me₃GeOAlCl₂ and Me₃GeOPOCl₂, respectively.

By dehydrocondensation of B(OH)₃ with Et₃GeH in 1962 Lesbre and Satge obtained tris(triethylgermyl)borate (Et₃GeO)₃B.

Cleavages of the Ge—O bond in Ge—O—Ge and Ge—O—Si groups are much easier than that for Si—O—Si groups. This indicates that the Ge—O bond is highly reactive. However, the heterolytic cleavage of Sn—O and Pb—O bonds was much easier (see Sections III and IV) than that for the Ge—O bond.

In 1967 Armer and Schmidbaur obtained metallogermanoxanes (Me₂GeOMMe₂)₂ with M = Al, Ga, In as well as (Me₂GeOGaPh₂)₂, (Ph₃GeOGaMe₂)₂ and (Ph₃GeOGaPh₃)₂. All these compounds seemed to be dimers. Subsequently, Davies and coworkers synthesized the similar tin and lead derivatives Ph₃GeOSnEt₃ and Ph₃GeOPbPh₃.

Organogermanes possessing a germthiane Ge—S bond were first prepared at the Dennis laboratory in 1927. These were three-dimensional polyarylgermosesquithianes (RGeS₁₅)n with R = Ph, 4-MeC₆H₄, Et₂NC₆H₄, produced by the action of H₂S on the corresponding (RGeO₁₅)n. At the time the compounds were considered to be the sulfur analogs of anhydrides of arylgermanoic acids, (RGeS)=S₂.

Five years later a series of organylgermsesquithianes (R₃GeS₁₅)n (R = Ph, 4-MeC₆H₄, 1-C₁₀H₇, Me₂NC₆H₄, Et₂NC₆H₄) was synthesized by the same method by Bauer and Burschkes and later by an easier method by Reichle.

In 1967, when studying the reaction of MeGeBr₃ and H₂S in the presence of Et₃N, Moedritzer prepared oligomeric (MeGeS₁₅)₄, apparently of tetrahedral structure.

Cyclic perorganycyclogermthianes oligomers (R₂GeS)ₙ became known much later. In 1948–1950 Rochow obtained the first (Me₂GeS)ₙ by the reaction of H₂S and Me₂GeCl₂ in a 6N H₂SO₄ solution. The crystalline product which has a specific pepper and onion smell was slowly hydrolyzed to H₂S when exposed to atmospheric moisture, and also in boiling water. In dilute acids the hydrolysis is much faster. This was patented later by an easier method by Reichle.

In 1956, Anderson synthesized the first four-membered tetraisopropylcyclogermthiane (i-Pr₂GeS)₂ by the reaction of i-Pr₂GeI₂ with Ag₂S. In 1965 its analog (Bu₂GeS)₂ was obtained by passing gaseous H₂S through a solution of Bu₂Ge(OR)₂ (R = Bu, i-Bu) in the corresponding alcohol. When R = i-Bu the reaction occurred only in the presence of PhSO₃H.

In 1963, Schmidt and Schumann found that heating Bu₄Ge with sulfur at 250°C gave (Bu₂GeS)₃ and Bu₂S. Bu₄-ₙGeSBuₙ, n = 1, 2 were the intermediate products. A similar reaction of sulfur and Ph₄Ge at 270°C gave elementary germanium and Ph₂S, the final thermolysis products of the intermediate (Ph₂GeS)₃. The latter was first obtained by Reichle in 1961 by the reaction of (Ph₂GeO)₃ with H₂S in st atu nascendi in aqueous media. In 1963, Henry and Davidson obtained (Ph₂GeS)ₙ with n = 2, 3 by the reaction of Ph₂Ge(SNa)₂ and PhCOCl.

Investigations of the chemical transformations of (R₂GeS)ₙ started in 1953. West succeeded in reducing (Me₂GeS)₃ to Me₂GeH₂ by reaction with zinc amalgam and HCl in an alcoholic media. In 1956, Anderson described the reactions of (i-Pr₂GeS)₂ with silver bromide, cyanide and acetate. Moedritzer and van Wazer investigated the exchange reactions of (Me₂GeS)₃ with Me₂GeX₂ (X = Cl, Br, I), and with (Me₂SiS)₃.

Monomeric organogermanium compounds having digermthiane (Ge—S—Ge) groups, i.e. hexaorganyldigermthianes R₃GeSGeR₃, R = Et, Ph, 4-MeC₆H₄, 4-PhC₆H₄ and...
1. Genesis and evolution in the organic chemistry of Ge, Sn, and Pb compounds

PhCH₂ were produced for the first time by Burschkies in 1936 via the reaction of the corresponding R₃GeBr with aqueous or alcoholic Na₂S solutions. The reaction of (c-C₆H₁₁)₃GeBr and Na₂S resulted in hexacyclohexyldigermperthiane (c-C₆H₁₁)₃GeSSGe(c-C₆H₁₁-c)₃.

In 1956, Anderson synthesized (i-Pr)₃GeSGe(i-Pr)₃ by reacting Ag₂S with i-Pr₃GeI. In 1965–1966, Satge and Lesbre and Cumper and coworkers produced hexaalkyldigermthianes R₃GeGeR₃, R = Et, Bu in high yield by the same method.

In 1966 Abel, Brady and Armitage, and in 1968 Wieber and Swarzmann used the reaction of triorganylhalogermanes with H₂S in the presence of nitrogen bases for the synthesis of hexaorganyldigermthianes in analogy to the widely used method in organosilicon chemistry.

In 1963, Ruidisch and Schmidt discovered that the thermal decomposition of lithium trimethylgermanthiolate afforded Me₃GeGeMe₃ and Li₂S. They found that Me₃GeSSiMe₃ thermally disproportionated to Me₃GeGeMe₃ and Me₃SiSSiMe₃. In 1966, Vayzankin and coworkers decomposed Et₃GeSH at 130°C to H₂S and Et₃GeSGeEt₃. The latter product also produced in the reaction of Et₃GeSH with Et₃Hg. Finally, hexaorganyldigermthianes R₃GeGeR₃ were obtained by the reaction of R₃GeSLi with R₃GeX (R = Me, Ph; X = Cl, Br).

In 1962, Henry and Davidson synthesized octaphenyltrigermdithian Ph₃GeGePh₂SGePh₃, one of the first perorganyloligogermdithianes. They also obtained hexaphenyl-digermperthiane Ph₃GeSSGePh₃ having a Ge-S-S-Ge group by the oxidation of Ph₃GeSH with iodine. We note that the first compound of this type was described by Burschkies as early as 1936.

The trialkylgermylthio derivatives of Group 14 elements R₃GeSMR₃ (M = Si, Sn, Pb) are analogs of hexaalkyldigermthiane. They were first synthesized in the Schmidt laboratory. For example, R₃GeSMR₃ (M = Si, Sn, Pb; R = Me, Ph) was obtained by the reaction of R₃GeSLi with R₃MCl. Unsymmetrical compounds R₃GeSMR₃ were obtained by the reaction of R₃GeSLi with R₃MX (M = Si, Sn). In 1966, Vayzankin and coworkers obtained Et₃GeSSnEt₃ by dehydrocondensation of Et₃GeSH and Et₃SnH.

Triorganyl(organylthio)germanes R₃GeSR' should be considered as organogermanium compounds having a Ge-S-M group, when M = C. Anderson was the first to synthesize nine representatives of the Et₃GeSR series by heterofunctional condensation of triethylacetooxygermanes with aliphatic and aromatic thiols RSH, R = C₆-C₁₂ Alk, Ar.

In 1956, Anderson obtained triethyl(organylthio)germanes by cleavage of Et₃GeOEt with aromatic and aliphatic thiols. Later, Satge and Lesbre used this reaction for synthesis of Et₃GeSbU. In 1966, Abel and coworkers employed the reaction for the preparation of Me₃GeSCMe₃ from Me₃GeOGeMe₃ and Me₃CSH. They also demonstrated that the reaction of Me₃GeOEt and PhSH resulted in Me₃GeSPh. Satge and Lesbre obtained Bu₃GeSPh, Bu₃GeSC₆H₁₇-n and Et₂Ge(SPh)₂ by the reaction of PhSH or n-C₈H₁₇SH with Bu₃GeOMe and Et₂Ge(OMe)₂. They also cleaved (Et₃GeO)n with thiophenol to form Et₃Ge(SPh)₂. Similar transformations of a Si-O bond to a Si-S bond did not occur with organosilicon compounds. Anderson discovered re-thiylation of trialkyl(organylthio)germanes by higher alkanethiols and areneethiols. This process occurred smoothly only on heating > 170°C and when a sufficiently wide range exists between the boiling points of the starting and the resultant thiols. Following Anderson, other researchers used this reaction. Ph₃GeSH was also used in the reaction. The re-thiylation reaction resembles the reaction of PhSH with Et₃GeSGeEt₃ at 180–190°C which gives Et₃GeSPh and H₂S.
Satge and Lesbre\textsuperscript{346} used the reaction of thiols with $R_3GeNM$e$_2$ for the synthesis of triorganyl(alkylthio)germanes $R_3GeSR'$ ($R$ = $i$-Pr, $t$-Bu; $R'$ = $Bu$). A year after, Abel, Armitage and Brady\textsuperscript{375} employed the reaction of $Me_3GeNEt_2$ and $BuSH$ to produce $Me_3GeSBu$.

In 1962, Davidson, Hills and Henry\textsuperscript{437} obtained triphenyl(organylthio)germanes $Ph_3GeSR$ by the reaction of $Ph_3GeSNa$ with organic halides ($R$ = Me, Bu, CH$_2$Ph, COPh, CH$_2$SM$e$), and by reaction of the latter halides with $Ph_3GeSH$ in the presence of pyridine. For the synthesis of organogermanium halides with mercaptanes or with sodium mercaptides $RSNa$\textsuperscript{369,375} in the presence of organic bases\textsuperscript{369,438} were used. The reaction of $Me_3GeSLi$ and $Me_3CSH$ resulting in $Me_3GeSCMe_3$ was also described. Lead alkanethiolates $Pb(SR')_2$ with $R'$ = Et, $Bu$\textsuperscript{346,369,429} were also employed for the synthesis of $R_4Ge(SR')_n$ ($n$ = 1, 2) from $R_4GeX_n$ ($X$ = Cl, Br). Abel, Armitage and Brady\textsuperscript{375} succeeded in substituting the bromine atom in $Me_3GeBr$ by an alkylthio group by the action of $Me_3SiSR$ ($R$ = Et, $i$-Pr).

By using dimethyl dichlorogermane and aliphatic or aromatic dithiols, Wieber and Schmidt\textsuperscript{391,392,439} designed new heterocyclic systems in 1963–1964. In 1968, the reaction of $Me_2GeCl_2$ with $HS(CH_2)_nSH$ ($n$ = 2, 3) in the presence of $Et_3N$ enabled them to obtain the first of 2,2-dialkyl-1,3-dithia-2-germacycloalkanes\textsuperscript{392,439}. By the reaction of $Me_2GeCl_2$ or $MeCH_2(Cl)GeCl_2$ with 4-methylbenzene-1,2-dithiol in the presence of $Et_3N$ they produced the two isomeric ring-methyl derivatives 2,2-dimethyl-4,5-benza-1,3-dithia-2-germacyclopentane and 2-chloro-2-dimethyl-5,6-benza-1,4-dithia-2-germacyclohexane, respectively\textsuperscript{392}. Similarly, 2,2-dimethyl-1-oxa-3-thia-2-germacyclopentane\textsuperscript{391} was obtained from 2-mercaptoethanol.

In 1962, Lesbre and Satge\textsuperscript{360} first carried out the dehydrocondensation of organogermanium compounds having the Ge–H bond with thiols, by reacting $Ph_3GeH$ with $BuSH$ in the presence of a platinum catalyst to give $Ph_3GeSBu$. They later used this reaction in the presence of nickel catalyst\textsuperscript{346}. Thus, $Et_3GeSch_2CH_2SGeEt_3$ was formed by the dehydrocondensation reaction of $Et_3GeH$ with $HSC(CH_2)_2SH$. In addition, Satge and Lesbre\textsuperscript{346} discovered that triethylgermane cleaved Me$SSMe$ to give $Et_3GeSMe$ and Me$SH$.

Several reactions of triorganyl(alkylthio)germanes were investigated in 1962–1965. The Ge–S bond in these compounds was found to be chemically more stable than an Si–S bond, but much more reactive than Sn–S and Pb–S bonds. According to Satge and Lesbre\textsuperscript{346} and Hooton and Allred\textsuperscript{440}, long exposure to triorganyl(alkylthio)germanes ($Et_3GeBu$\textsuperscript{346}, $Me_3GeMe$ and $Ph_3GeMe$\textsuperscript{440}) to water either caused no change or only a slight hydrolysis (for $Et_3GeMe$\textsuperscript{346}). The alcoholysis of $R_3MSR'$ ($M$ = Ge) was much more difficult than that for $M$ = Si\textsuperscript{346,440}. Compounds $R_3GeSR'$ are easily oxidized by hydrogen peroxide up to $R_3GeOGeR_3$\textsuperscript{440}; $LiAlH_4$ reduces them to $R_3GeH$\textsuperscript{456} and aniline does not react with them. The Ge–S bond of $Ph_3GeSMe$ was so reactive that it was cleaved with methyl iodide to $Ph_3Ge$I and $Me_3S^+I^{-}$\textsuperscript{440}. Similarly, dimethyl sulfate transforms $Me_3GeSMe$ to $Me_3GeO$S$O_2$OMe\textsuperscript{440} and $Me_3S^+[MeS_4O_4]^{-}$. When organolithium or organomagnesium compounds $R'M$ ($R'$ = alkyl; $M$ = Li\textsuperscript{335}, MgX\textsuperscript{346}) reacted with $R_3GeSMe$ ($R$ = Et, Ph), the $SMe$ group was replaced by alkyl groups giving $R_3GeR'$ derivatives.

Triorganylgermanethiols $R_3GeSH$ were latecomers in organogermanium chemistry. The first representative of this class, i.e. $Ph_3GeSH$, was produced only in 1963 by Henry and Davidson\textsuperscript{428} by the reaction of $Ph_3GeBr$ with $H_2S$ in the presence of pyridine.

In 1966, Vyazankin and coworkers\textsuperscript{367,368} found that triethylgermanethiol $Et_3GeSH$ was formed by heating $Et_3GeH$ with sulfur at 140°C. Attempts of Henry and Davidson\textsuperscript{428} to obtain diphenylgermanedithiol from $Ph_2GeBr_2$ had failed, although they suggested that a rather labile $Ph_2Ge(SH)2$ could exist in the reaction mixture.
The first alkali metal triorganylgermanethiolate \( R_3GeSM \) was \( Ph_3GeSNa \), synthesized by Henry, Davidson and coworkers by the reaction of \( Ph_3GeBr \) with excess \( Na_2S \) in an alcoholic solution.

Ruidisch and Schmidt developed a new synthesis of lithium trimethylgermanethiolate \( Me_3GeSLi \) in quantitative yield by the reaction of \( (Me_2GeS)_3 \) with \( MeLi \). Later, Vyazankin and coworkers produced the analog \( Et_3GeSLi \) by the reaction of \( Li \) with \( Et_3GeSH \) in THF. \( Ph_3GeSLi \) was synthesized by the reaction of \( Ph_3GeLi \) with sulfur in THF.

Unlike the labile \( Ph_2Ge(SH)_2 \), its di-sodium salt, which was isolated by Henry and Davidson as the trihydrate \( R_2Ge(SNa)_2 \cdot 3H_2O \) from the reaction of \( Ph_2GeBr_2 \) with \( Na_2S \), turned out to be rather stable.

The chemical transformations of \( Et_3GeSH \) and \( Ph_3GeSH \) have been extensively investigated by Vyazankin and coworkers and by Henry and Davidson. The latter authors showed that the reaction of \( Ph_3GeSH \) with \( PhCOCl \) and \( (SCN)_2 \) resulted in \( Ph_3GeSCOPh \) and \( Ph_3GeSCN \), respectively. They failed in an attempted addition of \( Ph_3GeSH \) to an activated double bond.

Organogermanium compounds with \( Ge-NUL \) bond were prepared much later than their sulfur analogs. All of them were obtained in Schmidt’s and the Vyazankin’s laboratories. The first compound was hexamethylcyclotrimagermane \( (Me_2GeSe)_3 \), which Schmidt and Rui obtained by the reaction of \( Me_2GeCl_2 \) with \( Na_2Se \) in 1961, together with higher cyclogermaneselenanes \( (Me_2GeSe)_n \) and a minor amount of the linear polymer \( Cl(Me_2GeSe)_nCl \). Two years later \( (Me_2GeSe)_3 \) was synthesized again in Schmidt’s laboratory. Its analogs and homologs \( (R_2GeSe)_n \) as well as all the organylgermsesquiselenanes \( (RGeSe)_{1,5} \) were not described until 1970.

In 1963, Ruidisch and Schmidt generated the first hexaalkyldigermselenane \( R_3GeSeGeR_3 \), \( R = Me \), together with \( Li_2Se \) by thermal decomposition at \( >65^\circ C \) of \( Me_3GeSeLi \). The precursor \( Me_3GeSeLi \) was quantitatively produced by cleavage of \( (Me_2GeSe)_n \) with methylolithium or by the action of selenium on \( Me_2GeLi \). \( Ph_3GeSeLi \) was obtained similarly. \( Me_3GeSeGeMe_3 \) was also synthesized from \( Me_3GeSeLi \) and \( Me_3GeCl \). Lithium triethylgermaneselenolate was prepared by the reaction of \( Et_3GeSeH \) with \( Li \) in THF whereas the reaction of \( MeMgI \) upon \( Et_3GeSeH \) resulted in \( Et_3GeSeMgI \). The reaction of the latter with \( Et_3GeBr \) gave \( Et_3GeSeGeEt_3 \).

In 1965, \( Ph_3GeSeGePh_3 \) was synthesized in the same laboratory by reaction of \( Ph_3GeSeLi \) with \( Ph_3GeBr \). In 1966, Vyazankin and coworkers found that \( Et_3GeSeGeEt_3 \) was obtained in 22% yield upon heating \( Et_3GeH \) and \( Se \) at 200°C. It was suggested that \( Et_3GeSeH \) was an intermediate in the reaction and, indeed, it was obtained in 63% yield at 200°C. Heating \( Et_3GeSeH \) at 130°C for a long time gave 37% of \( Et_3GeSeGeEt_3 \). When trialkylgermanes \( R_3GeH \) reacted with \( Se \) at 200°C, \( R_3GeSeH \) (\( R = i-Pr, c-C_6H_11 \)) were obtained in 67% and 31% yield, respectively, together with the corresponding hexaorganyldigermselenanes \( R_3GeSeGeR_3 \). A more effective synthesis of \( Et_3GeSeGeEt_3 \) in 45% yield was the thermal (200°C) reaction of \( Et_3GeSeH \) with \( Et_3Se \). A convenient synthesis of hexaethylgermaneselenane was the reaction of \( Et_3GeSeLi \) and \( Et_3GeBr \). The reaction of \( Et_3GeSeH \) with \( Et_2Hg \) at 20°C afforded \( Et_3GeSeGeEt_3 \).

Triethyl(organyl}seleno)germanes \( Et_3GeSeR \) with \( R = Bu \), \( CH_2Ph \), \( CH_2CH_2Ph \) and \( CH_2CH_2COOEt \) became known in 1967–1969. Compounds with \( R = Bu \) and \( CH_2Ph \) were produced by the reaction of \( Et_3GeSeLi \) with \( BuBr \) and \( PhCH_2Cl \). Unexpectedly, the reaction of \( Et_3GeSeLi \) and 1,2-dibromoethane gave \( Et_3GeSeGeEt_3 \) and \( CH_2=CH_2 \). Other compounds were prepared by hydroselenation (i.e. by photochemical addition of \( Et_3GeSeH \) to styrene and ethyl acrylate). \( Et_3GeSeBu \) was also synthesized.
by the reaction of \((\text{Et}_3\text{Ge})_2\text{Hg}\) and \(\text{BuSeH}\)\(^{449}\). Compounds having a Ge–Se–M group \((M = \text{Si}, \text{Sn}, \text{Pb})\) were first obtained in Schmidt’s\(^{247,442,445,450}\), laboratory in 1963–1965. These were \(\text{R}_3\text{GeSeM}_3\), with \(M = \text{Si}^{445}, R = \text{Me}; M = \text{Sn}^{247,442,450}, \text{Pb}^{247}, R = \text{Ph}\), and were produced by the reaction of the corresponding \(\text{R}_3\text{GeSeLi}\) and \(\text{R}_3\text{MX} (X = \text{Cl}, \text{Br})^{247}\). \(\text{Ph}_3\text{GeSePh}_3\) was also synthesized, but with the ‘opposite’ reagents \(\text{Ph}_3\text{GeBr}\) with \(\text{Ph}_3\text{SnSeLi}^{442,450}\). Finally, the Vyazankin group obtained \(\text{Et}_3\text{GeSeGeEt}_3\) by the condensation of \(\text{Et}_3\text{GeSeH}\) with \(\text{Et}_3\text{SnH}^{367}\) or of \(\text{Et}_3\text{GeSeLi}\) with \(\text{Et}_3\text{SnCl}^{369}\).

In 1968, Mazerolles and coworkers\(^{451}\) found that selenium inserted into the C–Ge bond of octaorganylgermacyclobutanes \(\text{R}_2\text{Ge}(\text{CR}_2)_3\) gave octaorganyl-1-seleno-2-germcyclopentane.

The Vyazankin group studied some cleavage reactions of the Ge–Se bond. The reaction of \(\text{Et}_3\text{GeSeGeEt}_3\) with bromine resulted in \(\text{Et}_3\text{GeBr}\) and \(\text{Se}\), that with \(\text{HCl}\) led to \(\text{Et}_3\text{GeCl}\) and \(\text{H}_2\text{Se}^{449}\) and, with sulfur, \(\text{Et}_3\text{GeSGeEt}_3^{452}\) was formed.

Organogermanium compounds having Ge–Te bonds were also first prepared in Schmidt’s and Vyazankin’s laboratories in 1965–1967. Seven compounds \([\text{R}_3\text{GeTeGeR}_3 (R = \text{Et, Ph, } c\text{-C}_6\text{H}_11), \text{R}_3\text{GeTeR} (R = \text{Et}) \text{and } \text{R}_3\text{GeTeMR}_3 (M = \text{Si, Sn, Pb}; R = \text{Et, Ph})]\) were prepared in which the germanium atom was bound to the Group 14 element by the tellurium atom. \(\text{Ph}_3\text{GeTeLi}\) was synthesized along with these compounds by the reaction of \(\text{Ph}_3\text{GeLi}\) with tellurium in THF\(^{247,436,442,443}\). The reaction of \(\text{Ph}_3\text{GeTeLi}\) with \(\text{Ph}_3\text{GeBr}, \text{Ph}_3\text{SnCl}\) and \(\text{Ph}_3\text{PbCl}\) gave the corresponding \(\text{Ph}_3\text{GeTeMPh}_3 (M = \text{Ge, Sn, Pb})^{247}\).

Hexaethyldigermtellurane was obtained by heating \(\text{Et}_3\text{GeH}\) either with tellurium at 190–210\(^\circ\text{C}^{447}\) or with diethyltelluride at 140\(^\circ\text{C}^{368,447}\) in 75% and 58% yields, respectively. It was synthesized by the reaction of \(\text{Et}_3\text{GeH}\) with \((\text{Et}_3\text{Si})_2\text{Te}^{452}\). \(\text{Et}_3\text{GeTeEt}\) was obtained for the first time (in 28–39% yield) by heating \(\text{Et}_3\text{GeH}\) with \(\text{Et}_2\text{Te}\) at 140\(^\circ\text{C}^{368,447}\). The reaction of \(\text{Et}_3\text{GeTeEt}\) with \(\text{Et}_3\text{MH} (M = \text{Si, Ge, Sn})\) at 20\(^\circ\text{C}\) resulted in 60% \(\text{Et}_3\text{GeTeMEt}_3^{368,447}\). When \(\text{Et}_3\text{GeSeGeEt}_3\) reacted with \(\text{Et}_3\text{SnH}\) at 170\(^\circ\text{C}\), \(\text{Et}_3\text{GeH}\) and \((\text{Et}_3\text{Sn})_2\text{Te}\) were produced\(^{368}\).

Vyazankin and coworkers\(^{452}\) found that in the reaction of elementary S and Se with \(\text{Et}_3\text{GeTeGeEt}_3\) the tellurium atom was replaced by the other chalcogen.

### G. Organogermanium Pnicogen Derivatives

Among organogermanium derivatives in which the Ge atom is bound to Group 15 elements (pnicogens), the compounds having Ge–N bonds were the first to be studied.

The first compound of this family was tris(triphenylgermyl)amine \((\text{Ph}_3\text{Ge})_3\text{N}\), prepared by Kraus and Foster\(^{161}\) in 1927 by the reaction of \(\text{Ph}_3\text{GeBr}\) and liquid ammonia. In Kraus’s laboratory\(^{197,198,224,370}\) all the triphenylgermylamines of the \((\text{Ph}_3\text{Ge})_n\text{NH}_3–n\) series, namely \(\text{Ph}_3\text{GeNH}_2\), \((\text{Ph}_3\text{Ge})_2\text{NH}\) and \((\text{Ph}_3\text{Ge})_3\text{N}\), were synthesized. The hydrolytically very unstable \(\text{Ph}_3\text{GeNH}_2\) was produced by the reaction of gaseous ammonia and \(\text{Ph}_3\text{GeBr}\) in an inert solvent\(^{370}\). It was also synthesized by reaction of \(\text{Ph}_3\text{GeBr}\) and \(\text{KNH}_2\). With excess of \(\text{KNH}_2\) the product was \(\text{Ph}_3\text{GeNHK}^{370}\), which could be converted back to \(\text{Ph}_3\text{GeNH}_2\) with \(\text{NH}_2\text{Br}\). Kraus and coworkers found that \(\text{Ph}_3\text{GeNH}_2\) was formed as a side product of the reaction of \(\text{Ph}_3\text{GeNa}\) with aryl halides\(^{197}\) or methylene dihalides\(^{196,329}\) in liquid ammonia. They pointed out that by eliminating ammonia, \(\text{Ph}_3\text{GeNH}_2\) could be condensed to the first representative of hexaorganyldigermanazes i.e. \(\text{Ph}_3\text{GeNHNHGePh}_3^{370}\). When heating to 200\(^\circ\text{C}\), \(\text{Ph}_3\text{GeNH}_2\) was entirely converted to \((\text{Ph}_3\text{Ge})_3\text{N}^{370}\).

In 1930 Kraus and Brown\(^{226}\) synthesized \((\text{Ph}_2\text{GeNH})_n\), \(n = 3\) or 4 (although they considered the product to be ‘diphenylgermanium imine’ \(\text{Ph}_2\text{Ge} = \text{NH}\)), by the reaction of \(\text{Ph}_2\text{GeCl}_2\) and liquid \(\text{NH}_3\). The compound was hydrolytically unstable.
The first hexaalkyldigermazane Et₃GeNHGeEt₃ was obtained in 1932 by Kraus and Flood by reaction of Et₃GeBr with Na in liquid ammonia. Its hydrolysis gave hexaethylgermanoxane Et₃GeOGeEt₃. Ammonolysis of Et₃GeBr₂ gave (Et₃GeNH)₃, which was hydrolyzed extremely easily to (Et₃GeO)n (n = 3, 4) by fluoride. Flood in 1932, and much later Rijkens and van der Kerk, obtained (R₂GeNH)₃, R = Et, Bu by the reaction of Na in liquid ammonia with Et₂GeBr₂ and Bu₂GeCl₂, respectively. In 1933, Flood found that during ammonolysis of Et₂GeX₃ (X = I, Br) a solid product corresponding to Et₂GeN, ‘ethylgermanium nitride’, was formed. Its hydrolysis resulted in polyethylgermazanes (Et₃GeO₁.₅)n, ‘ethylgermanoic anhydride’. Therefore, Flood had prepared the first three-dimensional polyethylgermazane.

In 1931, Thomas and Southwood obtained pseudo-organic organyl- and diorganylamine derivatives of two- and four-valence germanium such as Ge(NHR)₂ (R = Et, Ph), Ge(NEt₂)₂, Ge(NHPh)₄ and Ge(NC₅H₉-c)₄.

Laubengayer and Reggel, in 1943, synthesized Me₃GeNMMe₂, the first organogerma-nium compound having a Ge—NR₂ group, by reacting Me₃GeBr and LiNMe₂. Analogous compounds with R = SiMe₃ were produced much later from Me₃GeCl or Me₂GeCl₂ and NaN(SiMe₃)₂.

In 1952, Anderson synthesized a series of ethyl(dialkylaminogermanes EtGe(NR₂)₃ (R = Me, Et) by the direct reaction of EtGeCl₃ with dialkylamines. In 1949–1951 he discovered a new class of organogerma-nium compounds having Ge—N bonds, the alkylisocyanatogermanes R₄-nGe(NCO)ₙ (R = Et, Pr, i-Pr, Bu; n = 1–3). They were obtained from R₄-nGeClₙ and AgNCO. Rochow was an invisible participant in the work, since he gave Anderson Et₂GeCl₂ and EtGeCl₃. In 1956, Anderson obtained i-Pr₂Ge(NCO)₂ from the reaction of i-Pr₂GeCl₂ and AgNCO, Anderson hydrolyzed the alkylisocyanatogermanes, and their hydrolysis rates appeared to be the faster for the compounds with higher values of n. The cleavage of the Ge—N bond in ethylisocyanatogermanes with alcohols R’OH resulted in R₄-nGe(O(R'))ₙ (R = Me, Et, Bu; R’ = Me, Et; n = 1, 2) and formation of H₂NCOOR. At the same time Anderson synthesized the first alkylisothioisocyanatogermanes R₄-nGe(NCS)ₙ (R = Et, Pr, Bu; n = 2, 3). Compounds such as R₃GeNCS and R₂Ge(NCS)₂, R = Et, Pr, Bu were obtained in 1951 by cleavage of R₃GeOGeR₃ and (R₂GeO)₃ with HNCS generated in situ. Analogously, i-Pr₂Ge(NCS)₂ was obtained from (i-Pr₂GeO)₃. Exchange processes have also been studied, such as those of Et₅GeNCS with AgNCO and of Et₃GeCN with AgNCS.

It is remarkable that the rather intensive investigations on nitrogen-containing organogerma-nium compounds during a quarter of a century were followed by reduced activity. From 1952 till 1963 they were mentioned only in seven publications, five of which devoted to compounds having the Ge—NC bond (Y = O, S). No new compounds having the digermazane group (Ge—N—Ge) have been reported during this period.

The activity in the field was then resumed. In 1963, Onyszchuk carried out the reaction of Me₃GeBr, Et₂GeCl₂ and Ph₂GeCl₂ with liquid ammonia at −78°C which gave the 1 : 1 adducts. On raising the temperature the products were converted to the corresponding ammonolysis products [Me₃GeNH]⁺Br⁻ and (R₂GeNH)ₙ (n = 2, 3).

In 1964, Ruidisch and Schmidt synthesized hexamethyldigermazane by the reaction of Me₃GeCl and gaseous NH₃ in diethyl ether. At −60°C a considerable quantity of (Me₃Ge)₃N was formed. In the same year the authors also obtained organogerma-nium azides Me₄-nGe(N₃)ₙ (n = 1, 2) by reacting Me₄-nGeClₙ and NaN₃. At the same time Thayer and West as well as Reichle synthesized Ph₃GeN₃ from Ph₃GeBr.

In 1964, Rijkens and van der Kerk obtained hexabutylcyclogermazane (Bu₂GeNH)₃ by the reaction of Bu₂GeCl₂ with a Na solution in liquid NH₃.
In 1964–1966, Satge and coworkers\textsuperscript{36,37} used reactions of alkylhalogermanes with amino lithium and organomagnesium derivatives to generate Ge–N bonds.

Satge and Baudet\textsuperscript{462} synthesized in 1966 hexaethyldigermazone by the reaction of Et\textsubscript{3}GeCl and LiNH\textsubscript{2} in THF. The extremely unstable Et\textsubscript{3}GeNH\textsubscript{2} was a probable intermediate in the reaction.

At the same year Massol and Satge\textsuperscript{356} discovered that the ammonolysis of Et\textsubscript{3}GeH\textsubscript{n}Cl (n = 1, 2) led to the corresponding trigermethylamines (Et\textsubscript{3}GeH\textsubscript{n})\textsubscript{3}N (when n = 1, Et\textsubscript{2}GeHNHGeEt\textsubscript{2} was also formed). By contrast, Et\textsubscript{3}GeCl (n = 0) did not give (Et\textsubscript{3}Ge)\textsubscript{3}N on reaction with ammonia. That indicated a steric effect of the R\textsubscript{3}GeH\textsubscript{n} group on the chlorides during ammonolysis. Accordingly Me\textsubscript{3}GeNMe\textsubscript{2}, which has less bulky substituents than Et\textsubscript{3}Ge, underwent ammonolysis to give (Me\textsubscript{3}Ge)\textsubscript{3}N. The latter was formed also by the reaction of Me\textsubscript{3}GeCl and LiNMe\textsubscript{3} or LiN\textsubscript{3}\textsuperscript{462} as well as by the reaction of MeLi and (ClMe\textsubscript{2}Ge)\textsubscript{3}N\textsuperscript{461}.

According to Wieber and Schwarzmann\textsuperscript{434}, ammonolysis of ClCH\textsubscript{2}Me\textsubscript{2}GeCl resulted in ClCH\textsubscript{2}Me\textsubscript{2}GeNHGeMe\textsubscript{2}CH\textsubscript{2}Cl, the first carbon functionalized hexaalkyldigermazone derivative.

In 1964–1965, Rijkens and coworkers synthesized a series of nitrogen heterocycles (pyrrole, pyrazole, imidazole, triazole, succinimide, phthalimide), N-triorganylgermyl derivatives, and studied their properties\textsuperscript{76,466}.

In 1969, Highsmith and Sisler\textsuperscript{467} attempted to repeat the reaction of Ph\textsubscript{3}GeBr and ammonia, described by Kraus and Foster\textsuperscript{161}, but they obtained only Ph\textsubscript{3}GeNHGePh\textsubscript{3} instead of (Ph\textsubscript{3}Ge)\textsubscript{3}N.

Since the first synthesis of organogermanium nitrogen derivatives it was found that the Ge–N bonds display high reactivity, especially an easy protolysis with water, alcohols, phenols, carboxylic acids, hydrohalic acids, SH–, NH–, PH– and CH–acids, etc\textsuperscript{36,37,77,346,347}. All these reactions were initiated by electrophilic attack of the reactant proton on the nitrogen atom\textsuperscript{76,468,469}.

In particular, Anderson\textsuperscript{457} in 1952 found out that the Ge–N bond in EtGe(NMe\textsubscript{2})\textsubscript{3} was cleaved by HI to give EtGeI\textsubscript{3}. From 1964 ammonolysis\textsuperscript{76,347}, aminolysis\textsuperscript{347}, amido-lysis\textsuperscript{347} and hydrazinolysis reactions of trialkyl(dimethylamino)germanes R\textsubscript{3}GeNMe\textsubscript{2} (R = Me, Et) resulting in R\textsubscript{3}GeNHGeR\textsubscript{3}, R\textsubscript{3}GeNHR\textsubscript{0}, R\textsubscript{3}GeNHCOR\textsubscript{0} and R\textsubscript{3}GeNHNHR\textsubscript{0}, respectively, were discovered.

Under strict reaction conditions (sometimes in the presence of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}) peralkyl-germazanes (R\textsubscript{3}Ge)nNH\textsubscript{3}\textsubscript{76,462} (n = 2, 3) were cleaved.

Schmidt and Ruidisch\textsuperscript{471} in 1964 were the first to cleave the Ge–N–Ge group with organometallic reagents in the reaction of (Me\textsubscript{2}GeNMe\textsubscript{3}) and MeLi, which gave Me\textsubscript{3}GeN(Li)Me.

In 1964–1969, cleavage reactions of the Ge–N bond by anhydrides, carboxylic acids chloroanhydrides\textsuperscript{347}, chloramine\textsuperscript{472}, metal halides\textsuperscript{473}, and trimethylchlorometalanes Me\textsubscript{3}MCl (M = Si, Ge, Sn, Pb) were described.

The addition reactions of trialkyl(dimethylamino)germanes to activated double and triple bonds were discovered in 1967–1968\textsuperscript{474,475}.

The first investigations of Satge and coworkers on the introduction of organic and inorganic compounds having M= Y groups\textsuperscript{470} (CO\textsubscript{2}, CS\textsubscript{2}\textsuperscript{347}, PhNCO, PhNCS\textsuperscript{476}, F\textsubscript{3}CCOCF\textsubscript{3}\textsuperscript{477}) into the Ge–N bond are of particular interest. Glockling and Hooton\textsuperscript{478} were the first to obtain in 1963 organogermanium compounds having Ge–P bonds (e.g. Et\textsubscript{3}GePPh\textsubscript{2}) by reaction of Et\textsubscript{3}GeBr with Ph\textsubscript{2}PLi. A year later Satge and coworkers\textsuperscript{347,462} synthesized the same compound by cleavage of Et\textsubscript{3}GeNMe\textsubscript{2} with diphenylphosphine.

In 1969, Schumann-Ruidisch and Kuhlmey\textsuperscript{479} carried out analogous reactions of Me\textsubscript{3}GeNMe\textsubscript{2} with RPH\textsubscript{2} (R = Me, Ph), which resulted in (Me\textsubscript{3}Ge)\textsubscript{2}PR and Me\textsubscript{3}GePHPH.
Norman proposed a new approach to the synthesis of compounds $R_3GePH_2$ by reaction of $R_3GeCl$ with LiAl($PH_2$)$_4$.

In 1965, Brooks and coworkers discovered that the reaction of Ph$_4-n$GeBr$_n$ ($n = 2, 3$) and Ph$_2$PLi afforded Ph$_4-n$Ge(PPh$_2$)$_n$. Satge and Couret similarly synthesized Et$_3GePEt_2$ from Et$_3GeCl$ and Et$_2$PLi.

In 1965–1966, Schumann and coworkers carried out the condensation of Ph$_3GeCl$ with PH$_3$ and PhPH$_2$, which led to (Ph$_3Ge$)$_3P$ and (Ph$_3Ge$)$_2PPh$, respectively. Ph$_3GeOH$ was formed by cleavage of these compounds by an alcoholic KOH solution. (Me$_3Ge$)$_3P$ was synthesized by the reaction of Me$_3GeNMe_2$ with PH$_3$.

The Ge-P bond turned out to be extremely active. For example, R$_3GePR_2$ (R = R' = Et, Ph) was easily cleaved by water, alcohols, carboxylic acids, HCl, HBr, thiols, aniline and ammonia. Oxidation of Et$_3GePPh_2$ by oxygen involved insertion into the Ge-P bond as well and resulted in Et$_3GeOPPOH_2$. The latter was also produced in the reaction of Et$_3GeGeEt_3$ and Ph$_2$POOH. When Et$_3GePPh_2$ reacted with bromine, Et$_3GeBr$ and Ph$_2PBr$ were formed. Butyllithium cleavage of Et$_3GePPh_2$ led to Et$_3GeBu$ and Ph$_2PLi$. It is noteworthy that the Ge-P bond in Et$_3GePPh_2$ was cleaved even by methyl iodine to give Et$_3GeI$ and Ph$_2PMe$. The reaction of Ph$_2PMe$ and excess of MeI gave [Me$_2Ph$_2P]$_3$I. When Et$_3GePPh_2$ and AgI were added to the reaction mixture, the complex [Et$_3GePPh_2$ AgI]$_4$ was produced.

CS$_2$, PhNCS, PhNCO, PrCHO, PhCHO, CH$_2$DO, CH$_2$CN and PhC=CH inserted into the Ge-P bond of Et$_3GePR_2$ (R = Et, Ph) similarly to their insertion into the Ge-N bond. Et$_3GeP$Et$_2$ added to $\alpha,\beta$-unsaturated aldehydes at the 1,4-positions.

There was only one report before 1970 on organogermanium arsenic derivatives. In 1966, Schumann and Blas prepared (Me$_3Ge$)$_3As$ by the reaction of Me$_3GeNMe_2$ with AsH$_3$ and described some of its properties.

H. Compounds having a Hypovalent and Hypervalent Germanium Atom

The formation of inorganic compounds of hypovalent (divalent) germanium such as dihalo germanium GeX$_2$ (i.e. dihalogermylenes) was already noted by Winkler in the 19th century. He reported the existence of GeCl$_2$ in HCl solution and of GeF$_2$ as the reduction product of K$_2$GeF$_6$ by hydrogen. However, only in the beginning of the 20th century did fundamental investigations of dihalo germanium, including monomeric GeX$_2$, start.

In 1926–1934, some methods for the gas-phase generation of monomeric inorganic derivatives of divalent germanium such as H$_2$Ge$^{432,492}$, F$_2$Ge$^{493,494}$, Cl$_2$Ge$^{495,496}$ and Br$_2$Ge$^{497}$ were developed. Dennis and Hance obtained solid GeI$_2$ for the first time in 1922. It turned out not to be a monomer, since the germanium atom was surrounded octahedrally with six iodine atoms in its crystal lattice. However, at a high temperature GeI$_2$ dissociated to form the monomeric molecules.

Interesting complexes of GeI$_2$ and CH$_3$NH$_2$ or Me$_4$NI have been described. The reaction of GeI$_2$ with NH$_3$ gave germanium(II) imide Ge=NH, which could be hydrolyzed to Ge(OH)$_2$, i.e. (H$_2$O·GeO) and NH$_3$. Complexes of GeF$_2$ with Et$_2$O and with Me$_2$SO$^{502}$ were described in 1960–1962 and series of complexes of GeF$_2$, GeCl$_2$, GeBr$_2$, and GeI$_2$ were obtained as well. Thus, the inorganic chemistry of germylenes was born almost simultaneously with their organogermanium chemistry.

Organogermanium derivatives R$_2$Ge, which are often regarded as monomers, proved to be cyclic oligomers or linear polymers. The first attempt to synthesize monomeric diorganylgermylenes was made by Kraus and Brown. In 1930 they tried to obtain diphenylgermylene by reduction of Ph$_2$GeCl$_2$ with sodium metal in boiling xylene, but...
the product was a mixture of cyclic oligomers \((\text{Ph}_2\text{Ge})_n\). Only in 1963 did Neumann and Kühllein\cite{199} determine that the main product of the reaction was octaphenylcyclotetragermane \((\text{Ph}_2\text{Ge})_4\), i.e. a tetravalent germanium derivative.

In the 1960s, Nefedov, and his coworkers, Kolesnikov\cite{201–207,507}, Neumann and coworkers\cite{175,199,200,508,509} started to study the generation of diorganylgermylenes. However, the reduction reactions of diorganyldihalogeranes by alkali metals, as well as the reaction of dihalogeranes with organometallic compounds (cf. Section II.B.) always resulted in the formation of cyclic oligomers, linear polymers or the insertion products of the \(R_2\text{Ge}\) moiety into bonds of the solvents or the reagents. For example, in 1954 Jacobs\cite{240} tried to produce dialkylgermylenes by reaction of \(\text{GeI}_2\) with a series of organometallic compounds (\(\text{EtLi}, \text{BuLi}, \text{Bu}_2\text{Zn}, \text{Et}_2\text{Hg}, \text{Bu}_2\text{Hg}\)). However, the only organogermanium compound that he was able to isolate was \(\text{IBu}_2\text{GeGeBu}_2\text{I}\). The latter was also formed along with metallic mercury in the reaction of \(\text{GeI}_2\) and \(\text{Bu}_2\text{Hg}\).

In spite of these failures, all the authors had no doubts that diorganylgermylenes were the intermediates in the reactions studied.

Nefedov and coworkers\cite{204,207,507} confirmed the generation of dimethylgermylene \(\text{Me}_2\text{Ge}\) in the reaction of \(\text{Me}_2\text{GeCl}_2\) and \(\text{Li}\) based on the fact that its addition product to ethylene was formed. According to Vyazankin and coworkers\cite{512} diethylgermylene was evidently an intermediate in the thermal \((200^\circ\text{C})\) decomposition of \(\text{Et}_2\text{GeGeEt}_3\) with \(\text{AlCl}_3\) catalyst which resulted in \((\text{Et}_2\text{Ge})_n\) and \(\text{Et}_4\text{Ge}\). In 1966, Bulten and Noltes\cite{513} observed an analogous decomposition of \(\text{ClEt}_2\text{GeGeEt}_2\text{Cl}\) and \(\text{Et}_3\text{GeGeEt}_2\text{Cl}\). In both cases one of the products obtained was \((\text{Et}_2\text{Ge})_n\), formed along with \(\text{Et}_2\text{GeCl}_2\) or \(\text{Et}_3\text{GeCl}\), respectively. The intermediate generation of \(\text{Et}_2\text{Ge}\) was confirmed by its insertion into the \(\text{Ge}–\text{Cl}\) bond of the precursor chloride with the formation of oligomers such as \(\text{Et}_3\text{Ge}(\text{Et}_2\text{Ge})_n\text{Cl}\) \((n = 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20)\).

Neumann and Kühllein\cite{175,199,509} found in 1963 another precursor of diorganylgermylenes, the organomercurygermanium polymer \(\left(–\text{Ph}_2\text{GeH}–\text{Hg}–\right)_n\), which was synthesized by the reaction of \(\text{Ph}_2\text{GeH}_2\) and \(\text{Et}_2\text{Hg}\). Unfortunately, in the early 1960s the Neumann laboratory did not have available spectroscopic techniques for the identification of the highly reactive short-lived diorganylgermylenes and other labile intermediates.

Nefedov and coworkers\cite{202} had proven in their first publication that \(\text{Me}_2\text{Ge}\) was the intermediate formed in the reaction of \(\text{Me}_2\text{GeCl}_2\) and \(\text{Li}\), since when the reaction was conducted in the presence of styrene, \(1,1\text{-dimethyl}-3,4\text{-diphenyl}-1\text{-germacyclopentane}\) was formed in \(40\%\) yield.

The possibility of thermal generation of diorganylgermylene was established for the first time at the Nefedov laboratory in 1964–1965\cite{203,205,207,507}. Thermolysis of \((\text{Me}_2\text{Ge})_n\) where \(n\) is \(ca\ 55\) at \(350–400^\circ\text{C}\) led to \(\text{Me}_2\text{Ge}\) which was identified by its addition products to tolan and ethylene, together with its dimeric and polymeric biradicals\cite{207} and to \((\text{Me}_2\text{Ge})_n\) \((n = 6, 5, 4, 3)\) as well. Shorigin, Nefedov and coworkers\cite{206} were the first to obtain the UV spectra of polydiorganylgermylenes \((\text{Me}_2\text{Ge})_n\).

The publications of Glockling and Hooton\cite{249} and of Summers\cite{239} were of special interest, because they reported the formation of diphenylgermylene from \(\text{Ph}_2\text{GeHOMe}\) by \(\alpha\)-elimination of methanol. This led to the conclusion that the intermediate products in the formation of \(\text{R}_2\text{Ge}\) from \(\text{R}_2\text{GeX}_2\) or \(\text{GeX}_2\) \((\text{X} = \text{halogen})\) were \(\text{R}_2\text{Ge}(\text{X})\text{M}\) \((\text{M} = \text{Li}, \text{Na}, \text{K}, \text{MgX})\), which further decomposed to \(\text{MX}\) by an \(\alpha\)-elimination process.

It was surprising that Neumann did not investigate the thermal and photochemical reactions of the decomposition of \((\text{Ph}_2\text{Ge})_n\).

Cited as follows, publications of Nefedov and Kolesnikov\cite{201–207,507}, Neumann\cite{175,199,200,508,509} and their coworkers can be regarded as the beginning of the chemistry of diorganylgermylenes.
1. Genesis and evolution in the organic chemistry of Ge, Sn, and Pb compounds

Entrapping and subsequent investigations of diorganylgermylenes in hydrocarbon or argon matrices were carried out only in the 1980s. Metlesics and Zeiss showed the possible existence of organylhalogermylenes. They considered PhClGe to be the intermediate formed in the reaction of PhGeCl3 and Li amalgam.

Kinetically stable diorganylgermylenes [(Me3Si)2CH]2Ge and [2,4,6-(Me3C)3C6H8- c]2Ge were obtained and described in the last quarter of the 20th century. Different transformations of diorganylgermylenes (especially their insertion and dimerization reactions) were studied in the 1980s. New precursors of diorganylgermylenes such as 7,7-diorganyl-7-germabenzonorbornadienes, Ar2Ge(SiMe3)2, Me2Ge(N3)2, and some heterocyclic compounds having endocyclic Ge–Ge bonds were discovered at that very time, but we cannot dwell on these investigations in more detail.

Short-lived Ge-centered free radicals of R3Ge belong to the hypovalent (trivalent) germanium derivatives. In 1953–1957, Gilman and coworkers, based on the dissociation of hexaphenylethane to free Ph3C radicals, tried to obtain the Ph3Ge radical by dissociation of Ph3GeMPh3 (M = C, Si, Ge, Sn).

The stability of the Ge/Ge bond in Ph3GeGePh3 to homolytic cleavage to Ph3Ge radicals was evidenced from the fact that the compound melted at 336 °C without decomposition. Hexaethyldigermane was thermally stable as well and could be distilled under atmospheric pressure at 265 °C.

The results of thermal decomposition of polydimethylgermylenes (Me2Ge)n provide evidence in favor of the formation of Ge-centered biradicals, (Me2Ge)n. It is suggested that the initial step of the thermal decomposition (>400 °C) of tetraalkyldigermans R4Ge (R = Me, Et), which are widely used in producing germanium films, involves the formation of free radicals R3Ge. We note that Gaddes and Mack in 1930 were the first to carry out thermal cleavage of Et4Ge starting at ca 420 °C. The final cleavage products seemed to be Ge and C4H10. It is very likely that the data on Ge-centered organogermanium free radicals reviewed in the period under discussion are limited to what was reported in the references mentioned above.

Compounds R2Ge=Y (Y = GeR2, CR2, NR, O, S), in which the Ge atom is three-coordinated and is bonded by a π(p–p) bond with a Ge atom or with another element, can be considered as hypovalent germanium derivatives. The simplest concept of germanium atoms binding in the R2Ge=GeR2 molecule can be presented in the following way: R2Ge=GeR2.

Information about compounds having Ge=Y bonds were published much later than the period considered above of organogermanium chemistry evolution. We only refer to some pertinent reviews.

Hypervalent germanium derivatives are compounds having penta-, hexa- and sometimes heptacoordinate germanium atom. Numerous publications are devoted to inorganic and pseudo-organic (with no C–Ge bonds) derivatives of this type.

Of particular interest are pseudo-organic compounds of hypervalent germanium such as germanium tetrahalide complexes with amines, complexes of GeX4 with β-diketones, polyatomic alcohols and phenols, phthalocyanines, and others. The first labile hypervalent organogermanium compound Ph3Ge(NH3)3Na was obtained by Kraus and Foster by cleavage of Ph3GeGePh3 with sodium in liquid ammonia.

The formation of organic derivatives of penta- and hexacoordinate germanium is due to a later time when the reactions of organohalogermanes were studied with ammonia and amines (see Section II.F). When these reactions were conducted at low temperatures, 1 : 1 and 1 : 2 adducts were formed. When heated >0 °C, the complexes of organohalogermanes with ammonia, primary and secondary amines decomposed to give compounds.
with a Ge–N bond and quaternary ammonium salts\textsuperscript{331}. Such reactions were described for the first time in 1926–1933\textsuperscript{148},\textsuperscript{188},\textsuperscript{453},\textsuperscript{529–533}. However, Kraus and Flood\textsuperscript{148} found that the only reaction product of Et\textsubscript{3}GeBr and liquid ammonia was the monoadduct [Et\textsubscript{3}GeNH\textsubscript{3}]\textsuperscript{+}Br\textsuperscript{−}. Organohalogermaines and tertiary amines formed rather stable 1 : 1 or 1 : 2 complexes, which were unstable toward hydrolysis.

Sowa and Kenny\textsuperscript{534} in 1952 patented the unusual complex compounds [R\textsubscript{4−n}Ge(N\textsuperscript{−})\textsubscript{n}]X\textsuperscript{−} (n = 1–4) obtained from R\textsubscript{4−n}GeX\textsubscript{n} and tertiary amines.

The first stable intramolecular complexes of pentacoordinate organogermaine derivatives (1-organylgermatranes RGe(OCH\textsubscript{2}CH\textsubscript{2})\textsubscript{3}N) having a transannular Ge–N bond were synthesized in the Voronkov laboratory in 1965\textsuperscript{397}. Their synthesis was based on the direct use of RGeCl\textsubscript{3} and (RGeO\textsubscript{1.5})\textsubscript{n}\textsuperscript{397,398}. Their molecular and crystalline structure\textsuperscript{83,535,536}, UV spectra\textsuperscript{537}, \textsuperscript{1}H\textsuperscript{538}, \textsuperscript{13}C\textsuperscript{539} and \textsuperscript{15}N\textsuperscript{540} NMR spectra as well as their biological activity\textsuperscript{398,541–543} have been investigated. Mironov, Gar and coworkers\textsuperscript{82,84} later contributed to the investigations of germatranes and their biological activity.

Beginning from 1989, another interesting series of intramolecular organogermaine complexes, such as Ge-substituted N-germylmethylactames, were investigated extensively by Baukov, Pestunovich, Voronkov, Struchkov and others\textsuperscript{544,545}.

I. Biological Activity

The biological activity of germanium compounds and their influence on the biosphere have been considered in detail in an excellent monograph of Latvian and Russian chemists published in 1990 (in which 767 references are cited\textsuperscript{86}) as well as in earlier reviews by the same authors\textsuperscript{82,546–548}.

Investigations of the effect of inorganic germanium compounds on living organisms began in 1922 when it was discovered that germanium dioxide stimulated erythropoiesis (production of red blood cells). In the same year the toxicity of GeO\textsubscript{2} was determined for the first time\textsuperscript{549–553}. The results of germanium dioxide toxicological studies were published in 1931–1944\textsuperscript{553–556}. The growing interest in the chemistry of germanium, especially in the middle of the 20th century, led to numerous investigations of the biological activity of inorganic compounds of this element (GeO\textsubscript{2}, RGeOOH and its salts, metal hexafluorogermanates, GeH\textsubscript{4}, GeCl\textsubscript{4}, GeF\textsubscript{4}, GeS\textsubscript{2}), which were undertaken mostly after 1953\textsuperscript{48,75,86}.

Even in the first half of the last century it was already established that many organogermaine compounds did not suppress Trypanosoma, Spirochaeta, Pneumococcus, Streptococcus\textsuperscript{557,558} and test rat sarcoma\textsuperscript{559}. Moreover, in 1935 Carpenter and coworkers\textsuperscript{560} found that (Me\textsubscript{2}GeO)\textsubscript{n} stimulated the growth of many kinds of microorganisms. Much later, Rochow and Sindler\textsuperscript{561} found that (Me\textsubscript{2}GeO)\textsubscript{4} did not show either toxic or irritating action on mammals (hamsters, rabbits). However, this oligomer exerted a teratogenic effect on chicken embryos and was more toxic to them than acetone\textsuperscript{576,562}. The toxicity of (R\textsubscript{2}GeO)\textsubscript{n} (R = Me, Et, Bu; n = 3, 4) was determined by Rijkens and van der Kerk\textsuperscript{77} and by Caujolle and coworkers\textsuperscript{563} in 1964–1966.

In 1936, Rothermundt and Burschkies\textsuperscript{557} tried to establish the possibility of chemotherapeutic use of organogermaine compounds. They determined the toxicity of many types of substances such as R\textsubscript{4}Ge, R\textsubscript{3}GeX, R\textsubscript{3}GeGeR\textsubscript{3}, (RGeO\textsubscript{1.5})\textsubscript{n} and (ReGeS\textsubscript{1.5})\textsubscript{n}, where R = alkyl, cyclohexyl, aryl or benzyl. The conclusion reached was that organogermanes are of moderate therapeutic use because of their total low toxicity. In another article Burschkies\textsuperscript{431} has reported that these compounds are of no chemotherapeutic use. Nevertheless, Rijkens and coworkers\textsuperscript{76,564} thought that this statement was premature.
In 1962, Kaars first investigated the fungicidal activity of trialkyl(acetoxy)germanes. In contrast to analogous tin and lead derivatives, they were inactive. Triethyl(acetoxy)germane appeared to be considerably less toxic to rats (LD$_{50}$ 125–250 mg kg$^{-1}$ per-os) than isostructural tin and lead compounds. Its homologs, R$_3$GeOOCMe ($R = Pr, Bu$), did not show any toxic action. In general, no specific biological activity of compounds of type R$_3$GeOOCMe has been found. The toxicity of alkylhalogermanes Bu$_4-n$GeCl$_n$ ($n = 0–3$) or RGeI$_3$ ($R = Me, Et, Pr$) was within a range of 50–1300 mg kg$^{-1}$ on intraperitoneal administration.

The toxicity of hexaalkyldigermoxanes R$_3$GeOGeR$_3$ ($R = Me$–Hex) was determined in 1963–1964.

Italian pharmacologists in 1963–1966 studied extensively the toxicity of tetraalkylgermanes. All the compounds were practically nontoxic (LD$_{50}$ 2300–8100 mg kg$^{-1}$), except i-Pr$_4$Ge (LD$_{50}$ 620 mg kg$^{-1}$). It is noteworthy that the toxicity of Et$_3$GeCH$_2$CH$_2$ (LD$_{50}$ 114 mg kg$^{-1}$) was 40 times lower than that of its saturated analog Et$_3$GePr.

In 1969, diphenyl(iminodiacetoxy)germane was recommended for use as an insecticide. The lower toxicity of organic germanium compounds compared to that of isostructural silicon compounds was reasonably confirmed by Voronkov and coworkers in 1968; they found that 1-phenylgermatrane was 100 times less toxic than 1-phenylsilatrane (LD$_{50}$ 0.3–0.4 and 40 mg kg$^{-1}$, respectively), although it showed an analogous physiological action.

Nevertheless, PhGe(OCH$_2$CH$_2$)$_3$N was not the most toxic organogermanium derivative. Toxicological investigations in 1979 with other 1-organylgermatranes RGe(OCH$_2$CH$_2$)$_3$N showed that most of them had low toxicity (LD$_{50}$ 1300–10000 mg kg$^{-1}$). Compounds with $R = H$ and BrCH$_2$ showed LD$_{50}$ of 320 and 355 mg kg$^{-1}$, respectively. The most toxic compounds were 1-(2-thienyl)germatrane and 1-(5-bromo-2-thienyl)germatrane (LD$_{50}$ 16.5 and 21 mg kg$^{-1}$, respectively). Nevertheless, their toxicity was 10–12 times lower than that of 1-(2-thienyl)silatrane (LD$_{50}$ 1.7 mg kg$^{-1}$). It is remarkable that 1-(3-thienyl)germatrane was several times less toxic (LD$_{50}$ 89 mg kg$^{-1}$) than that of its isomer mentioned above.

The discovery of a wide spectrum of biological activity of the organogermanium drug Ge-132 has stimulated extensive investigations in the field of synthesis and pharmacology of carbofunctional polyorganylgermsesquioxanes (RGeO$_{1.5}$)$_n$. For this purpose Asai established a special Germanium Research Institute and a clinic in Tokyo. It should be mentioned that a cytotoxic antitumor drug 2-(3-dimethylaminopropyl)-8,8-diethyl-2-aza-8-germaspiro[4,5]decane, ‘spirogermanyl’, was developed in 1974.

Further events in bio-organogermanium chemistry, which was born soon after bioorganosilicon chemistry, have been described in a monograph.

The practical application of organogermanium compounds has been developed since the last quarter of the 20th century. They were used in medicine and agriculture as drugs and biostimulants as well as in the microelectronic industry to produce thin films of elementary germanium.

III. ORGANOTIN COMPOUNDS

A. How it All Began

The chemistry of organotin compounds was born in the middle of the 19th century almost simultaneously with the birth of the chemistry of organolead compounds. Organic derivatives of these two Group 14 elements started to develop three quarters of a century earlier than those of germanium, their neighbor in the Periodic Table. Due to this large
The review of the evolution of organotin compounds will cover a period of only 110 years, up to the beginning of the 1960s.

Carl Jacob Löwig (1803–1890), a professor at Zürich University, laid the foundation for the chemistry of organotin compounds. He is honored by the synthesis of the first organic compounds of tin in 1852. Polydiethylstannylene \((\text{Et}_2\text{Sn})_n\) was obtained in his unpretentious laboratory before other organotin compounds by the reaction of ethyl iodide with an alloy of tin containing 14% of sodium (he found that the optimal Sn:Na ratio is 6:1). Triethylidostannane and hexaethyldistannane were formed together with it. At a later date it was discovered that another reaction product was tetraethylstannane. Consequently, Löwig became the founder of the direct synthesis of organotin compounds. During his investigations he observed that the polydiethylstannylene obtained was easily oxidized in air to a white precipitate, which by modern concepts is a mixture of perethyloligocyclostannoxanes \((\text{Et}_2\text{SnO})_n\). The latter was prepared by the reaction of \(\text{Et}_2\text{SnI}_2\) with \(\text{Ag}_2\text{O}\) or with aqueous ammonia. Löwig found that the action of alcoholic HCl solution on \((\text{Et}_2\text{SnO})_n\) led to \(\text{Et}_2\text{SnCl}_2\). By the reaction of a solution of KOH saturated with hydrogen sulfide with \(\text{Et}_2\text{SnCl}_2\), Löwig obtained oligodiethylcyclostannathianes \((\text{Et}_2\text{SnS})_n\), as an amorphous precipitate having a penetrating foul smell. However, all the other compounds obtained had not quite a sweet smell, and they irritated the eyes and mucous membranes.

The reaction of \(\text{Et}_2\text{Sn}\) with bromine and chlorine (with iodine, a fire was created) resulted in the corresponding \(\text{Et}_2\text{SnX}_2\) \((X = \text{Cl, Br})\). When \(\text{Et}_2\text{Sn}\) reacted with HCl, \(\text{Et}_2\text{SnCl}_2\) was also formed.

Triethylidostannane was converted to hexaethyldistannoxane by treatment with aqueous ammonia, and hexaethyldistannoxane was converted to triethylchlorostannane by reaction with HCl.

Löwig and then Cahours obtained diethylstannyldinitrate \(\text{Et}_2\text{Sn(ONO}_2\text{)}_2\) and triethylstannylnitrate \(\text{Et}_3\text{SnONO}_2\), by the reaction of HNO\(_3\) with \(\text{Et}_2\text{SnO}\) and \(\text{Et}_3\text{SnOSnEt}_3\), respectively. The reaction of diethylidostannane with \(\text{Ag}_2\text{SO}_4\) gave diethylstannylensulfate \(\text{Et}_2\text{SnOSO}_2\).

In spite of the rather tedious investigations of Löwig which were conducted at the level of 19th century chemistry, they resulted both in syntheses and the study of reactivities of the first organotin compounds. He interpreted his results by the then predominant theory of radicals and used the obsolete values of 6 and 59, respectively, for the carbon and tin atomic weights.

Though a very experienced detective is required to investigate the Löwig publications, it is clear that Löwig had in his hands the first representatives of the main classes of the organotin compounds, i.e. \((\text{R}_2\text{Sn})_n\), \(\text{R}_3\text{SnSnR}_3\), \((\text{R}_2\text{SnO})_n\), \(\text{R}_3\text{SnOSnR}_3\), \(\text{R}_3\text{SnX}\), \(\text{R}_2\text{SnX}_2\), as their ethyl derivatives. It is rather interesting to compare the Löwig formulas and names for his organotin compounds with the modern ones (Table 2).

It is regretful that the Löwig papers devoted to organotin compounds were published only during one year. He then stopped the investigations in this field. Evidently, this was caused by his leaving Zürich for Breslau, where he was invited to take Bunsen’s position.

Bunsen, who accepted the chair in Heidelberg University, left his new laboratory in Breslau to his successor. Löwig’s termination of his organotin investigations possibly reflects his unwillingness to impose severe hazards upon himself and the people surrounding him by the poisoning and irritating vapors of the organotin and organolead compounds to which he was exposed in Zürich. Nevertheless, Löwig did not forget the organic tin and lead compounds and his publications, where he did not fail to mention his priority and which are part of the history of organometallic compounds, bear witness to this fact.
1. Genesis and evolution in the organic chemistry of Ge, Sn, and Pb compounds

In spite of Löwig’s outstanding research, which laid the foundation of organotin chemistry, it should be noted that he shared the laurels of the discoverer with two other founders of organometallic chemistry: Edward Frankland (1825–1899), a professor of the Royal Chemical College in London, and August Cahours (1813–1891), a professor of the Ecole Centrale in Paris. It is generally believed that Frankland’s first article devoted to the organotin synthesis appeared in 1853. Actually, the results of his pioneer research were published a year earlier in a journal that was of little interest to chemists. There is no reference to this article in monographs and reviews dealing with organotin compounds. Frankland reported in this article that he used his earlier discovered organozinc method for the syntheses of organotin compounds. In the course of his investigations Frankland, together with Lawrence, first discovered the cleavage reactions of the C\(\rightarrow\)Sn bond.

In the reaction of Et\(_4\)Sn with sulfur dioxide in the presence of air oxygen he obtained ethyl triethyllylsulfonate Et\(_3\)SnOSO\(_2\)Et (‘stantriethylic ethylsulfonate’). The action of H\(_2\)SO\(_4\) on the latter led to bis(triethyllylanyl) sulfate (Et\(_3\)SnO)\(_2\)SO\(_2\) (‘stantriethylic sulphate’). Finally, Frankland prepared polydiethyllylnylene (Et\(_2\)Sn)\(_n\) by the reduction of Et\(_2\)SnI\(_2\) with zinc in hydrochloric acid. All these data were reproduced and extended in his later publications. In 1853, he isolated crystals of Et\(_2\)SnI\(_2\) and some amount of Et\(_3\)SnI by heating a tin foil with ethyl iodide at 180 °C in a sealed tube. He observed this reaction also under sunlight, i.e. he reported the first photochemical process in organometallic chemistry. In 1879, Frankland and Lawrence demonstrated that the action of R\(_2\)Zn (R = Me, Et) on Et\(_2\)SnI\(_2\) resulted in Et\(_2\)SnMe\(_2\) and Et\(_4\)Sn, respectively. He found that HCl cleaved Et\(_2\)SnMe\(_2\), but the cleavage products were not identified. Frankland’s research is also a corner stone of organotin chemistry. He favored the valence ideas and the use of modern graphic formulas of organotin compounds. Moreover, his research destroyed the border between inorganic and organic chemistry.

In 1852, simultaneously Cahours together with Löwig and Frankland became interested in organotin compounds. Together with Löwig and Frankland he belongs to the great pioneers of organotin chemistry in the 19th century and he made an essential contribution to its development. His first organotin investigation concerned the synthesis of diethyllylnylene (almost simultaneously with those described by Löwig and Frankland) and other reactions followed. In 1853, Cahous showed that MeI reacted with Sn at 150–180 °C to give Me\(_4\)Sn and Me\(_3\)SnI. The hydrolysis of Me\(_3\)SnI gave Me\(_3\)SnOSnMe\(_3\), whose cleavage with aqueous acids (HX, H\(_n\)Y) resulted in Me\(_3\)SnX.

<table>
<thead>
<tr>
<th>Modern formula</th>
<th>Löwig’s formula</th>
<th>Löwig’s name (in German)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et(_3)SnSnEt(_3)</td>
<td>Sn(_4)(C(_4)H(_5))(_3)</td>
<td>Acetstannäthyl</td>
</tr>
<tr>
<td>Et(_4)Sn</td>
<td>Sn(_4)(C(_4)H(_5))(_5)</td>
<td>Äethstannäthyl</td>
</tr>
<tr>
<td>Et(_3)SnOEt</td>
<td>Acetstannäthyl-oxyd</td>
<td></td>
</tr>
<tr>
<td>Et(_3)SnCl(_2)</td>
<td>Chlor-Elaylstannäthyl</td>
<td></td>
</tr>
<tr>
<td>Et(_3)SnBr(_2)</td>
<td>Brom-Elaylstannäthyl</td>
<td></td>
</tr>
<tr>
<td>Et(_3)SnI(_2)</td>
<td>Iod-Elaylstannäthyl</td>
<td></td>
</tr>
<tr>
<td>(Et(_2)SnO)(_n)</td>
<td>Et(_2)SnO</td>
<td>Elaylstannäthyl-oxyd</td>
</tr>
<tr>
<td>Et(_2)SnOSnEt(_3)</td>
<td>Et(_2)SnO</td>
<td>Methylstannäthyl-oxyd</td>
</tr>
<tr>
<td>Me(_3)SnONO(_2)</td>
<td>Sn(_2)(C(_4)H(_5))(_3)O,NO(_4)</td>
<td>Salpetersäure Methstannäthyl-oxyd</td>
</tr>
<tr>
<td>Et(_3)SnONO(_2)</td>
<td>Sn(_4)(C(_4)H(_5))(_4)O,NO(_5)</td>
<td>Salpetersäures Elaylstannäthyl-oxyd</td>
</tr>
<tr>
<td>(Et(_3)SnO)(_2)SO(_2)</td>
<td>Sn(_2)(C(_4)H(_5))(_3)SO(_3)</td>
<td>Schwefelsäure Methstannäthyl-oxyd</td>
</tr>
<tr>
<td>Et(_3)SnONO(_2)</td>
<td></td>
<td>Salpetersäure Acetstannäthyl-oxyd</td>
</tr>
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</table>
(X = Cl, Br, I, S, OOCMe, NO₃) and \((\text{Me}_3\text{Sn})_n\text{Y}(\text{Y} = \text{S}, \text{CO}_3, \text{OOC}_2, n = 2; \text{PO}_4, n = 3)\). By hydrolysis of \(\text{Me}_2\text{SnI}_2\), \((\text{Me}_3\text{SnO})_n\) was obtained, and it was cleaved with the corresponding acids to \(\text{Me}_2\text{SnX}_2\). Cahours was the first to demonstrate the possibility of replacing the halogens in alkylhalostannanes \((\text{Et}_3\text{Sn}, \text{Et}_2\text{SnI}_2)\) by the anions of the corresponding silver salts \((\text{AgCN, AgNCO, AgSCN})\) using their reactions with \(\text{Et}_3\text{SnI}\) as an example. He also obtained hexaethyldistannatniane \(\text{Et}_3\text{SnSSnEt}_3\) by the reaction of \(\text{Et}_3\text{SnCl}\) with \(\text{H}_2\text{S}\) in alcoholic media.

Following these three fathers of organotin chemistry, other luminaries of the chemical science of the 19th century such as Buckton, Ladenburg, and then at the turn of the century Pope and Peachey and Pfeiffer and coworkers, were engaged in the development of organotin chemistry. In the 20th century this development is associated with the names of well-known scientists such as Krause, Schmidt and Neumann (in Germany), Kraus, Druce, Bullard, Gilman, Rochow, Anderson, Seyferth and West (in the USA), Kocheshkov, Nesmeyanov, Razuvaev, Nefedov, Koton, Kolesnikov and Manulkin (in the USSR), van der Kerk (in the Netherlands), Lesbre (in France) and Nagai and Harada (in Japan) and their numerous colleagues. Together they synthesized about 1800 organotin compounds up to 1960, in ca. 950 publications.

We shall now follow systematically these developments.

### B. Direct Synthesis

The reactions of metals, their intermetal derivatives or alloys (often in the presence of a catalyst or a promoter) with organic halides and with some other organic compounds such as lower alcohols and alkylamines can be regarded as a direct synthesis of the organometallic compounds. As mentioned in Section III.A, Löwig and, to a lesser extent, Frankland were the originators of the direct synthesis of organotin compounds. Since 1860, they were followed by Cahours, who used the reaction of alkyl iodides with a tin–sodium alloy (10–20%) in a sealed tube at 100–200 °C. Cahours obtained \(\text{Et}_2\text{SnI}_2\) by the reaction of \(\text{EtI}\) with tin metal at 140–150 °C as well as at 100 °C under sunlight irradiation (according to Frankland). He also established that by increasing the Na content (from 5 to 20%) in the Sn–Na alloy, the reaction of \(\text{EtI}\) with the alloys led to the formation of \(\text{Et}_3\text{SnI}\) and then to \(\text{Et}_4\text{Sn}\). Cahours synthesized a series of trialkyliodostannanes \(\text{R}_3\text{SnX}\) and tetralkylstannanes \(\text{R}_4\text{Sn}\) \((\text{R} = \text{Me, Et, Pr})\) by the reaction of alkyl iodides with the Sn–Na alloy. Among other products he observed the formation of the corresponding dialkylidiodostannanes and hexaalkyldistannoxanes. He found that increasing the sodium content of the alloy led predominantly to tetralkylstannanes, and decreasing its content led to dialkylidiiodostannanes. He also demonstrated that EtBr reacted analogously to alkyl iodides to give \(\text{Et}_3\text{SnBr}\). Cahours prepared a series of tetraalkylstannanes \((\text{C}_n\text{H}_{2n+1})_4\text{Sn}\) \((n = 1, 2, 3, 4, 5)\) by heating the corresponding alkyl iodides and bromides with the Sn–Na alloy in a sealed tube. A simultaneous formation of the corresponding trialkyliodostannanes and trialkylbromostannanes was observed. Other researchers then synthesized tetraalkyl- and dialkylidihalostannanes by the reaction of alkyl halides with an Sn–Na alloy. Neiman and Shushunov investigated the kinetics of the reaction of tin alloys containing 8.8 and 18.2% Na with EtBr at a wide range of temperatures and pressures in 1948. Depending on the alloy compositions and reaction conditions, the products were \(\text{Et}_4\text{Sn}\) or \(\text{Et}_2\text{SnBr}_2\). When using this process, they were the first to discover a topochemical reaction with a longer induction period at higher rather than lower temperatures. Following Cahours, they also found that using an alloy with a high Na content led to \(\text{Et}_4\text{Sn}\). When the sodium content in the alloy...
corresponded to a NaSn$_4$ composition, Et$_4$Sn was formed at a temperature $<$60°C, but at $>$60–160°C the main product was Et$_2$SnBr$_2$.

Pure tin was also used for the direct synthesis of organotin compounds. In 1948, unlike previous investigations, Harada obtained sodium stannite Na$_2$Sn not by the metal fusion, but by the reaction of tin with sodium in liquid ammonia. The reaction of Na$_2$Sn with EtBr led to ($\text{Et}_2\text{Sn}$)$_n$.

Following Frankland, Cahours established that alkyl halides reacted with melted tin to give dialkyldihalostannanes. Consequently, both authors became the founders of the direct synthesis of organylhalostannanes from metallic tin. Nevertheless, the first attempts to use alkyl bromides in the reaction with tin were unsuccessful. In 1911, Emmert and Eller first obtained carbofunctional organotin compounds ($\text{EtCOOCH}_2$)$_2\text{SnI}_2$ by the reaction of metallic tin with ethyl iodoacetate. In 1928–1929, Kocheshkov discovered that dibromomethane and dichloromethane reacted with tin at 180–220°C to give almost quantitative yields of MeSnX$_3$ ($X = \text{Cl, Br}$) according to equation 4.

$$3\text{CH}_2\text{X}_2 + 2\text{Sn} \rightarrow 2\text{MeSnX}_3 + \text{C}$$

He suggested that CH$_2$SnX$_2$ was an intermediate product in the process and that MeSnX$_3$ was formed by addition of HX to the intermediate, which, in turn, was the insertion product of Sn into CH$_2$X$_2$. The reaction of CH$_2$I$_2$ with Sn at 170–180°C led only to carbon and SnI$_4$. It is noteworthy that benzyl chloride acted with tin powder in water or in alcohol under mild conditions to give (PhCH$_2$)$_3\text{SnCl}$ in 85% yield.

In 1958, Kocheshkov and coworkers showed that alkylbromostannane can be prepared from tin and alkyl bromides under ionizing irradiation.

The development of the direct syntheses of organotins involves a mysterious and even detective story, as told by Letts and Collie. They wanted to prepare diethylzinc according to Frankland by heating ethyl iodide with zinc metal. To their great surprise, tetraethylstannane was the main reaction product. They could not guess that so much tin was present in the commercial zinc that they purchased. Their further experiments with mixtures of tin and zinc led to the same result. They also found that heating tin powder with EtZnI at 150°C resulted in Et$_4$Sn. Consequently, Letts and Collie proposed the following scheme (equations 5 and 6) for the reaction.

$$\text{Et}_2\text{Zn} + \text{Sn} \rightarrow \text{Et}_2\text{Sn} + \text{Zn}$$

$$2\text{Et}_2\text{Sn} \rightarrow \text{Et}_4\text{Sn} + \text{Sn}$$

Anyway, it is doubtful whether Letts and Collie thought about zinc as the catalyst of the reaction of tin with alkyl halides (in spite of their demonstration) since this fact was established considerably later. The authors also found that the reaction of EtI with a Sn–Zn alloy (33–50%) containing 5% of Cu gave a maximum yield of Et$_4$Sn. Thus, long before Rochows’s finding the catalytic influence of copper in the direct synthesis of organometallic compounds was observed.

Since 1927, Harada studied the influence of addition of zinc to the Sn–Na alloy in its reaction with haloalkanes (MeI, EtI, PrI, BuBr, SnCl$_2$ and others). Among other factors, he found that boiling ethyl bromide with an Sn alloy containing 14% of Na and 12–22% of Zn resulted in remarkable Et$_4$Sn yields. The promotion by zinc during the direct synthesis was further studied by other researchers. In particular, it was shown that Bu$_3$SnCl was the product of the reaction of BuCl and tin–sodium alloy containing 2% of Zn. In 1957, Zietz and coworkers found that the reaction of higher alkyl chlorides with an Sn–Na alloy containing 2% of Zn at 150–180°C led to a mixture of R$_4$Sn and R$_3$SnCl ($R = \text{Pr, Bu, Am}$) with a high tin conversion. Under milder
conditions, in the same reaction with exactly the same Sn–Na alloy, the product (R₂Sn)_n with R = Et, Bu, was formed. Cu, Cd, Al were suggested in 1958 as activators of the alloys of the compositions Na₄Sn (43.5% Na) and Na₂Sn (28% Na). In the presence of these metals, even higher alkyl chlorides (C₈–C₁₂) also reacted with the alloys.

From the end of the 19th century, alkyl chlorides and bromides (often under pressure) successfully reacted with melted tin, preferably in the presence of catalytic amounts of copper or zinc. These data are mostly presented in patents.

In 1953, Smith patented the reaction of MeCl with Sn, which led to Me₂SnCl₂ at 300 °C. However, already in 1949–1951 Smith and Rochow thoroughly investigated the reaction of gaseous MeCl with melted tin under ordinary pressure, but they did not publish the results though they were presented in a thesis submitted by Smith to Harvard University. The existence of the above patent induced them to report their result in 1953. Smith and Rochow studied the influence of added 25 elements to the reaction of methyl chloride with melted tin at 300–350 °C. The best catalysts found were Cu, Ag and Au.

Naturally, copper was further used as a catalyst. Under appropriate conditions, the main reaction product was Me₂SnCl₂ but small quantities of Me₃SnCl and Me₃SnCl were also formed. The yield of Me₂SnCl was increased by the addition of sodium to tin. Methyl bromide reacted with liquid tin at 300–400 °C to form Me₂SnBr₂, whereas in these conditions (385 °C) methyl iodide was completely decomposed. The products of the thermolysis were gaseous hydrocarbons and iodine. The iodine reacts with Sn to give SnI₂ and the reaction of SnI₂ with MeI gave MeSnI₃. In the same article Smith and Rochow reported that under conditions analogous to those used for the direct synthesis of Me₂SnCl₂, tin reacted very slowly with EtCl and BuCl underwent a complete thermal decomposition. They also found that MeX (X = Cl, Br, I) reacted with tin monoxide containing 10% Cu at 300 °C to form Me₃SnX.

In 1954, van der Kerk and Luijten found that in the direct synthesis of tetraorganylstannanes the tin—sodium alloy can be replaced with a tin–magnesium alloy. A mercury catalyst (Hg or HgCl₂) was required for this variant and the process was conducted at 160 °C under pressure.

In further investigations it was possible to conduct this reaction at atmospheric pressure in a solvent capable of influencing the ratio of the reaction products R₄Sn and R₃SnX. The method of the alloy preparation played an important role, with the content of magnesium being at most 21–29% (Mg₂Sn). In the absence of the catalyst (mercury salts or amines) alkyl chlorides did not react with these alloys. In the reaction of a Sn–Na alloy (containing 4–5% Cu) with alkyl bromides or iodides in solution, up to 60% of dialkyldialostannanes R₂SnX₂ as well as R₄Sn and R₃SnX were formed.

The direct synthesis of aromatic tin compounds was realized for the first time in the 19th century. In 1889 Polis and in 1926 Chambers and Schere obtained tetraphenylstannane by a long-time boiling of bromobenzene with an Sn–Na alloy in the presence of the initiator ethyl acetate or without it. In the reaction of PhBr with an alloy of Li₄Sn composition the yield of Ph₄Sn was only 13%. Aryl halides did not react with tin alone at temperatures <200 °C. In 1938, Nad’ and Kocheshkov obtained tetraphenylstannane by heating Ph₃SnCl with an Sn–Na alloy. The formation of tetraarylstannanes in the reaction of aryl halides with Sn–Na alloy was probably preceded by arylation of the tin with sodium aryls, which were the intermediates of this process. This mechanism was confirmed by the alkylation of tin with phenylmagnesium bromide. Consequently, organometallic compounds were actually used to synthesize tetraarylstannanes from metallic tin or its alloys with sodium. Thus, in 1938, Talalaeva and Kocheshkov obtained...
tetraarylstannanes in a reasonable yield by boiling lithium aryls with tin powder or its amalgam. Nad' and Kocheshkov\textsuperscript{665} carried out the reaction of PhHgCl with an Sn–Na alloy in boiling xylene with better results (50% yield of Ph\textsubscript{2}Sn). They found that the reaction between PhHgCl and Na\textsubscript{2}Sn involved the intermediate formation of (Ph\textsubscript{2}Sn)\textsubscript{n} and Ph\textsubscript{3}SnSnPh\textsubscript{3}. The latter disproportionated to Ph\textsubscript{3}Sn and Ph\textsubscript{2}Sn. According to their data, the reaction of PhHgCl with Sn gave Ph\textsubscript{2}SnCl\textsubscript{2}, which was disproportionated to Ph\textsubscript{3}SnCl and SnCl\textsubscript{4}\textsuperscript{665}. The data on the direct synthesis of organotin compounds are summarized in a monograph\textsuperscript{650}.

C. Organometallic Synthesis from Inorganic and Organic Tin Halides

Frankland\textsuperscript{588,589,591} was the first to synthesize in 1852 organotin compounds using the reaction of Et\textsubscript{2}Zn with SnCl\textsubscript{2} to give Et\textsubscript{4}Sn (Section II.A). One year later Cahours\textsuperscript{575} obtained Et\textsubscript{4}Sn by the reaction of Et\textsubscript{3}SnI with Et\textsubscript{2}Zn. He synthesized the first mixed tetraalkylstannane Me\textsubscript{3}SnEt\textsuperscript{583} by the reaction of Me\textsubscript{3}SnI with Et\textsubscript{2}Zn and in 1862 he analogously prepared Et\textsubscript{3}SnMe\textsuperscript{596}. Under Butlerov’s guidance Morgunov\textsuperscript{668} obtained Me\textsubscript{2}SnEt\textsubscript{2} by the reaction of Me\textsubscript{2}SnI\textsubscript{2} with Et\textsubscript{2}Zn, although they did not succeed in synthesizing it from Et\textsubscript{2}SnI\textsubscript{2} and Me\textsubscript{2}Zn in the pure form according to Frankland. In 1900, Pope and Peachey\textsuperscript{608} also used the organozinc method to prepare Me\textsubscript{3}SnEt\textsubscript{2}. During 12 years they obtained the first organotin compound containing asymmetric tin atom (MeEtPrSnI) using the appropriate dialkyl zinc. The asymmetric iodide was converted into an optically active salt with \([\alpha]_D = +95^\circ\) by the reaction with silver d-camphorsulfonate.

Buckton in 1859 was the first to use tin tetrachloride to synthesize organotin compounds\textsuperscript{603}. At that time, the reaction of SnCl\textsubscript{4} with Et\textsubscript{2}Zn was the common route to Et\textsubscript{4}Sn. Pope and Peachey\textsuperscript{608} used this method only after four decades. In 1926, Chambers and Scherer\textsuperscript{662} obtained Ph\textsubscript{4}Sn by the organozinc method. Kocheshkov, Nesmeyanov and Potrosov\textsuperscript{669} synthesized (4-ClC\textsubscript{6}H\textsubscript{4})\textsubscript{4}Sn in the same way in 1934. However, at the beginning of the 20th century the organozinc method of organotin compounds synthesis lost its importance.

The use of Grignard reagents led to revolutionary developments in the synthesis of organotin compounds. It started in 1903 when Pope and Peachey\textsuperscript{611} obtained R\textsubscript{4}Sn, R = Et, Ph in a good yield from SnCl\textsubscript{4} and RMgBr. Just one year later this method was used by Pfeiffer and Schnurmann to synthesize Et\textsubscript{4}Sn, Ph\textsubscript{4}Sn and (PhCH\textsubscript{2})\textsubscript{3}SnCl\textsuperscript{670}. In 1904, Pfeiffer and Heller\textsuperscript{615} reacted SnI\textsubscript{4} with the Grignard reagent MeMgI to obtain Me\textsubscript{3}SnI. In 1954, Edgell and Ward\textsuperscript{671} used Et\textsubscript{2}O and, in 1957, Seyferth\textsuperscript{672} and Stone\textsuperscript{673} used THF as the solvent in this reaction and that improved the yield of R\textsubscript{4}Sn.

From 1914, the Grignard method of synthesis completely displaced the organozinc method and was widely used\textsuperscript{674}. Up to 1960, fifty publications reporting the use of this method appeared\textsuperscript{125,675}.

In 1927, Kraus and Callis\textsuperscript{643} patented the method of preparing tetraorganylstannanes by the reaction of Grignard reagents with tin tetrahalides. In 1926, Law\textsuperscript{676} obtained mixed tetraorganylstannanes, such as Et(PhCH\textsubscript{2})\textsubscript{2}SnBu and Et(PhCH\textsubscript{2})\textsubscript{2}SnBu\textsubscript{2} from Et(PhCH\textsubscript{2})\textsubscript{2}SnI and Et(PhCH\textsubscript{2})SnI\textsubscript{2}, by the Grignard method. In 1923, Böseken and Rutgers\textsuperscript{677} demonstrated that a Grignard reagent was able to cleave the Sn–Sn bond: the reaction of PhMgBr with (Ph\textsubscript{2}Sn)\textsubscript{n} led to Ph\textsubscript{4}Sn, Ph\textsubscript{3}SnSnPh\textsubscript{3} and Ph\textsubscript{12}Sn\textsubscript{5} (the first linear perorganylpolystannane).

It is noteworthy that in 1912 Smith and Kipping\textsuperscript{678} applied the Barbier synthesis, i.e. the addition of organic halide to a mixture of Mg and SnCl\textsubscript{4} in ether (without preliminary preparation of the Grignard reagent) to obtain organylchlorostannanes in a good yield\textsuperscript{678,679}. 

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Organolithium synthesis of organotin compounds, in particular (4-MeC₆H₄)₄Sn from SnCl₄, was first described by Austin in 1932. In 1942, Talalaeva and Kocheshkova used this method to obtain Ar₃Sn (e.g., Ar = 4-PhC₆H₄) when Grignard reagents failed to react. Bähr and Gelius used the appropriate aryllithiums to synthesize tetra(9-phenanthryl)- and tetra(1-naphthyl)stannane from SnCl₄. Organolithium compounds were also used to synthesize 1,1-diorganylstannacycloalkanes.

An interesting spirocyclic system was created by the reaction of SnCl₄ with 1,2-bis(2'-lithiumphenyl)ethane by Kuivila and Beumel in 1958. Spirocyclic compounds were also obtained in the reaction of SnCl₄ with 1,4-dilithium-1,2,3,4-tetraphenylbutadiene or with ethyl bis(2-lithiumphenyl)amine.

In some cases the organolithium compounds cleaved the C–Sn bond. However, these obstacles were successfully overcome by converting the organolithium compounds to the Grignard reagent by adding a magnesium halide.

The organolithium synthesis was also extensively used, especially for attaching vinyl and aryl groups to the tin atom. It should be noted that in 1955, Gilman and Wu obtained 4-Ph₃SnC₆H₄NMe₂ by the reaction of Ph₃SnCl with 4-Me₂NC₆H₄Li. In 1958, Bähr and Gelius prepared (4-PhC₆H₄)₃SnBr by reacting 4-PhC₆H₄Li with SnBr₄ in a 3.5:1 molar ratio.

Both organolithium and organomagnesium syntheses of tetra(tert-butyl)stannane had failed. Up to 1960 organolithium compounds were seldom used to synthesize aliphatic tin derivatives. In 1951, the reaction of PhLi with SnCl₂ allowed Wittig and coworkers to obtain (Ph₂Sn)₄ in a good yield. With excess PhLi, Ph₃SnLi was also formed. Immediately after Wittig’s work in 1953, Gilman and Rosenberg developed a method to synthesize Ar₃SnLi from ArLi and SnCl₂. The reaction of Ar₃SnLi with appropriate aryl halides gave Ar₄Sn. This method was also successfully used to synthesize tetraarylstannanes.

In 1956, Fischer and Grübner obtained for the first time dicyclopentadienyltin by the reaction of cyclopentadienyllithium with SnCl₂. Ladenburg first used organosodium synthesis (i.e., the Wurtz reaction) of organotin compounds in 1871. He synthesized Et₃SnPh by the reaction of Et₃Sn with Na and PhBr in ether medium. That was the first aromatic tin compound. He obtained EtPhSnCl₄ in the same way. In 1889, Polis found that the reaction of SnCl₄ with Na and PhCl in boiling toluene did not result in Ph₄Sn. Nevertheless, when a 25% Na—75% Sn alloy reacted with PhBr, using the MeCOOEt as an initiator, he obtained Ph₄Sn. However, during the following century this method was forgotten. Nevertheless, Dennis and coworkers used the reaction of aryl bromides and Na with SnCl₄ in ether, benzene or toluene to prepare tetraarylstannanes and the method was even patented.

In 1926, Chambers and Scherer obtained the first organotin compound containing an Sn–Na bond. By reacting Ph₃SnBr with Na in liquid ammonia, they synthesized Ph₃SnNa and investigated its transformations. For example, the reactions of Ph₃SnNa with aryl halides resulted in Ph₃SnAr, with CICH₂COONa, Ph₃SnCH₂COONa was formed, and PhHgI gave Ph₃SnHgPh. They were the first to cleave the C–Sn bond by metallic Na, demonstrating that Ph₄Sn reacted with Na in liquid ammonia to form consecutively...
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Ph$_3$SnNa and Ph$_2$SnNa$_2$. The reaction of the latter with Ph$_2$SnBr$_2$ in liquid ammonia gave the polymeric substance (Ph$_3$Sn)$_n$.$^{662}$

The Würzt-type reaction was applied in the syntheses of organotin compounds, containing an Sn—Sn bond. Law prepared hexabenzyldistannane (PhCH$_2$)$_3$SnSn(Ch$_2$Ph)$_3$ for the first time in 1926 by the reaction of Na with (PhCH$_2$)$_3$SnCl in toluene.$^{676}$

Just a few reactions of R$_{4-n}$SnCl$_n$ (n = 1—4) with silver,$^{719,720}$ mercury, aluminum, thallium and lead were described.$^{676,721}$ As early as 1878, Aronheim$^{722}$ found that prolonged heating of Ph$_2$Hg with SnCl$_4$ resulted in Ph$_2$SnCl$_2$ (33% yield). Only three quarters of a century later PhSnCl$_3$$^{723,724}$ was similarly obtained. In 1930 and 1931, Nesmeyanov and Kocheshkov$^{725-727}$ demonstrated that tin dihalides can react with organomercury compounds. In the reaction of Sn$_2$ (X = Cl, Br) with Ar$_2$Hg in ethanol or acetone they obtained diaryldihalostannanes Ar$_2$SnX$_2$. In 1922, Goddard and coworkers$^{728,729}$ found that the reaction of SnCl$_4$ with Ph$_3$P led to Ph$_3$SnCl$_2$ and Ph$_2$PbCl$_2$. By the reaction of Ph$_3$SnCl with AgC≡CCH(OEt)$_2$, Johnson and Holum$^{730}$ obtained Ph$_3$SnC≡CCH(OEt)$_2$ in 1958. Finally, in 1957 and 1959, Zakharkin and Okhlobystin$^{720,731}$ found that the reaction of SnCl$_4$ with R$_3$Al$^{720,731}$ could be employed to synthesize tetraalkylstannanes.

In conclusion it should be noted that organometallic synthetic methods of organylhalostannanes were not as widely used as in the synthesis of the isostructural compounds of silicon and germanium. Section III.E explains the reason for this.

D. Organotin Hydrides

In 1922, Kraus and Greer$^{732}$ synthesized trimethylstannane Me$_3$SnH, the first organotin compound containing an Sn—H bond, by the reaction of sodium trimethylstannane with ammonium bromide in liquid ammonia. In 1926, Chambers and Scherer$^{662}$ used this method for the synthesis of triphenylstannane R$_3$SnH and diphenylstannane R$_2$SnH$_2$. In 1943, Malatesta and Pizzotti$^{733}$ obtained Et$_3$SnH and Ph$_3$SnH by the same method. In 1951, Wittig and coworkers$^{706}$ used Ph$_3$SnLi in this reaction. The chemistry of organotin hydrides started to develop extensively when, in 1947, Finholt, Schlesinger and coworkers$^{336,648}$, who developed the reduction method of organometallic halides by LiAlH$_4$, used this method for the synthesis of trimethyl-, dimethyl- and methylstannane from Me$_{4-n}$SnCl$_n$ (n = 1—3). This method was widely applied later to obtain organotin hydrides.$^{48,125,675,734}$ Thus, in 1955—1958, Et$_3$Sn$^{735}$, Ph$_3$SnCl$^{736}$, Et$_2$SnCl$_2$$^{737}$ and Pr$_2$SnCl$_2$$^{738}$ were reduced to the appropriate hydrides by LiAlH$_4$. In 1953, West$^{334}$ failed to reduce triphenylstannanes with zinc in hydrochloric acid, unlike the reduction of triphenylbromogermane. In 1957—1958, Kerk and coworkers$^{738,739}$ developed the reduction method of R$_3$SnCl to R$_3$SnH (R = Et, Pr, Bu, Ph) with amalgamated aluminum in aqueous medium. As a result of this research 20 organotin hydrides R$_{4-n}$SnH$_n$ (n = 1—3) became known up to 1960.

Beginning from 1929, Ipatiev and his nearest coworkers Razuvaev and Koton tried to hydrogenate Ph$_4$Sn under drastic conditions (60 atm, 220° C)$^{740-744}$, but neither formation of the compounds containing an Sn—H bond nor hydrogenation of the aromatic cycle was observed. Instead, hydrolysis of the C—Sn bond with formation of metallic tin and benzene took place. In this respect we note that, when in 1989 Khudobin and Voronkov$^{745}$ tried to reduce Bu$_2$SnCl$_2$ by R$_3$SiH in the presence of colloidal nickel, the products were metallic tin, butane and R$_3$SiCl. R$_3$SiH reduced tetrachlorostannane to SnCl$_2$ to give R$_3$SiCl and H$_2$. Organotin hydrides R$_{4-n}$SnH$_n$ are not among the stable organotin compounds. Their stability increases (i.e. their reactivity decreases) on decreasing the number $n$$^{737}$ of hydrogens at the tin atom. Even the early researchers observed that many organotin hydrides R$_{4-n}$SnH$_n$ (especially with R = Me,
Et and \( n = 2, 3 \) were slowly decomposed at room temperature and easily oxidized by air oxygen\(^{336,732,735-737,746} \). However, \( \text{Me}_3\text{SnH} \) and \( \text{Me}_2\text{SnH}_2 \) are little changed when stored in a sealed ampoule at room temperature during 3 months and 3 weeks, respectively\(^{336} \). \( \text{Me}_3\text{SnH} \) decomposed under these conditions less than 2%\(^{747} \) during 16 days. Distillation of butylstannane under atmospheric pressure at ca 100 °C failed because of its complete decomposition. However, at 170 °C and 0.5 mm the high-boiling triphenylstannane was so stable that its distillation succeeded\(^{736,738} \) but it decomposed under sunlight exposure. In 1926, Chambers and Scherer\(^{662} \) found that diphenylstannane \( \text{Ph}_2\text{SnH}_2 \) decomposed to \( \text{Ph}_2\text{Sn} \) at \(-33 °C \). In contrast, van der Kerk and coworkers\(^{748} \) found that \( \text{Ph}_2\text{SnH}_2 \) decomposed to \( \text{Ph}_4\text{Sn} \) and metallic tin only on heating \( >100 °C \) in vacuum. Apparently, this process involves the intermediate formation of \( \text{Ph}_2\text{Sn} \) which further disproportionated. \( \text{Et}_2\text{SnH}_2 \) was decomposed with explosion in contact with oxygen. In 1926–1929 it was shown that oxidation of trialkylstannanes and triphenylstannanes gave different products under different conditions. Bullard and coworkers\(^{749,750} \) and later Anderson\(^{735} \) obtained trialkylstannanol. According to Chambers and Scherer\(^{662} \), \( \text{Ph}_3\text{SnH} \) gave hexaphenyldistannane. The latter is the product of reaction of \( \text{Ph}_3\text{SnH} \) with amines, as Noltes and van der Kerk\(^{751} \) had found. Diphenylstannane was dehydrocondensed into the yellow modification of \( (\text{Ph}_2\text{Sn})_n \) in the presence of amines. In contrast, the reaction of \( \text{Ph}_3\text{SnH} \) with thiols gave hexaphenyldistannathiane \( \text{Ph}_3\text{SnSSnPh}_3 \)\(^{751} \). In 1950, Indian researchers\(^{752} \) found that the reaction of \( \text{Pr}_3\text{SnH} \) with aqueous-alcoholic NaOH solution gave \( \text{Pr}_3\text{SnOH} \). In 1922, Kraus and Greer\(^{732} \) found that the reaction of \( \text{Me}_3\text{SnH} \) with concentrated HCl led to \( \text{Me}_3\text{SnCl} \). In 1951, Wittig and coworkers\(^{706} \) converted \( \text{Ph}_3\text{SnH} \) to \( \text{Ph}_3\text{SnCl} \) by the same method. Noltes showed in his dissertation (1958) that triorganystannanes reacted analogously with carboxylic acids to form \( \text{R}_3\text{SnOOCR} \) and that organotin hydrides reacted vigorously with halogens to give the corresponding halides. In 1955, Gilman and coworkers\(^{267,736} \) found that \( \text{Ph}_3\text{SnH} \) in the presence of benzoyl peroxide formed \( \text{Ph}_4\text{Sn} \) without precipitation of metallic tin. However, in the presence of excess (PhCOO)\(_2\) the product was \( \text{Ph}_3\text{SnOCOPh} \). According to Kraus and Greer, and to Chambers and Scherer, \( \text{R}_3\text{SnH} \) (\( \text{R} = \text{Me}^{732}, \text{Ph}^{662} \)) reacted with Na in liquid NH\(_3\) to give \( \text{R}_3\text{SnNa} \). In 1949, Gilman and Melvin\(^{753} \) pointed out that \( \text{Ph}_4\text{Sn} \) and LiH were formed in the reaction of PhLi on \( \text{Ph}_3\text{SnH} \). In contrast, Wittig and coworkers\(^{706} \) found that the reaction of \( \text{Ph}_3\text{SnH} \) with MeLi led to \( \text{Ph}_3\text{SnLi} \) and \( \text{CH}_4 \). Nevertheless, in 1953, Gilman and Rosenberg\(^{754} \) found that this reaction resulted in \( \text{Ph}_3\text{SnMe} \) and LiH. Lesbre and Buisson\(^{755} \) developed the reaction of trialkylstannanes with diazo compounds \((\text{R}‘\text{CHN}_2)\), which gave \( \text{R}_3\text{SnCH}_2\text{R}‘ \) (\( \text{R} = \text{Pr}, \text{Bu} \); \( \text{R}‘ = \text{H}, \text{COOEt}, \text{COMe}, \text{COPh}, \text{CN} \)) along with nitrogen.

The hydrostannylation reaction\(^{756} \) is of great importance in organotin chemistry. This term was proposed by Voronkov and Lukevics\(^{52,53} \) in 1964. The reaction is based on the addition of organotin compounds, containing at least one Sn–H bond to multiple bonds (\( \text{C} = \text{C}, \text{C} = \text{C}, \text{C} = \text{O} \) etc.)\(^{52,53,77,265} \). It is of special interest for the synthesis of carbofunctional organotin compounds. This reaction was first carried out by van der Kerk, Noltes and coworkers\(^{748,751,757,758} \) in 1956. They found that trialkylstannanes \( \text{R}_3\text{SnH} \) (\( \text{R} = \text{Pr}, \text{Bu} \)) were easily added to the double bonds in \( \text{CH}_2=\text{CHR}‘ \) (\( \text{R}‘ = \text{Ph}, \text{CN}, \text{COOH}, \text{COOMe}, \text{CH}_2\text{CN}, \text{CH(OEt)}_2 \)), to give the adducts \( \text{R}_3\text{SnCH}_2\text{CH}_2\text{R}‘ \) in 95% yield. Hydrostannylation proceeded easily in the absence of catalysts by heating mixtures of both reagents at 80–100 °C for several hours. In 1958, monosubstituted ethylene derivatives with \( \text{R}‘ = \text{CONH}_2, \text{CH}_2\text{OH}, \text{COCMe}, \text{CH}_2\text{OOCMe}, \text{4-C}_5\text{H}_4\text{N}, \text{OPh}, \text{Hex}, \text{C}_6\text{H}_4\text{CH} = \text{CH}_2 \) were involved in the reaction with \( \text{Ph}_3\text{SnH} \). It was found that \( \text{Ph}_3\text{SnH} \) was involved in the hydrostannylation process more easily than trialkylstannanes \( \text{R}_3\text{SnH} \) with \( \text{R} = \text{Pr}, \text{Bu} \)\(^{759} \). For example, the attempted addition of \( \text{R}_3\text{SnH} \) to \( \text{CH}_2=\text{CHCH}_2\text{OH} \)}
had failed, while Ph₃SnH was easily added to allyl alcohol. In 1959, van der Kerk and Noltes carried out the first hydrostannylation of dienes. The addition of dialkylstannanes to dienes and acetylenes gave polymers in some cases. However, in 1959, Noltes and van der Kerk obtained the cyclic diadduct 1,1,2,4,4,5-hexaphenyl-1,4-distannacyclohexane by the addition of Ph₂SnH₂ to PhC=CH. He also hydrostannylated Ph₃GeCH=CH₂ and Ph₂Si(CH₂=CH₂)₂ with triphenyl- and diphenylstannane. The reaction of Me₃SnH with HC≡CH led to Me₃SnCH=CHPh. Only the trans-adduct was isolated by hydrostannylation of phenylacetylene by triphenylstannane, but its addition to propargyl alcohol gave a mixture of cis- and trans-adducts. The hydrostannylation of alkynes proceeded more easily than that of alkenes, as confirmed by the lack of reactivity of Ph₃SnH with HexCH=CH₂, whereas it easily added to BuC≡CH. Nevertheless, in the reaction of R₃SnH with acetylenic hydrocarbons the diadducts could also be obtained. Dialkylstannanes R₂SnH₂ (R=Pr, Bu) were first used as hydrostannyliant agents in 1958, and Ph₂SnH₂ in 1959. The addition of R₂SnH₂ to the monosubstituted ethylenes CH₂=CHR’ at 60–80°C resulted in the diadducts R₂Sn(CH₂CH₂R’), Ph₂SnH₂ to F₂C=CF₂ at 80°C proceeded similarly. Analogously, organylstannanes RSnH₃ were added to three molecules of unsaturated compounds. Unlike the hydrosilylation reaction, neither Pt nor H₂PtCl₆ catalyzed the hydrostannylation reactions. Addition of hydroquinone did not inhibit this reaction, thus arguing against a free radical mechanism. Dutch researchers concluded that the hydrosilylation is an ionic process.

Since 1957 the triorganylstannanes Bu₃SnH and Ph₃SnH attracted scientists’ attention as effective reducing reagents. They easily reduced alkyl-, alkynyl- and aryl halides, amines and mercaptans to the corresponding hydrocarbons, but reduced ketones to the corresponding alcohols. Hydrostannylation of the carboxylic group was not observed, distinguishing it from the hydrosilylation. However, Neumann found that in the presence of radical reaction initiators triorganylstannanes were added easily to aldehydes R’CH₂O with the formation of the R₃SnOCH₂R’ adducts (R=Alk; R’=Alk, Ar). Kuivila and Beumel established that the ability of organotin hydrides to reduce aldehydes and ketones was decreased along the series: Ph₂SnH₂ > Bu₂SnH₂ > BuSnH₃ > Ph₃SnH > Bu₃SnH. In 1957, Dutch chemists showed that benzoyl chloride was reduced to benzaldehyde with Ph₃SnH, and Anderson discovered that Et₃SnH reduced halides and oxides of Group 13 elements to their lowest oxidation state or even to the free metals. Noltes reported that Pr₃SnH reduced BF₃ and AlCl₃ to the free elements. At the end of the last century, organotin hydrides were widely applied for the reduction of different organic, organometallic and inorganic compounds.

**E. Organylhalostannanes. The C–Sn Bond Cleavage**

Among the first organotin compounds of special importance are the organylhalostannanes R₄₋ₙSnXₙ. We would like to review here their development and approach to their synthesis in the absence of metallic tin, other metals or organometallic compounds, which have not been considered in the previous sections. Their properties will be considered as well.

Historically, the first and basic nonorganometallic method for the synthesis of organylhalostannanes was the C–Sn bond cleavage reaction by halogens and inorganic halides. As reported in section IIIA, Frankland and Cahours first observed the C–Sn bond cleavage of tetraalkylstannanes by halogens in 1859 and 1860–1862, respectively. In 1867, following Frankland, Morgunov demonstrated that the reaction of iodine
with \(\text{Me}_2\text{SnEt}_2\) resulted in \(\text{Et}_2\text{SnI}_2\). In 1871, Ladenburg\(^768\) found that, depending on the reagent ratio (1 : 1, 1 : 2, 1 : 3), the reaction of \(\text{Et}_4\text{Sn}\) with \(\text{I}_2\) resulted in \(\text{Et}_3\text{SnI}, \text{Et}_2\text{SnI}_2\) and \(\text{Et}_2\text{SnEtI}_2\), respectively. The cleavage of \(\text{Et}_3\text{SnPh}\) by iodine led to \(\text{Et}_3\text{SnI}\) and \(\text{PhI}\). Thus, he was the first to show that the Sn—Ar bond is weaker than the Sn-alkyl bond. In 1872, he cleaved \(\text{Me}_4\text{Sn}\) by iodine and obtained \(\text{Me}_3\text{SnI}\)\(^607\). Ladenburg\(^768\) also found that, contrary to Frankland\(^591\), the reaction between iodine and \(\text{Me}_2\text{SnEt}_2\) led to \(\text{MeEt}_2\text{SnI}\) and \(\text{Et}_2\text{SnI}_2\). He demonstrated the Sn—Sn bond cleavage by alkyl iodides, e.g. by the reaction of \(\text{Et}_3\text{SnEt}_3\) with \(\text{EtI}\) at 220°C, which gave \(\text{Et}_3\text{SnI}\) and \(\text{C}_4\text{H}_{10}\)\(^768\).

In 1900 Pope and Peachey\(^608\), who intended to synthesize a mixed trialkyliodoostannane having an asymmetric tin atom, cleaved \(\text{Me}_3\text{SnEt}\) and \(\text{Me}_2\text{SnEtPr}\) by iodine and obtained \(\text{Me}_2\text{SnEtI}\) and \(\text{MeEtPrSnI}\), respectively. In 1912, Smith and Kipping\(^678\) demonstrated that it was easier to cleave a PhCH\(_2\)-Sn than an Et-Sn bond and that cleavage of a Ph-Sn bond was easier in the reaction of \(\text{R}_3\text{SnCH}_2\text{Ph}\) (\(\text{R} = \text{Ph}, \text{Et}\)) with iodine, which led to \(\text{Ph_3SnI}\) and \(\text{R}_2(\text{PhCH}_2)_2\text{SnI}\), respectively. Sixteen years later Kipping\(^679\) found the following decreasing cleavage ability of the \(\text{R}_3\text{Sn}\) bond: \(2\text{-MeC}_6\text{H}_4 > 4\text{-MeC}_6\text{H}_4 > \text{Ph} > \text{PhCH}_2\). He obtained four organotin compounds containing the asymmetric tin atoms: \(\text{Ph}(4\text{-MeC}_6\text{H}_4)(\text{PhCH}_2)\text{SnI}, \text{Ph}(4\text{-MeC}_6\text{H}_4)(\text{PhCH}_2)\text{SnOH}, \text{BuPh}(\text{PhCH}_2)_2\text{SnI}\) and \(\text{EtBu(PhCH}_2)_2\text{SnI}\) during the multistage process of the C—Sn bond cleavage by iodine followed by a new C—Sn bond formation with a Grignard reagent. Unfortunately, he failed to isolate them as pure optically active isomers. In 1924, Krause and Pohland\(^769\) showed that one of the phenyl groups was cleaved in the reaction of iodine with triphenylhexylstannane. In 1889, Polis\(^651\) found that iodine did not cleave the Ph-Sn bond in \(\text{Ph}_4\text{Sn}\) and this was confirmed by Bost and Borgstrom\(^770\). Steric factors were evidently predominant, i.e. the Ar—Sn bond in \(\text{ArSnR}_3\) (\(\text{R} = \text{Me}, \text{Et}\)) was easier to cleave by iodine than the Sn—R bond.

Manulkin\(^771\) together with Naumov\(^772\) extensively studied for the first time the cleavage of alkyl radicals at the tin atom by iodine. They found that their cleavage from \(\text{R}_4\text{Sn}\) (\(\text{R} = \text{Me}, \text{Et}, \text{Pr}, \text{Bu}, \text{i-Am}\)) to form \(\text{R}_3\text{SnI}\) became more difficult (i.e. required higher temperature) on increasing their length. The same was demonstrated for the homologous series of tetraalkylstannanes \((\text{C}_n\text{H}_{2n+1})_4\text{Sn}\) with \(n = 1–7\), and for the mixed series \(\text{R}_3\text{SnR}_0\), where \(\text{R}, \text{R}_0\) were alkyl groups of various length\(^773,774\). Contrary to Cahours\(^595,597\), Manulkin showed that the reaction of iodine with \(\text{Me}_3\text{SnR}\) (\(\text{R} = \text{Et}, \text{Bu}, \text{Am}, \text{i-Bu}, \text{i-Am}\)) led to \(\text{Me}_2\text{RSnI}\) and that \(\text{Et}_3\text{SnBu}\) was transformed to \(\text{Et}_3\text{BuSnI}\)\(^775\). He was also able to cleave two or even all four \(\text{R}\) groups from the tin atom in \(\text{R}_4\text{Sn}\) (\(\text{R} = \text{Me}, \text{Et}\)) under more drastic conditions (160–170°C). Thus, he was the first to find that in the reaction of halogens \(\text{X}_2\) with \(\text{R}_4\text{Sn}\), one or two \(\text{R}\) substituents were first cleaved in consequent steps whereas the remaining two groups were cleaved simultaneously with the formation of \(\text{SnX}_4\). He was unsuccessful in stopping the process at the \(\text{R}_3\text{SnX}_3\) formation. In 1957, Koton and Kiseleva\(^776\) were the first to demonstrate that the allyl group was easily cleaved from tin atom by iodine: the reaction of iodine with \(\text{CH}_2=\text{CHCH}_2\text{SnPh}_3\) led to \(\text{Ph}_3\text{SnI}\) and \(\text{CH}_2=\text{CHCH}_2\text{I}\).

Only few publications\(^651,777\) were devoted to the use of chlorine to obtain organylchlorostannanes. In 1870, Ladenburg\(^778\) obtained \(\text{Et}_2\text{SnCl}_2\) by chlorination of hexaethyldistannane \(\text{Et}_3\text{SnEt}_3\), i.e. a cleavage of both the C—Sn and Sn—Sn bond took place. In the reaction of hexaethyldistannane with chloroacetic acid at 250°C he obtained \(\text{Et}_2\text{SnCl}_2\) as well as \(\text{C}_2\text{H}_4\) and \(\text{C}_4\text{H}_{10}\)\(^778\).

In the 20th century the cleavage reaction of \(\text{R}_4\text{Sn}\) by halogens (mainly by bromine and iodine) was widely used for the syntheses of \(\text{R}_3\text{SnX}\) and \(\text{R}_2\text{SnX}_2\), at yields which were dependent on the reaction conditions and the ratios of the reagents. Thus, the first syntheses of organylhalostannanes by the cleavage of \(\text{R}_4\text{Sn}\) and \(\text{R}_3\text{SnX}\) were carried out in
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1900–1925 609,610,630,678,732,769,777,779–782. Sixty publications in the period before 1960, reporting the use of the cleavage of R₄Sn for organylbromo- and organyliodonstannane syntheses by halogens (mainly bromine and iodine), were reviewed 125,675.

Bromine was mostly used to easily cleave aryl substituents from the tin atom. In 1899 Polis 651 synthesized Ph₂SnBr₂ by the reaction of bromine and Ph₄Sn and in 1918 Krause 779 obtained Ph₃SnBr by the same reaction. The cleavage of Ph₄Sn by bromine and chlorine to form Ph₃SnX was carried out by Bost and Borgstrom 770 in 1929. Unlike iodine, ICl reacted extremely easily with Ph₄Sn to give Ph₃SnCl and PhI. In 1931 Bullard and Holden 783, and in 1941–1946 Manulkin 771,773–775 began to investigate in detail the hydrocarbon radical cleavage from the tin atom. The Manulkin studies showed that the tin–alkyl bond became more difficult to cleave as the alkyl group length increased (and it was more difficult when its tail was branched). Secondary alkyl groups (e.g. Me₂CH) were cleaved more easily from the tin atom than primary ones 773. These investigations enabled one to arrange the substituents according to the ease of their cleavage by halogens from the tin atom as follows: All > Ph > PhCH₂ > CH₂=CH > Me > Et > Pr > i-But > Bu > i-Am > Am > Hex ≫ Heptyl > Octyl.

Following Frankland 591, Buckton 604,784 in 1859 demonstrated the possibility of the C–Sn bond cleavage in tetraalkylstannanes by hydrohalic acids. In 1870, Ladenburg 778 found that HCl cleaved the C–Sn and Sn–Sn bonds in Et₃SnSnEt₃ with the formation of Et₃SnCl and that HCl cleaved the phenyl group from PhSnEt₃ with the formation of Et₃SnCl 605. In 1878, Aronheim 722 showed that HCl could cleave two phenyl groups of Ph₂SnCl₂ with the formation of SnCl₄. He also reported that the reaction of Ph₂SnCl₂ with the gaseous HBr and HI was not accompanied by the Ph–Sn bond cleavage, but was an exchange reaction, which resulted in Ph₂SnClX (X = Br, I). The reaction between Ph₂SnX₂ (X = Br, I) and HBr and HI led to SnX₄.

In 1927, Bullard and Robinson 785 studied the cleavage reaction of Ph₂SnMe₂ by hydrogen chloride, which resulted in Me₂SnCl₂. Four years later Bullard and Holden 783 isolated MeEtSnCl₂ from the reaction of HCl with Me₂SnEt₂. This result showed that both ethyl and methyl groups were cleaved. Under the action of HCl on Et₂SnR₂, R = Pr, Ph the products EtPr₂SnCl and Et₂SnCl₂ 783 were obtained, respectively. The facility of alkyl group cleavage from the tin atom with hydrogen halides decreased in line with the above-mentioned substituent order with the halogens. However, the order may be different in cleavage by HCl and by iodine. For example, in 1928 Kipping 679 found that HCl could cleave the Ph(CH₂)₃SnEt cleaved the ethyl group, but the reaction of halogens led to the benzyl group cleavage. He also demonstrated that in the reaction of concentrated HCl with tetraarylstannanes two aryl groups might be cleaved 679. During the action of hydrogen halides on the silicon organotin derivatives R₂Sn(CH₂SiMe₃)₂, R = Me, Bu the (trimethylsilylmethyl)methyl group was the first to be cleaved 672. In contrast, halogens cleaved preferentially the R–Sn bond of these compounds. In 1938, Bashinskaya and Kocheshkov 596 studied the facility of the reaction of HCl with Ar₂SnAr' and found that the C–Sn bond cleavage by hydrogen chloride became more difficult in the following order (the ‘electronegative row’ of substituents): 2-thienyl > 4-MeOC₆H₄ > 1-C₁₀H₇ > Ph > c-C₆H₁₁. In 1946, Manulkin 774 showed that Me₂EtSnCl was formed in the reaction of HCl with Me₂SnEt. In 1958, Bähr and Gelius 703 cleaved by HCl all the three isomers of (PhC₆H₄)₄Sn to (PhC₆H₄)₂SnCl₂. Finally, in 1957, Koton and Kiseleva 776 demonstrated for the first time that an allyl group easily cleaves from the tin atom under the action of alcoholic HCl solution. The ease of the cleavage followed the order of compounds: (CH₂=CHCH₂)₄Sn > (CH₂=CHCH₂)₂SnPh₂ > CH₂=CHCH₂SnPh₃. The cleavage of tetraalkylstannane with HCl at room temperature to SnCl₄ was especially easy in this series. Further, the high reactivity in homolytic processes of the C–Sn bond
in the CH$_2$=CHCH$_2$Sn moiety was extensively used in synthesis\textsuperscript{786–788}. In 1957–1958, Seyferth\textsuperscript{672} demonstrated that, under the action of hydrogen halides, a vinyl group was cleaved more easily from the tin atom than an alkyl one, less easily than the phenyl group. In this process an addition of HX to the double bond was not observed. In the 20th century the application of the C–Sn bond cleavage by hydrogen halides was limited. From 1928 to 1948 it was used only in 7 laboratories\textsuperscript{774,783,785,791–794}.

Developed in 1859 by Buckton\textsuperscript{604} and then studied by Cahours\textsuperscript{596} in 1862, by Ladenburg\textsuperscript{605,606} in 1871, by Pope and Peachey\textsuperscript{308} in 1903 and by Goddard and Goddard\textsuperscript{729} in 1922, the cleavage reaction of tetraorganylstannane by tin tetrahalides became the most important method for the synthesis of organylhalostannanes. Neumann\textsuperscript{90} named it the co-proportionation reaction (originally ‘komproportionierung’). In general, it may be presented by equation 7.

$$R_4Sn + \frac{n}{4-n}SnX_4 \rightarrow 4 \frac{4-n}{4-n}R_4SnX_n (R = \text{Alk}, \text{Ar}; X = \text{Cl, Br, I}; n = 1–3)$$ \hspace{1cm} (7)

The first stage of this process is the cleavage of one organic substituent R with the formation of R$_3$SnX and R$_2$SnX$_2$. A further reaction of the latter led to R$_2$SnX$_2$ and an excess of SnX$_4$ led to R$_3$SnX$_3$\textsuperscript{653}. In 1871, Ladenburg\textsuperscript{606} was the first to show that the presence of both aryl and alkyl groups at the tin atom in the reaction with SnCl$_4$ led to the reaction described in equation 8.

$$Et_3SnPh + SnCl_4 \rightarrow Et_2SnCl_2 + EtPhSnCl_2$$ \hspace{1cm} (8)

Unlike the synthesis of organylhalostannanes based on dealkylation by halogens, hydrohalic acids and other inorganic and organic halides of R$_4$Sn and R$_3$SnX, the co-proportionation reaction enabled one to keep all the organic substituents in the products, i.e. the number of R–Sn bonds is the same in the precursor and in the products. In 1929–1945, this reaction was studied extensively by Kocheshkov and his coworkers\textsuperscript{633,727,795–806}. In particular, by the reaction of tetraarylstannanes and diarylhalostannanes with SnCl$_4$ under severe conditions (150–220 °C) they obtained aryltribromostannanes for the first time. In 1938, Kocheshkov and coworkers synthesized (4-PhC$_6$H$_4$)$_2$SnBr$_2$ by the reaction of (4-PhC$_6$H$_4$)$_4$Sn with SnBr$_4$ at 160–210 °C. According to Zimmer and Sparmann\textsuperscript{693} (1954) the reaction of SnBr$_4$ with Ph$_4$Sn at 220 °C led to Ph$_2$SnBr$_2$. The reaction of diaryldibromostannanes with SnBr$_4$ at 150 °C enabled Kocheshkov\textsuperscript{633,795} to obtain a number of aryltribromostannanes in 1929. Two years later he showed that both SnCl$_4$ and SnBr$_4$ could be widely used to synthesize ArSnX$_3$ (X = Cl, Br)\textsuperscript{806}. In 1933 he reacted R$_4$Sn, R$_3$SnX, R$_2$SnX$_2$ (R = Me, Et, Pr) with SnX$_4$ (X = Cl, Br)\textsuperscript{796}. In 1950, Razuvaev\textsuperscript{807} first conducted the photochemical reaction of SnCl$_4$ with Ph$_4$Sn and obtained Ph$_2$SnCl$_2$ almost quantitatively. This allowed the temperature of the reaction to be reduced to 200 °C\textsuperscript{633,795} and it also showed that the process proceeded via a free-radical mechanism. Unfortunately, these data remained unknown to the general circle of researchers. During the first 60 years of the 20th century the co-proportionation reaction had been referred to in 50 publications\textsuperscript{631,653,798}. In 1957, Rosenberg and Gibbons\textsuperscript{808} used tetravinylstannane in the reaction with SnX$_4$ at 30 °C which led to (CH$_2$=CH)$_2$SnCl$_2$.

For the first time tetraiodostannane was used in the reaction with tetraalkylstannanes by Pope and Peachey\textsuperscript{308,611} in 1903. They demonstrated that heating Me$_4$Sn with SnI$_4$ at >100 °C led to Me$_3$SnI and MeSnI$_3$. Ph$_4$Sn did not react with SnI$_4$ even at 240 °C.

In 1871, Ladenburg\textsuperscript{606} was the first to study the reaction of SnCl$_4$ with a nonsymmetric tetraorganystannane. As a result Et$_2$SnCl$_2$ and EtPhSnCl$_2$ were obtained from Et$_3$SnPh.
In 1945, Pavlovskaya and Kocheshkov showed that in the reaction of SnCl$_4$ with triaryllalkylstannanes Ar$_3$SnR, ArSnCl$_3$ and RSnCl$_3$ were easily formed. In 1933 Kocheshkov, and in 1963 Neumann and Burkhardt as well as Seyferth and Cohen found that dialkyldihalostannanes R$_2$SnX$_2$ (X = Cl, Br) and alkyltrihalostannanes reacted with SnCl$_4$ analogously to tetraalkylstannanes and trialkylhalostannanes, but at a higher temperature (200–215°C).

In 1878, Aronheim was able to disproportionate (i.e. 'retrokomproportionierung') organylhalostannanes when Ph$_2$SnCl$_2$ was transformed to Ph$_3$SnCl and SnCl$_4$, as well as to study the catalytic influence of NH$_3$ and sodium amalgam on this reaction. He also showed that the reaction of Ph$_2$SnCl$_2$ with NaOH led to Ph$_3$SnCl and SnO$_2$, and that the reaction of NaNO$_3$ with Ph$_2$SnCl$_2$ in acetic acid solution resulted in Ph$_3$SnCl.

During the first half of the 20th century it was found that the C–Sn bond in tetraorganystannanes could be cleaved by the halides of mercury, aluminum, phosphorus, arsenic, bismuth and iron with formation of the corresponding organylhalostannanes. In this case tetraorganystannanes acted as alkylating and arylating agents and could be used for preparative purposes.

In 1936 Kocheshkov, Nesmeyanov and Puzyreva found that HgCl$_2$ cleaved the Sn–Sn bond in both R$_3$SnSnR$_3$ and (R$_2$Sn)$_n$ with the formation of R$_3$SnCl and R$_2$SnCl$_2$, respectively.

In 1903 and 1904 Pfeiffer and Heller developed a new synthetic approach to organyltrihalostannanes. By conducting the reaction of SnI$_2$ with MeI in a sealed tube at 160°C, they obtained MeSnI$_3$. In 1911, Pfeiffer decided to replace in the reaction the SnI$_2$ by Et$_2$Sn, which he probably regarded as a monomer. Indeed, heating of (Et$_2$Sn)$_n$ with EtI at 150°C led to Et$_3$SnI. In 1936, Lesbre and coworkers modified Pfeiffer’s reaction. They replaced tin dihalides with the double salts with the halides of heavy alkaline metals MSnX$_3$ (M = K, Rb, Cs; X = Cl, Br), which enabled them to obtain organyltrichloro- and -tribromostannanes. The reaction of KSnCl$_3$ with excess of RI at 110°C led to R$_3$SnI, R = Me, Et, Pr with 44, 37 and 25% yields, respectively. In 1953, Smith and Rochow found that the reaction of SnCl$_2$ with MeCl led to MeSnCl$_3$.

In 1935, Nesmeyanov, Kocheshkov and Klimova found that the decomposition of the double salts of aryldiazonium chlorides and SnCl$_4$, i.e. [(ArN$_2$)$_2$Cl]$_2$SnCl$_4$ (more exactly, [(ArN$_2$)$_2$]$^2^+$[SnCl$_6$]$^{2^-}$), by tin powder gave Ar$_2$SnCl$_2$. Sometimes the reaction product turned out to be ArSnCl$_3$. Two years later Waters simplified this method by allowing the tin powder to act directly on phenyldiazonium chloride. Later, he found that the reaction proceeded via decomposition of PhN$_2$Cl into Ph$^+$ and Cl$^-$ radicals, whose interaction with tin led to Ph$_3$SnCl$_2$. In 1957–1959 Reutov and coworkers found that the decomposition of double chloronium, bromonium and iodonium salts of tin dichloride Ar$_2$XCl·SnCl$_2$ by the tin powder led to Ar$_2$SnCl$_2$, ArX (X = Cl, Br, I) and SnCl$_2$. This reaction was simplified by decomposing the mixture of Ar$_2$XCl and SnCl$_2$ by the tin powder. In 1959 Nesmeyanov, Reutov and coworkers obtained diphenyldichlorostannane by decomposition of complexes of diphenylhalonium dichlorides and SnCl$_4$, i.e. [Ph$_2$Y]$_2^2^+$SnCl$_6^{2^-}$ (Y = Cl, Br), by the tin powder.

The attempt of Aronheim to obtain Ph$_2$SnCl$_3$ by the thermal reaction of SnCl$_4$ with benzene (analogously to the Michaelis synthesis of PhPCl$_2$) had failed in 1878. The reaction products at 500°C were biphenyl, SnCl$_2$ and HCl. The chemical properties of organylhalostannanes began to be studied extensively after their synthesis. The first property was their ability to be hydrolyzed by water, especially in the presence of bases. As early as 1852–1860 Löwig, Frankland and Cahours obtained (R$_2$SnO)$_n$ with R = Me, Et, Pr, Et$_3$SnSnEt$_3$ and R$_3$SnOH (R = Me, Et) by the reaction of alkylhalostannanes with aqueous-alcoholic alkaline solution.
In 1862, Cahours first showed that the halogen in organylhalostannanes could be easily substituted by a pseudohalide group in the reactions with silver pseudohalides, such as the reaction of \( \text{Et}_3\text{SnI} \) and \( \text{Et}_2\text{SnI}_2 \) with AgCN, AgNCO and AgSCN. In 1878 Aronheim substituted the chlorine atom in Ph\(_2\)SnCl\(_2\) by the action of HI, H\(_2\)O, NH\(_3\) and EtONa which resulted in Ph\(_2\)SnClI, Ph\(_2\)Sn(OH)Cl, Ph\(_2\)Sn\((\text{NH}_2)\)Cl and Ph\(_2\)Sn\((\text{OEt})_2\), respectively. The products Ph\(_2\)Sn(OH)Cl and Ph\(_2\)Sn(NH\(_2\))Cl were of special interest, since no stable isostructural silicon and germanium analogs had been known. The Ph\(_2\)Sn(OH)Cl was also obtained by the hydrolysis of Ph\(_2\)Sn(NH\(_2\))Cl and it was transformed to Ph\(_2\)SnCl\(_2\) by the action of HCl. The stability of Ph\(_2\)Sn(OH)Cl is amazing, as it does not undergo intramolecular dehydrochlorination. It is more amazing that, according to Aronheim’s data, the intermolecular heterofunctional condensation of Ph\(_3\)SnCl with Ph\(_3\)SnOH resulted in Ph\(_3\)SnOSnPh\(_3\). It might be assumed that compounds R\(_2\)Sn(X)Cl, X = OH, NH\(_2\) were either dimeric or bimolecular complexes R\(_2\)SnCl\(_2\) - R\(_2\)SnX\(_2\). In 1879, Aronheim continued to study exchange reactions of Ph\(_3\)SnCl. In this respect the interesting investigations of the Russian chemist Gustavson, who developed the exchange reactions of SnCl\(_4\) with mono-, di- and triiodomethanes, should be mentioned. The mixtures of SnCl\(_4\) with CH\(_3\)I, CH\(_2\)I\(_2\) and CHI\(_3\) were stored in the dark in sealed ampoules at room temperature for 7 years. No reaction was observed with CHI\(_3\), but in the mixture of CH\(_2\)I\(_2\) with SnCl\(_4\) 0.7–1.2% of the chlorine was displaced with iodine, while in the mixture of SnCl\(_4\) with CH\(_3\)I 33–34% of the chlorines were displaced. These data should be added to the Guinness Book of Records.

The substitution of alkylhalostannanes by the reaction with silver salts was first realized by Cahours. In 1852 he found that the reaction of \( \text{Et}_2\text{SnI}_2 \) with AgNO\(_3\) and AgSO\(_4\) resulted in \( \text{Et}_2\text{Sn(NO}_3)_2 \) and \( \text{Et}_2\text{SnSO}_4 \), respectively. Ten years later he synthesized \( \text{Et}_2\text{Sn(SCN)}_2 \) and \( \text{Et}_2\text{Sn(CN)}_2 \) in the same way, and \( \text{Et}_3\text{SnCN} \), \( \text{Et}_3\text{SnSCN} \) and \( \text{Et}_3\text{SnNCO} \) by the reaction of \( \text{Et}_3\text{SnI} \) with AgCN, AgSCN and AgNCO, respectively. In 1860, Kulmiz used a similar reaction with silver salts for the synthesis of a series of Et\(_3\)Sn derivatives (cyanide, carbonate, cyanoate, nitrate, phosphate, arsenate, sulfate).

In 1954, Anderson and Vasta studied the exchange reactions of \( \text{Et}_3\text{SnX} \) with silver salts AgY. They showed that the substitution ability of X by Y is decreased in the following order of Y (‘the Anderson row’): SMe > SSnEt\(_3\) > I > Br > CN > SNC > Cl > OSnEt\(_3\) > NCO > OCOMe > F. None of these groups could replace the F atom in Et\(_3\)SnF. In contrast, the SMe group in Et\(_3\)SnSMe can be replaced by any group Y in this series. The simplest synthesis of organylfluoro- and iodostannanes was by the exchange reaction of an appropriate organylchloro- and bromostannanes with alkali metal halides (KF, NaI etc.). The exchange of the halogen atoms of nonfluoro organylhalostannanes for fluorine, i.e. the preparation of organylfluorostannanes, was first realized by Krause and coworkers, in the reaction of KF and Ph\(_3\)SnCl in aqueous-alcohol medium. A number of researchers used the exchange reactions of organylchlorostannanes with the sodium salts of organic and inorganic acids. For example, Kocheshkov and coworkers, found that PhSnCl\(_3\) (which could be easy hydrolyzed by boiling water) reacted with HX (X = Br, I) in water to give PhSnX\(_3\).

In the first half of the 20th century it was shown that the C–Sn bond in organotin compounds, especially in tetraorganylstannanes, was easily cleaved by both heterolytic and homolytic mechanisms. This fact makes the C–Sn bond quite different (regarding its thermal and chemical stability) from the C–Si and C–Ge bonds and brought it close to the C–Pb bond. In 1945, Waring and Horton studied the kinetics of the thermal decomposition of tetramethylstannane at 440–493 °C, or at 185 °C at a low pressure...
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(5 mm). Metallic tin, methane and some amounts of ethylene and hydrogen turned out to be the prevalent products of the thermolysis reaction. Indian researchers revised their data and concluded that the reaction is of a kinetic order of 1.5 and proceeds by a free-radical mechanism. Long investigated the mechanism of tetramethylstannane thermolysis in more detail.

In 1958, Prince and Trotman-Dickenson studied the thermal decomposition of \( \text{Me}_2\text{SnCl}_2 \) at 555–688 °C in the presence of toluene as the radical carrier. The process proceeded homolytically according to equation 9.

\[
\text{Me}_2\text{SnCl}_2 \rightarrow 2\text{Me}^* + \text{SnCl}_2
\]

In 1956 and 1959, Dutch researchers first observed the thermal cleavage of \( \text{Ph}_3\text{SnCH}_2\text{CH}_2\text{COOH} \), which led to \( \text{C}_6\text{H}_6 \) and \( \text{Ph}_2\text{SnCH}_2\text{CH}_2\text{COOH}^- \). The latter was the first zwitterionic organotin compound.

F. Compounds Containing an Sn–O Bond

As reported in Section III.A, oxygen-containing organotin compounds with the stannoxane Sn–O bond, such as \( \text{(R}_2\text{SnO)}_n \), \( \text{R}_3\text{SnOSnR}_3 \), \( \text{R}_3\text{SnOH} \), and \( \text{[R(HO)SnO]}_n \), became known in the second half of the 19th century. They appeared first in the laboratories of Löhig (1852), Frankland (1853), Cahours (1860), Aronheim (1878) and Meyer (1883). The main synthetic method of compounds of the \( \text{(R}_2\text{SnO)}_n \) and \( \text{R}_3\text{SnOSnR}_3 \) type was alkaline hydrolysis of diorganyldihalostannanes and triorganylhastannanes. In 1913, Smith and Kipping were the first to report that the so-called diorganyl tin oxides \( \text{R}_2\text{SnO} \) were not monomers, as previously considered. This is the reason why their archaic name has to be taken out of use. They concluded that these compounds were formed in a dehydrocondensation process of the primary hydrolysis products of \( \text{R}_2\text{SnX}_2 \) and were typical polymers, i.e. polydiorganylstannoxane-\( \alpha,\omega \)-diols \( \text{HO(R}_2\text{SnO)}_n\text{H} \), which are solids mostly insoluble in water and organic solvents. The authors succeeded in isolating a low molecular weight oligomeric intermediate, i.e. hexabenzylltristannoxane-1,5-diol \( \text{HOR}_2\text{SnOSnR}_2\text{OSnR}_2\text{OH} \) (\( \text{R} = \text{PhCH}_2 \)), from the dehydrocondensation of \( \text{R}_2\text{Sn(OH)}_2 \). According to Kipping’s nomenclature, it was named ‘di-unhydro-tri-(dibenzyltin)-dihydroxide’.

In 1951, Solerio reported that compounds with the \( \text{R}_2\text{SnO} \) formula could be monomeric as well, when the tin atom carries bulky substituents, such as diorganylstannanones \( \text{R}_2\text{Sn}=\text{O}, \text{R} = \text{C}_12\text{H}_{25} \). When the substituents \( \text{R} \) are less bulky, the substrates are still polymers. Thus, Solerio can be considered as the founder of the chemistry of diorganyl-stannanones \( \text{R}_2\text{Sn}=\text{O} \), the first organotin compounds of three-coordinated tin, bonded to one of its substituents by a double bond.

Many years after Löhig’s initial study of the oxidation of diethylstannylene to \( \text{Et}_2\text{SnO} \) by air oxygen, the reaction was studied properly in the 20th century by Pfeiffer, Krause and Becker and Chambers and Schere.

In 1952, Nesmeyanov and Makarova developed the synthetic method for ‘diaryl tin oxides’ \( \text{Ar}_2\text{SnO} \) by the reaction of \( \text{SnCl}_2 \) with \( \text{[ArN}_2\text{]}^+\text{[BF}_4^- \) and with zinc powder in acetone, followed by aqueous hydrolysis with ammonia. The yields of \( \text{(Ar}_2\text{SnO)}_n \) never exceeded 41%. Along with it small amounts of triarylstannanols and arylstannane acids were isolated. In 1957, Reutov and coworkers succeeded in significantly increasing the yields of \( \text{(Ar}_2\text{SnO)}_n \) up to 80% using the Harada reaction. In 1939–1949, Harada described a series of compounds with a composition of \( \text{R}_2\text{SnO} \cdot \text{R}_2\text{SnX}_2 \) whose molecular structure has not yet been determined.

The Sn–O bond in \( \text{(R}_2\text{SnO)}_n \) and in \( \text{R}_3\text{SnOSnR}_3 \) was very reactive. It was hydrolyzed by alkalis, and decomposed by alcohols, glycols and inorganic and organic acids.
In 1860, Cahours began to study nonprotolytic, heterolytic cleavage reactions of the Sn—O—Sn group and showed that polydiethylstannoxane reacted with PCl₅ to give diethylchlorostannane. The cleavage reactions of this group by SnCl₄, SiBr₄, HgCl₂, I₂ and H₂S were studied only in the 20th century.

During the period 1920–1940, studies of thermal reactions of organotin compounds having Sn—O bonds had started. All the reactions proceeded with a C—Sn bond cleavage followed by a disproportionation process. In 1926, Chambers and Scherer found that thermolysis of Ph₃SnOH gave (Ph₂SnO)n, Ph₄Sn and H₂O. According to Schmitz-DuMont, the product of the dehydrocondensation, i.e. Ph₃SnOSnPh₃, was also formed. In 1929, Kraus and Bullard observed an analogous thermal destruction of Me₃SnOH. According to Harada (1939–1940) thermolysis of triethylstannanol occurred in another way (equation 10).

$$\text{3Et₃SnOH} \xrightarrow{-C₂H₆} \text{3Et₂SnO} \xrightarrow{} \text{Et₃SnOSnEt₃ + SnO₂} \quad (10)$$

Kraus and Bullard found that Me₃SnOSnMe₃ thermolysis led to Me₄Sn and (Me₂SnO)n. They also showed that thermal decomposition of (Me₂SnO)n gave Me₄Sn, C₂H₆, SnO₂ and SnO. Unlike this, the thermolysis of (Et₂SnO)n led to Et₃SnOEt₃ and SnO₂.

The first trialkylstannanol R₃SnOH, R = Me, Et were synthesized by Frankland (in 1853), and Cahours and coworkers (in 1860) by the action of alkaline aqueous solutions on the corresponding trialkylhalostannanes. In 1928, Kipping used aqueous ammonia solution for this purpose. Ladenburg, Aronheim, Hjortdahl, Werner and Pfeiffer similarly obtained triorganylstannanols. Aronheim synthesized triphenylstannanol Ph₃SnOH in 1878. The first trialkylstannanol containing bulky substituents at the Sn atom, (t-Bu)₃SnOH, was synthesized by Krause and Weinberg in 1930. During the period from 1903 to 1960 trialkylstannanols were mentioned in 50 publications.

In some cases the Sn—OH bond was also formed by hydrolytic cleavage of the XCH₂Sn bond, when X was an electronegative substituent (N≡C, EtOOC).

Trialkylstannanols turned out to be rather stable compounds and this was their main difference from their isostructural silicon and germanium compounds. They could be dehydrated to hexaalkyldistannoxanes only in the presence of dehydrating agents. For example, Harada obtained hexamethyldistannoxane from trimethylstannanol only when it was distilled from sodium. Unlike R₃SiOH, the R₃SnOH (R = Alk) are strong bases. Nevertheless, triphenylstannanol, as well as its silicon analogs are still weak acids. According to the ebullioscopy data, the compounds R₃SnOH (R = Me, Et, PhCH₂) were associated to some extent in boiling benzene. Trialkylstannanols were not converted to stannolates even by the action of Na metal. According to Harada, the reaction of Me₃SnOH with Na in liquid ammonia did not give Me₃SnNa, but Me₃SnSnMe₃. Kraus and Neal also found that the latter was obtained in the reaction of Me₃SnOPh with Na in the same solvent. The reaction of R₃SnOH with inorganic acids (e.g. HCl, HBr, HI, H₂SO₄) enabled an easy replacements of the hydroxyl group by the anions of the acids.

The first attempts to obtain dialkylstannandiol R₂Sn(OH)₂ by the hydrolysis of dialkylhalostannanes were unsuccessful. These compounds turned out to be extremely unstable and they dehydrated immediately to amorphous polyperorganylstannoxane-α,ω-diols.
HO(R₂SnO)₂H. However, in the first half of the 20th century diorganyl stannanediols containing bulky substituents (R = c-Hex, t-Bu, t-Am) were synthesized.

In 1954, Anderson concluded that the basicity of organotin compounds having Sn—O bonds decreases on increasing the number of oxygen atoms surrounding the Sn atom, i.e. in the series: (R₃Sn)₂O > (R₂SnO)ₙ > (R₂SnO₁.₅)ₙ > SnO₂.

In the Krause laboratory it was established in 1924 and 1930 that the reaction of R₂Sn(OH)₂ with HCl or HBr resulted in R₂SnX₂ (X = Cl, Br). Simultaneously, an interesting disproportionation reaction was discovered according to equation 11.

\[ 2[R(MO)SnO]_n \rightarrow (R₂SnO)ₙ + nM₂SnO₃ (M = Na, K). \] (11)

In 1878, first Aronheim and then Kipping (1928) and Krause and Weinberg (1930) synthesized stable diorganyl halostannanols R₂Sn(OH)X, which are stable crystalline substances. Organotin compounds R(OH)₂SnOSn(OH)Cl and RSn(OH)₂Cl as well as compounds containing the >Sn(OH)Cl group were obtained only in the 1960s.

Silicon compounds having the >Si(OH)Cl group have not yet been identified. They immediately undergo disproportionation into hydrohalic acid and a short-lived highly reactive diorganylsilanones R₂Si=O, which in turn quickly oligomerize or are inserted into the bond of a trapping reagent. The higher stability of diorganyl halostannanols in comparison with their organosilicon analogs can be ascribed to two factors: (1) a longer distance between halogen and oxygen atoms, and (2) a higher stability of the O—H bond due to the higher basicity of the >SnOH group. It is more likely that these compounds are cyclic dimers [R₂Sn(OH)Cl]₂ or [R₂Sn(OH)₂ · R₂SnCl₂], or even high oligomers.

Organyl stannantriols RSn(OH)₃ have not yet been isolated. Consequently, organotin compounds R₂Sn(OH)₃ are less stable than their isostructural compounds of silicon and germanium, which in turn are not highly stable. However, their formation as intermediate compounds in hydrolysis reactions of R₂SnX₂ and RSnX₃ seems likely.

Meyer’s reaction can be described by equation 12.

\[ SnCl₂ + 3MOH \rightarrow Sn(OH)OM + 2MCl, -H₂O \rightarrow R(X)Sn(OH)OM \rightarrow RSnOM + CO₂, -H₂O \rightarrow RSnOOH + MHCO₃ \] (M = Na, K; X = I, Br)

At the same time Meyer also isolated ‘pyro acid’ of (MeSn)₄O₇H₂ composition. It appeared to be a cross-linked polymer, corresponding to the formula HO(MeSnO₁.₅)₄H.

At the beginning of the 20th century Pfeiffer and coworkers, then Druce, and Lambourne improved the Meyer method and synthesized a series of ‘alkylstannone acids’ and studied their
properties. Unfortunately, the Meyer reaction was hardly suitable for the synthesis of arenestannone acids. In 1903, Pfeiffer and Lehnardt, and others suggested another method for the synthesis of organylstannone acids. It was based on the reaction of alkyltrihalostannanes with aqueous alcoholic alkaline solutions. In 1929 following Pope, Kocheshkov and coworkers developed a method for the synthesis of arylstannone acids, based on hydrolysis of ArSnCl3. It is interesting to note that according to Kocheshkov, the hydrolysis of ArSnBr3 was more difficult than that of ArSnCl3. During the hydrolysis of ArSnX3 by alkali solutions the arylstannates salts were formed, but not the free acids, and then the free acids were isolated by the action of CO2. In 1957, Koton and Kiseleva obtained the first unsaturated allylstannone acid by heating tetraallylstannane with water in a sealed ampoule at 170 °C.

Zhukov following Pfeiffer and Lehnardt and Pope and Peachey (1903), Druce and then Kocheshkov and Nad’ showed that alkylstannone acids were easily decomposed by hydrohalic acids to RSnX3. This reaction was used extensively for the synthesis of pure organyltrihalostannanes. In 1938, in Kocheshkov laboratory it was found that the reaction of RSnOOH with HX proceeded with R/NUL bond cleavage to give RH and SnX4 under severe conditions. According to Pope and Peachey, MeSnOOH was transformed in boiling aqueous alkali to a mixture of (Me2SnO)n and Me3SnOH with simultaneous formation of CH4. In 1934, Lesbre and Glotz found that the transformation of alkylstannone acids RSnOOH to (R2SnO)n became easier with the decrease in the size of the alkyl radical R. Arenestannone acids did not undergo this reaction.

The so-called organylstannone acids are polymers, which could be assigned the structure of polyorganyl(hydroxy)stannoxanes [RSn(OH)O]n or HO[RSn(OH)O]nH. It is interesting that they were not hydrolyzed on heating and were not converted to polyorganylstannanesesquioxanes (RSnO1.5)n. The properties of their hydrolysis products were strikingly different from those of their isostructural organyltrichlorosilanes with regard to solubility in water and methanol and the high reactivity. They were easily decomposed by acids, alkalis, hydrogen sulfide or mercaptans.

Lambourne showed that the action of carboxylic acids RCOOH on ‘methylstannone acid’ gave 1,3,5-trimethylpentacycloxytristannoxanes Me(RCOO)2SnOSn(OCOR)MeOSn(OCOR)2Me, which hydrolyzed to the cyclic trimers 1,3,5-trimethyltricyclooctotristannoxanes [Me(RCOO)SnO]3. The data obtained led him to conclude that methylstannone acid was the cyclic trimer [Me(HO)SnO]3.

The first representative of hexaalkyldistannoxanes R3SnOSnR3 with R = Et (incorrectly named earlier ‘trialkyltin oxides’) was obtained by Cahours and Kulmiz in 1860. Unlike their isostructural silicon and germanium analogs, the preparation of lower hexaalkyldistannoxanes with R = Me, Et by hydrolysis of trialkylhalostannanes failed even in the presence of alkalis. This was caused by the fact that the Sn-O-Sn group in these compounds was extremely easily cleaved by water, so that the equilibrium of the trialkylstannanol dehydration with their primary alkaline hydrolysis products (equation 13) was almost completely to the left. Probably, this was the reason that, after the Cahours and Kulmiz reports, hexaethyldistannoxane appeared in chemical publications again only in 1939. Hexamethyldistannoxane was first synthesized in the Kraus laboratory in 1925–1929 (and then by Bähr), where it was obtained by Me3SnSnMe3 oxidation. In 1940, Harada synthesized Me3SnOSnMe3 by the reaction of Me3SnOH with metallic sodium. Krause and Pohland synthesized Ph3SnOSnPh3, the first representative of hexaaryldistannoxanes in 1924. In the last
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century, the higher hexaalkyldistannoxanes began to be obtained by dehydration of corresponding trialkylstannanols in the presence of dehydrating agents (P_2O_5, CaCl_2) or even at high temperature (preferably in vacuum). The higher hexaalkyldistannoxanes (beginning from \( R = Bu \)) were synthesized by the reaction of the corresponding trialkylhalostannanes with aqueous or alcoholic alkaline solutions. Anderson and Vasta obtained \( Et_3SnOSnEt_3 \) by the reaction of \( Ag_2O \) with \( Et_3SnX \) or with \( Et_3SnSSnEt_3 \).

\[
2R_3SnX + 2MOH \xrightarrow{-2MX} 2R_3SnOH \xrightarrow{\text{H}_2\text{O}} R_3SnOSnR_3 + H_2O \\
(M = Na, K; X = Cl, Br; R = Me, Et) \tag{13}
\]

The properties of hexaalkyldistannoxanes were very different in comparison with those of their silicon isostructural analogs \( R_3SiOSiR_3 \). The ability of the Sn–O–Sn group to be decomposed by water, alcohols, phenols, diols, organic and inorganic acids, SH acids (H_2S, RSH), organic and inorganic halides and pseudohalides is consistent with later investigations, which demonstrated the cleavage of the Sn–O bond in \( R_3SnOSnR_3 \), \( (R_2SnO)_n \), \( R_3SnOR \) and \( R_3SnOH \) by NH acids (RCONH_2, (RCO)_2NH, pyrrole, pyrazole, imidazole, benzotriazole), and by CH acids (RC=CH\_886–893; CH_2(CN)_2, CH_2(COOMe)_2\_894; fluorene), as well as by H_2O_2, CO_2, and RCOCl. The majority of reactions showed a significant difference between the Sn–O–Sn and Si–O–Si groups. The latter was not decomposed by SH, NH and CH acids, and usually reacted with weak OH acids only in the presence of catalysts.

Anderson showed that \( Et_3SnOSnEt_3 \) was decomposed by many halides and pseudohalides of B, Si, Ge and Sn, i.e. EtOBCl_2, Me_3SiOCOME, MeSi(OCCCF_3)_3, Me_2Si(OCCCF_3)_2, Ph_2SiF_2, MeOSi(NCO)_3, SiBr_4, Pr_3GeF, i-PrGeOH, GeCl_4, SnCl_4, SnBr_4, SnCl_2, Et_2SnCl_2, PCl_3, AsCl_3 and SbCl_3. Some classes of compounds having the Sn–O–M moiety (with M = C, metalloid or metal) can be combined to give a wide range of organotin compounds. The first class, having the Sn–O–C group, include organic compounds of tin with alkoxy, aryloxy or acyloxy groups at the Sn atom. Organylalkoxystannanes \( R_{4-n}Sn(OH)^n \), namely Me_3SnOEt, Et_3SnOEt and Ph_2Sn(OEt)_2, were first obtained by Ladenburg and Aronheim in the 1870s. However, the basic investigations of compounds containing the Sn–O–R group were carried out in the 20th century. They were obtained from the corresponding organylhalostannanes with sodium alcoholates or phenolates or by the reaction of organylstannanes, polydialkylstannoxanes, organylacetoxystannanes and organylhalostannanes with alcohols or phenols. In 1956, Koton showed the possibility of the Sn–C bond cleavage by alcohols. The studied reaction of \( (H_2C=CHCH_2)_4Sn \) led to the cleavage of all four Sn–C bonds to give \( Sn(OEt)_4 \).

Three years later, D’Ans and Gold found that triorganylaryloxystannanes with electron-withdrawing substituents in the aromatic ring (halogen, NO_2) could be obtained only by the reaction of the corresponding phenols with organylhalostannanes in the presence of sodium hydride in THF. Finally, R. and G. Sasin succeeded in cleaving the C–Sn bond of \( Et_3Sn \) by phenol to obtain \( Et_3SnOPh \). Organylalkoxystannanes were interesting synthons due to their high reactivity. Yakubovich and coworkers first showed the possibility of transforming organylalkoxystannanes to the corresponding organylhalostannanes by reaction with acyl halides in 1958. The reaction of \( (Et_2SnO)_2 \) with MeCOF consequently led to \( Et_2Sn(OEt)F \) and \( Et_2SnF_2 \) together with MeCOOEt.
The first organylacyloxystannanes $R_4\cdot Sn(OCOR')_n$ were obtained by Cahours\(^{583}\) (1860), Kulmiz\(^{584}\) (1860) and Frankland and Lawrence\(^{589}\) (1879). They were synthesized by the reaction of carboxylic acids or their anhydrides with $(R_2SnO)_n$, $R_2SnOH$ or $R_3SnOSnR_3$. Cahours\(^{583,588,600}\), obtained 30 $R_2Sn(OCOR')_2$ and $R_3SnOCOR'$ type compounds with $R = Me, Et, Pr, Bu, i-Bu, i-Am$; $R' = C_nH_{2n+1}$; $n = 0–11$, as well as the corresponding derivatives of hydroxycarboxylic acids (citrates and tartrates) by using this method. Kulmiz\(^{584}\) synthesized triethylacyloxystannanes $Et_3SnOCOR'$, $R' = H, Me, Pr, Ph$ and triethylstannyl esters of oxalic and tartaric acids, as well. He also used the reaction of $(Et_3Sn)_2SO_4$ with $Ba(OCOR')_2$ and of $(Et_3Sn)_2CO_3$ with $RCOOH$ for the synthesis of these compounds. Frankland and Lawrence\(^{589}\) were less 'pretentious' and had made only triethylacetoxystannane. Further, organylacyloxystannanes were obtained by the $Sn-O$ bond cleavage with carboxylic acids by Quintin\(^{909}\) (1930), Kocheshkov and coworkers\(^{820}\) (1936), Smyth\(^{910}\) (1941), Anderson\(^{911}\) (1957), Shostakovskii and coworkers\(^{881}\) (1958). By this method the two latter authors obtained trimethylacyloxystannane, which was used further for the synthesis of organotin polymers. Anderson\(^{911}\) synthesized 12 triethylacyloxystannanes by the cleavage of hexaethyldistannoxane with the corresponding esters.

Another approach to the synthesis of organylacyloxystannanes based on the reaction of organylhalostannanes with salts of carboxylic acids, including silver salts\(^{830}\), was first offered by Pope and Peachey\(^{608,609}\) in 1900, then used by Pfeiffer, Lehnard and coworkers\(^{617}\) in 1910. In 1955–1958 the re-esterification reaction\(^{905,912}\) started to be used for the synthesis of organylacyloxystannanes\(^{905,912}\). Anderson\(^{845,911}\) (1954, 1957) found that dialkylidiacyloxystannanes were formed in the reaction of $(R_2SnO)_n$ with esters. For the first time the ability of carboxylic acids to cleave the $C-Sn$ bond of $R_4Sn$ was explored by Lesbre and Dupont\(^{913}\) (1953), by R. and G. Sasin\(^{855}\) and then by Koton and Kiseleva\(^{776,907}\) (1957), Seyferth and coworkers\(^{672,789,790,818}\) (1957–1958) and Rosenberg and coworkers\(^{879}\) (1959).

In the second half of the last century a strong interest was developed in alkylacyloxystannanes due to the discovery of the high fungicide activity of $R_3SnOCOR'$ and the possibility that $R_2Sn(OCOR')_2$ could be applied as polyvinyl chloride stabilizers (see Sections III.J and III.K).

Organylanatostannanes $R_{4-n}Sn(OCN)_n$ belong to compounds containing the $Sn-O-C$ group. A series of such compounds with $n = 1$ were synthesized by Zimmer and Lübke\(^{914}\) (1952) and Anderson and Vasta\(^{830}\) (1954).

Some derivatives of oxygen-containing inorganic acids (such as $H_3BO_3$, $HNO_3$, $H_3PO_4$ and $H_2SO_4$) can be also classified as belonging to organotin compounds, having the $Sn-O-M$ bond, where $M$ is a metalloid. Unlike the isostructural organosilicon compounds, trialkylstannyl and dialkylstannyl derivatives of strong inorganic acids have an ionic structure, so they can be referred to as organotin salts. As early as 1898 Werner and Pfeiffer\(^{585}\) showed that diethylstannylenesulfate $Et_2SnSO_4$ (which has no monomeric organosilicon analog) and many other similar compounds were dissociated in water into $Et_2Sn^{2+}$ and $SO_4^{2–}$ ions. In the 19th century the first organotin salts of this kind were obtained by Löwie\(^{41}\) : $Et_2SnSO_4$, $Et_2Sn(NO_3)_2$, $Et_3SnNO_3$, $(Et_3Sn)_2SO_4$; by Cahours\(^{583,599}\) : $Me_2SnSO_4$, $(Me_3Sn)_2SO_4$, $(Et_3Sn)_2SO_4$, $Et_2SnSO_4$, $(i-Bu_3Sn)_2SO_4$, $Et_2Sn(No_3)_2$; by Buckton\(^{604}\) : $(Et_3Sn)_2SO_4$; by Kulmiz\(^{584}\) : $(Et_3Sn)_2CO_3$, $Et_3SnNO_3$, $(Et_3Sn)_2SO_4$, $(Et_3Sn)_3PO_4$, $(Et_3Sn)_3AsO_4$; by Frankland\(^{589}\) : $(Et_3Sn)_2SO_4$; and by Hjortdahl\(^{621,853}\) : $(Me_3Sn)_2SO_4$, $(Et_3Sn)_2SO_4$, $(Et_3Sn)_2SeO_4$. In 1898 Werner and Pfeiffer\(^{585}\) obtained $Et_2SnHPO_4$ and $Et_2SnSO_4$. Six years later Pfeiffer and Schnurmann\(^{870}\) described $(Et_3Sn)_2CO_3$ again.
After these investigations, organotin salts did not attract attention until almost the middle of the 20th century. In the second half of the 20th century interest in these compounds increased sharply owing to the discovery of some useful properties of organotin compounds having the Sn–O–M group. During these years numerous organotin salts with \( M = B^{915,916}, N^{917}, P^{979,918–921}, As^{922}, S^{623,673,782,905,923}, Se \) and \( P^{915,924} \) were synthesized (only the periodical publications are cited here). A large number of patents cited in a review\(^{631} \) were devoted to these salts.

Na and Li stanolates belong to these compounds, since they have Sn–O–M groups (\( M = \text{metal} \)). Unlike the isostructural compounds of silicon and germanium, the preparation of \( R_3\text{SnOM} \) (\( M = \text{Na, Li} \)) by the direct reaction of sodium and lithium with the appropriate stannanols had failed. Compounds of this type were synthesized by Chambers and Scherer\(^{662} \) in 1926, and later by Harada\(^{641} \) via the oxidation of \( R_3\text{SnNa} \) in 1939. In 1963 Schmidbaur and Hussek\(^{925} \) obtained \( R_3\text{SnOLi} \) by the cleavage of hexaorganodistannoxanes with organolithium compounds. \( Me_3\text{SnOLi} \) turned out to be a hexamer. The attempt of Harrison\(^{926} \) to obtain \( Bu_3\text{SnOLi} \) by cleavage of \( (Bu_2\text{SnO})_n \) with butyllithium resulted in the formation of \( Bu_4\text{Sn} \).

Dimethylstannylene salts of inorganic acids, which came to light in Rochow’s laboratory in 1952–1953\(^{915,924} \), could be assigned to organotin compounds, having the Sn–O–M group with \( M = \text{Sb, V, Mo, W} \). They were obtained by the reaction of \( Me_2\text{SnCl}_2 \) with the corresponding acids and their salts in the aqueous medium. Rochow attributed the ease of such reactions to the complete dissociation of \( Me_2\text{SnCl}_2 \) in water to the \( Me_2\text{Sn}^{2+} \) and \( Cl^- \) ions.

In 1959, Wittenberg and Gilman\(^{927} \) obtained dimethylstannylene salts of phosphorus, arsenic, molybdenic and tungsten acids by the reaction of \( Me_2\text{SnCl}_2 \) with the corresponding acids. In 1950–1960, many compounds containing the Sn–O–Si group were synthesized by the reaction of triorganosilanlates of alkaline metals with organylhalostannanes\(^{928–936} \). In 1952, \( Ph_3\text{SnOSiPh}_3 \) and \( (Me_3\text{SiO})_2\text{Sn} \)\(^{937} \) were synthesized by the reaction of \( Ph_3\text{SiONa} \) and \( Me_3\text{SiONa} \) with \( Ph_3\text{SnBr} \) and \( SnCl_2 \), respectively. In 1957, Papetti and Post\(^{928} \) obtained \( Ph_3\text{SnOSiPh}_3 \) by reacting \( Ph_3\text{SiONa} \) with \( Ph_3\text{SnCl} \). In 1961, Okawara and Sugita\(^{938} \) synthesized triethyl(trimethylsilyloxy)stannane \( Et_3\text{SnOSiMe}_3 \) and found that its reaction with \( CO_2 \) gave \( (Et_3\text{Sn}_2)\text{CO}_3 \). Okawara and coworkers\(^{939–941} \) (1950, 1961) obtained tetraalkyl-1,3-bis(trimethylsilyloxy)distannoxanes \( R_2(\text{Me}_3\text{SiO})\text{SnOSn(OSiMe}_3)R_2 \) (\( R = \text{Me, Et, Pr, Bu} \)), which turned out to be dimeric, by co-hydrolysis of \( R_2\text{SnCl}_2 \) with \( Me_3\text{SnCl} \) in aqueous ammonia. These compounds were recently shown to be centrosymmetric tricyclic ladder dimers in which all the tin atoms were pentacoordinated\(^{942} \). The synthesis of these compounds by co-hydrolysis of \( Me_3\text{SiCl} \) with \( ClR_2\text{SnOSnR}_2\text{Cl} \) were carried out in order to confirm their structures. Labile dialkylbis(trimethylsilyloxy)stannanes \( R_2\text{Sn(OSiMe}_3)_2 \) were obtained similarly. All these compounds tended to disproportionate to form \( \alpha,\omega\)-bis(trimethylsilyloxy)polydialkylstannoxanes. These investigations founded the basis for the chemistry of stannosiloxanes\(^{640,910,926,943,944} \) and their practical use.

In the middle of the 20th century synthetic methods started to develop, and the properties\(^{926} \) were studied of metal–stannoxane monomers and polymers having a Sn–O–M group, where \( M = \text{Ge, Pb, Ti, P} \), as well as their analogs, containing SnEM (\( E = S, Se, Te, NR \)) chains.

G. Compounds Containing an Sn–E Bond (\( E = S, Se, N, P \))

Unlike silicon and germanium, tin and lead belong to the family of chalcophile elements (according to the Goldshmidt geochemical classification), which have a high affinity to sulfur. In this connection the stability of the stannathiane Sn–S bond (in the Sn–S–Sn
group) and the ease of its formation differ strongly from the high reactivity of the Si–S and the Ge–S bonds. The Sn–S bond can be compared with the siloxane bond in the Si–O–Si group. Consequently, the distannathiane Sn–S–Sn group has a special place in organotin chemistry\textsuperscript{88,125,675,757,945} just like the disiloxane Si–O–Si group, which played a most important role in organosilicon chemistry.

The first reaction, which showed the easy conversion of the Sn–O to the Sn–S bond, is due to Kulmiz\textsuperscript{584,946}. In 1860, he found that triethylstannanol could be converted to hexaethyldistannathiane $\text{Et}_3\text{SnSSnEt}_3$ by reaction with hydrogen sulfide. In 1953, Sasin showed that hydrogen sulfide easily cleaved the distannoxane group in hexaalkyldistannoxanes\textsuperscript{882} with the formation of hexaalkyldistannathianes. Analogously, trialkylalkoxystannanes\textsuperscript{88} reacted with $\text{H}_2\text{S}$. Hydrogen sulfide also cleaved the Sn–O bonds in the oligomers ($\text{R}_2\text{SnO})_n$ and polymers [R(OH)SnO]$_n$. After Kulmiz’s investigations, organotin compounds containing the Sn–S bond did not attract the attention of chemists until the end of the 19th century, probably because of their low reactivity and the reluctance to work with hydrogen sulfide and its derivatives. However, in the first half of the last century the incredible ease of the Sn–S bond formation was supported again by the easy cleavage of the Sn–O bond and other Sn–X bonds (X = halogen, H, Sn and even C\textsuperscript{789,818}) by $\text{H}_2\text{S}$. In 1903, Pfeiffer and Lehnardt\textsuperscript{309,614} found that the action of $\text{H}_2\text{S}$ on methyltriblalıkostannanes gave an unknown polymethylstannasesquithiane $\text{MeSnS_1}_5\text{n}$, which was assigned the (MeSn=Sn)\text{S}_2\text{S} structure. Analogously, in 1931, Nesmeyanov and Kocheshkov\textsuperscript{727,806} obtained the first polyarylstannasesquithianes ($\text{ArSnS}_1\text{.5}_n$, by the reaction of $\text{H}_2\text{S}$ with arytrihialostannanes.

Pfeiffer and coworkers\textsuperscript{616} (1910), and then Kocheshkov\textsuperscript{796,947} and Nesmeyanov\textsuperscript{727,806,815} (1931–1933) carried out the easy hydrothiolysis of organotin halides $\text{R}_4\text{nSnX}_n$, $n = 1–3$ (equations 14–16).

\begin{equation}
2\text{R}_3\text{SnX} + \text{H}_2\text{S} \rightarrow \text{R}_3\text{SnSSnR}_3 + 2\text{HX}
\end{equation}

\begin{equation}
\text{R}_2\text{SnX}_2 + \text{H}_2\text{S} \rightarrow \frac{1}{n}(\text{R}_2\text{SnS})_n + 2\text{HX}
\end{equation}

\begin{equation}
\text{RSnX}_3 + 1.5\text{H}_2\text{S} \rightarrow \frac{1}{n}(\text{RSnS}_1\text{.5}_n) + 3\text{HX}, \text{ where X = Cl, Br, I}
\end{equation}

With organosilicon halides, the same reactions proceeded only in the presence of an acceptor of hydrogen halide. In the first half of the last century the monomeric structures were assigned to $\text{R}_2\text{Sn}=\text{S}$ and ($\text{Rn}=\text{S})_2\text{S}$, obtained in the reactions mentioned above. In 1942, Harada\textsuperscript{948,949} and later other investigators\textsuperscript{924,950,951} found that the compounds of the composition $\text{R}_2\text{SnS}$ (R = Ph) were cyclic trimers (Ph$_2\text{SnS})_3$, i.e. hexaphenylcyclotristannathianes. It is remarkable that the reactions of organylalostannanes with alkali metals or ammonium sulfides and hydrosulfides as well as with $\text{H}_2\text{S}$ proceed smoothly even in aqueous medium\textsuperscript{727,815}. This method for the synthesis of ($\text{Ar}_2\text{Sn})_3$ was first proposed by Kocheshkov\textsuperscript{802} and Nesmeyanov and Kocheshkov\textsuperscript{727,806} in 1931 and used later by them\textsuperscript{801,804,952} and by Harada\textsuperscript{642,948,949}, Seyferth\textsuperscript{672} and Edgar and Teer\textsuperscript{953} for the syntheses of compounds of the $\text{R}_3\text{SnSSnR}_3$ and ($\text{R}_2\text{SnS})_3$\textsuperscript{804} series. In 1938, first Nad' and Kocheshkov\textsuperscript{665} and then Pang and Becker\textsuperscript{954} obtained hexaaryldistannathianes. The first representatives of the hexaalkyldistannathiane series $\text{R}_3\text{SnSSnR}_3$, R = Me, Et, Pr were obtained by Harada\textsuperscript{948,949} in 1942. Organyln(organylthio)stannanes $\text{R}_4\text{nSn(SR'))}_n$ containing the Sn–S–C group were first obtained in the 1950s. It was found that the Sn–O bonds in the Sn–O–Sn and Sn–OH groups were easily cleaved by mercaptans like hydrogen sulfide. That was evidently proved by the reaction studied by Stefl and Best\textsuperscript{955} (1957) and Ramsden and coworkers\textsuperscript{956} (1954) (equation 17).
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\[ \frac{1}{n} [\text{R(OH)SnO}]_n + 3 \text{HSR'} \xrightarrow{125-150^\circ C} \text{RSn(SR')}_3 + 2 \text{H}_2\text{O} \] (17)

Cycloalkyldistannoxanes \((\text{R}_2\text{SnO})_2\) were also cleaved by thiols \(\text{R'SH}\) to give \(\text{R}_2\text{Sn(SR')}_2\)\(^956,957\). As is evident by the numerous patent data, not only alkane- and alkenethiols, but also their carbofunctional derivatives such as mercaptalcohols, mercaptoacids and their ethers and esters, were applied in the reaction with organotin compounds containing an Sn–O bond. Pang and Becker\(^954\) obtained the first triorganyl(organylthio)stannane \(\text{Ph}_3\text{SnSPh}\) in 1948. In 1953–1958, Sasin and coworkers\(^882,958\) synthesized a series oftrialkyl(organylthio)stannanes \(\text{R}_3\text{SnSR'}\) (\(\text{R} = \text{Et}, \text{Pr}; \text{R'} = \text{Alk}, \text{Bn}, \text{Ar}\)). In 1957–1961, compounds of this series\(^959\), including \(\text{Ph}_3\text{SnSPh}\)\(^960\), were obtained by the reaction of sodium thiolates with organotin halides. The first patents dealing with the methods of obtaining organyl(organylthio)stannanes by the reaction of the corresponding halides and mercaptans in the presence of an HHal acceptor were issued in 1953–1956\(^961-963\).

Whereas aliphatic and aromatic thiols cleaved the C–Sn bond in tetraalkylstannanes to give trialkylorganylthiostannanes\(^768,855\), the analogous reaction in organosilicon chemistry is absolutely unusual. According to Seyferth\(^789,818\) (1957), the vinyl group was especially easy to cleave from tin atom by mercaptans.

In 1933, Bost and Baker\(^964\) first carried out the C–Sn bond cleavage by elemental sulfur. They recommended the reaction of \(\text{Ar}_4\text{Sn}\) and \(\text{S}\) as a method for the synthesis of \(\text{Ar}_3\text{SnSAr}\). Furthermore, in 1962–1963 Schmidt, Bersin and Schumann\(^965,966\) (for a review, see Reference\(^967\)) studied the cleavage of \(\text{Bu}_4\text{Sn}, \text{Ph}_4\text{Sn}\) and \(\text{Ph}_3\text{SnCl}\) by sulfur. In spite of the high stability of the Sn–Sn bond group in comparison with the Sn–O–Sn group, in 1954 Anderson\(^845\) was able to cleave it by the action of \(n\)-\(\text{C}_12\text{H}_{25}\text{SiI}_3, \text{SiBr}_4, \text{GeCl}_4, \text{SnCl}_4, \text{SnCl}_2, \text{PCl}_3\) and \(\text{AsCl}_3\) on \(\text{Et}_3\text{SnSSnEt}_3\) with the formation of \(\text{Et}_3\text{SnX}\) (\(\text{X} = \text{Cl, Br, I}\)) together with the corresponding inorganic sulfides.

In 1950, Tchakirian and Berillard\(^874\) obtained for the first time organotin compounds containing the Sn–Se bond. Those were polyalkylstannasesquiselenanes \((\text{RSnSe})_1.5\)\(^n\) which were formed by the reaction of \([\text{R(OH)SnO}]_n\) with \(\text{H}_2\text{Se}\). Monomeric compounds containing the Sn–Se bonds were synthesized in the 1960s. The cleavage reactions of the Sn–O bonds by \(\text{H}_2\text{Se}\) were unprecedented.

The majority of organotin compounds containing the stannazane Sn–N bond appeared only in the early 1960s. Their late appearance was probably caused by the fact that the reaction of organylhalostannanes with ammonia, primary and secondary amines did not result in the corresponding amino derivatives (as for the isostructural Si and Ge derivatives), but in stable complexes containing a hypervalent tin atom (Section III. I). The first compound containing the Sn–N bond, triethylstannylisocyanide \(\text{Et}_3\text{SnNC}\), was synthesized by Kulmiz\(^584\) by the reaction of \(\text{Et}_3\text{SnI}\) with \(\text{AgCN}\) in 1860. He also obtained \(N\)-triethylstannylcarbamide and this synthesis was no longer reproduced. In 1927, Bullard and Robinson\(^875\) obtained a mixture of \((\text{Me}_3\text{Sn})_3\text{N}\) and \(\text{Me}_3\text{SnPh}\) by the reaction of \(\text{Me}_3\text{SnNa}\) with \(\text{PhBr}\) in liquid \(\text{NH}_3\), but they failed to isolate tris(trimethylstannyl)amine. Nevertheless, they can be considered as the founders of modern synthetic methods of organotin compounds having Sn–N bonds. In 1930, Kraus and Neal\(^968\) reported success in obtaining amino(trimethyl)stannane \(\text{Me}_3\text{SnNH}_2\) by the reaction of hexamethyldistannane or trimethylstannane with sodium amide in liquid ammonia. However, they could neither isolate it nor describe its properties. Between 1930 and 1960 only organotin sulfonamide derivatives\(^88,714,969-971\), trialkylstannylisocyanates \(\text{R}_3\text{SnNCO}\)\(^830\) and isocyanides \(\text{R}_3\text{SnNC}\)\(^714,795,830,924,972\) were synthesized, but many organotin complexes containing the \(\text{N} \rightarrow \text{Sn}\) bonds were obtained (Section III. I). Kettle\(^975\) (1959) pointed out the formation of
aminodimethylstannylsodium \( \text{Me}_2\text{Sn(NH}_2\text{)}\text{Na} \) by the reaction of dimethylstannane with sodium in liquid ammonia. Up to 1960 no compound of the type \( R_4-n\text{Sn(NR}_1\text{R}_2\text{)}_n \) had been synthesized.

A revolutionary breakthrough, which marks the birth of the most important compounds containing the Sn—N bond, was made by Wiberg and Rieger. They patented the preparation method of trialkyl(alkylamino)stannanes by the reaction of trialkylchlorostannanes with lithium alkylamides. In 1962, this method was improved by Abel and coworkers and Jones and Lappert and was further widely practiced. Jones and Lappert synthesized 23 compounds by this method and studied their numerous addition and insertion reactions. In the same period Sisido and Kozima developed a method for obtaining trialkyl(dialkylamino)stannanes based on the reaction of trialkylchlorostannane with dialkylaminomagnesium bromides. In 1962, Abel and coworkers also developed an original exchange method to synthesize trialkyl(alkylamino)stannanes by Sn—N bond cleavage using trialkylobromostannanes according to equation 18.

\[
\text{Me}_3\text{SnBr} + \text{Me}_3\text{SiNHEt} \xrightarrow{\Delta} \text{Me}_3\text{SnNHEt} + \text{Me}_3\text{SiBr}
\]  

The intermediate of this process was a complex of the precursor reagents, which decomposed to the final reaction products.

This pioneer research marked the start of vigorous development of the chemistry of organotin compounds containing Sn—N bonds. Numerous publications appeared in reviews, as well as in parts 18 and 19 of Gmelin’s Handbook.

The first compound containing the Sn—P bond was synthesized in 1947 by B. Arbuzov and Pudovik, who applied the A. Arbuzov reaction to organotin halides by demonstrating that \( R_3\text{SnX} \) reacted with \( \text{P(OR)}_3 \) at 105 °C with the formation of \( R_3\text{SnPO(OR)}_2 \) (\( R = R’ = \text{Me, Et} \)). The Sn—P bond in these compounds was easily cleaved by \( \text{Cl}_2 \), HCl, MeCOCl and aqueous KOH. The reaction of \( \text{Et}_3\text{Sn} \) with \( \text{NaPO(OEt)}_2 \) in EtOH gave \( \text{Et}_3\text{SnNHEt} \). In 1947 Arbuzov and Grechkin showed that \( \text{R}_2\text{SnX}_2 \) reacted with \( \text{P(OMe)}_3 \) with the formation of \( \text{R}_2\text{Sn[PO(OMe)}_2\text{]}_2 \). The reaction of \( \text{MeSnH}_3 \) and \( \text{P(OMe)}_3 \) resulted in \( \text{MeSn[PO(OMe)}_2\text{]}_3 \). The reaction of \( \text{Et}_2\text{SnI}_2 \) with \( \text{NaPO(OEt)}_2 \) proceeded in two directions with the formation of \( \text{Et}_2\text{Sn[PO(OEt)}_2\text{]}_2 \) and \( \text{Et}_2\text{Sn} \). The latter was oxidized to \( \text{Et}_2\text{SnO} \) by the air oxygen. In 1959, Kuchen and Buchwald obtained \( \text{R}_3\text{SnPPh}_2 \) by the reaction of \( \text{R}_3\text{SnBr} \) with \( \text{Ph}_2\text{PNa} \).

Organotin compounds having Sn—As and Sn—Sb bonds were mentioned briefly in a patent issued in 1935. Since 1963, a number of organotin compounds in which the tin atom was bonded to B, P, As and Sb atoms were synthesized. However, these studies are beyond the period of history covered in this chapter.

H. Compounds Containing Sn—Sn or Sn—M Bond

Compounds containing the Sn—Sn bonds corresponding in general to the \( R_3\text{SnSnR}_3 \) and \( (R_2\text{Sn})_n \) formulas appeared in the early days of organotin chemistry. Until the middle of the 20th century, these compounds were considered as the three-valent \( R_3\text{Sn} \) and two-valent \( R_2\text{Sn} \) tin derivatives.

As described in Section III.A, the first compound of this type was polydiethylstannane \( (\text{Et}_2\text{Sn})_n \), which was synthesized by Löwig in 1852 as one of the products of the reaction

* Hereafter, oligomers and polymers \( (R_2\text{Sn})_n \) will be denoted as \( R_2\text{Sn} \) unless otherwise noted, and monomers, i.e. (diorganylstannlenes), as \( R_2\text{Sn} \).
of ethyl iodide and a tin–sodium alloy, and by Frankland in 1853 by reducing \( \text{Et}_2\text{SnI}_2 \) with zinc in the HCl. In 1859–1860, Buckton and Cahours synthesized the same compound. Already in 1911, Pfeiffer obtained \( \text{R}_2\text{Sn}, \text{R} = \text{Me, Et} \) by reducing \( \text{R}_2\text{SnCl}_2 \) with sodium amalgam in ether. In 1859–1860, Buckton and Cahours synthesized the same compound. In 1925, Kraus and Greer synthesized \( \text{Me}_2\text{Sn} \) by the reaction of \( \text{Me}_2\text{SnBr}_2 \) and Na in liquid ammonia. Excess of Na gave \( \text{Me}_2\text{SnNa}_2 \). In 1925, Kraus and Greer synthesized \( \text{Me}_2\text{Sn} \) by the reaction of \( \text{Me}_2\text{SnNa}_2 \) and \( \text{Me}_2\text{SnBr}_2 \). In 1959, Kettle synthesized \( \text{Me}_2\text{Sn} \) by the reaction of metallic sodium and \( \text{Me}_2\text{SnH}_2 \) followed by decomposition of \( \text{Me}_2\text{SnNa}_2 \) obtained by ammonium bromide.

In 1920, Krause and Becker for the first time prepared \( \text{Ph}_2\text{Sn} \) by the reaction of \( \text{SnCl}_2 \) and \( \text{PhMgBr} \). In 1923, Böseken and Rutgers observed the formation of \( \text{Ph}_2\text{Sn} \) when \( \text{Ph}_2\text{SnNa}_2 \) reacted with \( \text{Ph}_2\text{SnBr}_2 \) in liquid ammonia. In 1926, Chambers and Scherer reacted \( \text{Ph}_2\text{SnBr}_2 \) and Na in liquid ammonia to synthesize \( \text{Ph}_2\text{Sn} \).

In 1939–1959 \( \text{Me}_2\text{Sn} \), \( \text{Et}_2\text{Sn} \), and their analogs were obtained by the methods described above.

It should be mentioned that the compounds of structure \( \text{R}_2\text{Sn} \), which were once considered as monomers and later proved to be oligomers or polymers \( (\text{R}_2\text{Sn})_n \), did not always correspond to this formula. In 1964, Neumann and König pointed out that when \( \text{Ph}_2\text{Sn} \) was synthesized by the reaction of alkali metals and \( \text{Ph}_2\text{SnX}_2 \), not only a Sn–Sn bond but also C–Sn bonds were created, making the structure of the formed polymers more complicated. The latter polymers were assigned the \( \text{R}_3\text{Sn} \), \( (\text{R}_2\text{Sn})_n \text{SnR}_3 \), and \( \text{R}_2\text{Sn} \), \( (\text{R}_2\text{Sn})_n \text{SnR}_3 \) \( (\text{R} = \text{Ph}) \) \( \text{R}_3\text{Sn} \), \( (\text{R}_2\text{Sn})_n \text{SnR}_3 \) \( (\text{R} = \text{Ph}) \) structures. However, at the same time the cyclic oligomer dodecaphenylcyclohexastannane \( (\text{Ph}_2\text{Sn})_6 \) was isolated in the reaction of \( \text{SnCl}_2 \) and \( \text{PhMgBr} \) together with the higher oligomers and polymers. In 1961, Kuivila and coworkers showed that \( \text{Ph}_2\text{SnH}_2 \) in the presence of amines underwent the dehydrocondensation to perphenylcyclostannanes \( (\text{Ph}_2\text{Sn})_n \). Neumann and König obtained a series of dodecaphenylcyclohexastannanes \( (\text{Ph}_2\text{Sn})_n \) in a high yield from the corresponding \( \text{Ar}_2\text{SnH}_2 \) in the presence of pyridine. In the dehydrocondensation of \( \text{Ph}_2\text{SnH}_2 \) they succeeded in obtaining \( (\text{Ph}_2\text{Sn})_n \). Consequently, four-, five-, six- and nine-membered peralkyl-, perbenzyl- and percyclohexylcyclostannanes \( (\text{R}_2\text{Sn})_n \) \( \text{R} = \text{t-Bu, PhCH}_2 \) \( (n = 4) \); \( \text{c-Hex} \) \( (n = 5) \); \( \text{Et, Bu, i-Bu} \) \( (n = 6, 9) \) were synthesized using this method. Thus, the investigations of Neumann and König clarified the structures of the compounds corresponding to the \( (\text{R}_2\text{Sn})_n \) composition.

The first representative of hexaorganyldistannanes \( \text{R}_3\text{SnSnR}_3 \) with \( \text{R} = \text{Et} \) was obtained in 1860 by Cahours and then in 1869–1872 by Ladenburg. Cahours isolated \( \text{Et}_3\text{SnSnEt}_3 \) from the reaction products of \( \text{EtI} \) with a tin–sodium alloy and Ladenburg synthesized it from the reaction of \( \text{Et}_3\text{SnI} \) and metallic Na. Ladenburg determined the molecular weight of the product of \( \text{Et}_3\text{Sn} \) with Na by its vapor elasticity. This enabled him to assign the \( \text{Et}_3\text{SnSnEt}_3 \) formula to the product, instead of \( \text{Et}_3\text{Sn} \), as was considered before and even some time later. In 1908, Rügheimer repeated this synthesis and carried out a precise measurement of the molecular weight (MW) of \( \text{Et}_3\text{SnSnEt}_3 \) in ether by the ebullioscopic method. He found that the MM value decreased on dilution. When the solvent to substance ratio was 5.55 : 1, the MW was 235, and when it was 38.7 : 1, \( \text{MW} = 368 \) (for \( \text{Et}_6\text{Sn}_2 \), \( \text{MM} = 411 \)). These data apparently indicated that hexaethyldistannane was dissociated to the free radicals \( \text{Et}_3\text{Sn} \) in the dilute solutions. Rügheimer followed Ladenburg by pointing out that this compound was the derivative of four-valent tin and contained an Sn–Sn bond. In 1917, Grüttners (the same method was used later by Kraus and Eatough) obtained \( \text{R}_3\text{SnSnR}_3 \) \( (\text{R} = \text{Et, Pr, i-Bu}) \) from \( \text{R}_3\text{SnCl} \) and Na at 120°C by a similar method and corroborated Ladenburg’s data when he determined the molecular mass of hexaethyldistannane by cryoscopy in benzene. He also
synthesized the mixed hexaalkyldistannanes of REt₂SnEt₂R (R = Pr, i-Bu)⁹⁹⁴ from RE₃SnBr and Na.

Only in 1925 did Kraus and Bullard⁹⁹⁶ and Kraus and Session⁷⁸² obtain hexamethyldistannane by the reaction of Me₃SnBr with Na solution in liquid ammonia. In 1929, Harada⁶⁴⁰ described the preparation of Me₃SnSnMe₃ by the reaction of Me₃SnO and sodium in liquid ammonia. In 1924, Krause and Poland⁷⁶⁹ obtained hexacyclohexyldistannane by the reaction of SnCl₄ and c-HexMgBr. In 1926, Law synthesized (PhCH₂)₃SnSn(CHO₂Ph)₃ by the reaction of Na with (PhCH₂)₃SnCl⁶⁷⁶. In 1937, Riccoboni⁹⁹⁷ developed a synthesis of R₃SnR₃ by the electrochemical reduction of R₃SnCl in methanol.

Krause and Becker⁷⁸¹ in 1920 synthesized the first representative hexaaryldistannane Ar₃SnSnAr₃ (Ar = Ph) by the reaction of triarylbromostannane and sodium in liquid ammonia. Krause and Weinberg⁸³² synthesized a series of other hexaaryldistannanes in 1929. According to Nad’ and Kocheshkov⁶⁶⁵ hexaaryldistannanes were among the reaction products of arylmercurichlorides and tin–sodium alloy. In 1920, Krause and Becker⁷⁸¹ (and later Bonner and coworkers⁹⁹⁸) established that when the reaction of SnCl₄ with PhMgBr was carried out under defined conditions, it lead to Ph₃SnSnPh₃.

Hexaaryldistannane with R = 2-PhC₆H₄⁹⁹⁹ was obtained analogously.

The attempt of Kraus and coworkers⁷⁸²,¹⁰⁰⁰,¹⁰⁰¹ to obtain compounds (R₃Sn)₄C by the reaction of CCl₄ and R₃SnNa (R = Me, Et, Ph) gave instead R₃SnSnR₃. In 1951, Razuvaev and Fedotova⁹⁸⁵ found that R₃SnSnR₃ could be prepared by the reaction of (R₃Sn)₄ and Ph₃CN = NPh. Wittig and his coworkers⁷⁰⁶ (1951) and Gilman and Rosenberg⁷⁶⁷,¹⁰⁰² (1952) offered a convenient method for the synthesis of Ph₃SnSnPh₃ by the reaction of Ph₃SnLi with Ph₃SnX (X = Cl, Br). In 1953, Gilman and Rosenberg⁷⁰⁷ also found that the main reaction product of (2-MeC₆H₄)₃SnLi with 2-iodotoluene was R₃SnSnR₃ (R = 2-MeC₆H₄).

In contrast, in the reaction of Ph₃SnLi with EtI or PhCH₂Cl they obtained Ph₄Sn and Ph₃SnR⁶⁷⁶ (R = Et, CH₂Ph). The interaction of Ph₃SnNa with O₂, CO₂, SO₂, PhCOCl and PhSSPh⁹⁶⁰ gave Ph₃SnSnPh₃.

Finally, Ph₃SnSnPh₃ was formed slowly in the reaction of Ph₃SnM (M = Li, Na) with Et₂O, THF, EtOH and BuOH. Wittig and coworkers⁷⁰⁶ showed that the action of lithium on Ph₃SnBr in liquid ammonia followed by treatment with NH₃Br led to a mixture of Ph₃SnSnPh₃ and Ph₃SnH. As reported in Section III.D, hexaphenyldistannane was formed by the dehydrocondensation of Ph₃SnH in the presence of aliphatic amines⁷⁵¹. Ph₃SnSnPh₃ was also formed on reduction of carbonyl compounds by triphenylstannane. It is remarkable that according to Johnson and coworkers¹⁰⁰³,¹⁰⁰⁴ 1,2-diiodotetraalkyldistannanes were formed in the reaction of R₂SnCl₂ with EtONa or with highly basic amines in ethanol. Finally, it must be remembered that dodecaorganylpentastannanes R(R₂Sn)₉SnR₃ containing 5 tin atoms (n = 4) in a linear chain were first synthesized by Böseken and Rutgers⁶⁷⁷ in 1923 (with R = Ph) and by Kraus and Greer⁹⁸³ in 1925 (with R = Me). The latter authors also described EtMe₂SnMe₂SnMe₂Et, which is unstable in air. In 1932, Kraus and Neal⁸⁶⁰ obtained dodecamethyldistannane (R = Me, n = 3). Individual linear peroorganylpolystannanes containing more than five Sn atoms in the chain were unknown until 195⁶¹⁰⁰⁵. Böseken and Rutgers⁶⁷⁷ synthesized the first bulky perorganyloligostannane, i.e. tetrakis(triphenylstannyl)stannane (Ph₃Sn)₄Sn, by the reaction of Ph₃SnNa and SnCl₄.

One cannot but mention that macrocyclic perethylcyclostannanes (Et₂Sn)ₙ with n = 8, ⁹¹⁰⁰⁶, ¹⁰¹⁰⁰⁷ were synthesized in 1963. Thus, the possibility that ten tin atoms can be bonded to each other in a closed chain was shown.
Peroorganylstannylmetals $\text{R}_3\text{SnMR}_3$ ($\text{M} = \text{Si, Ge}$) were first obtained in the laboratory of Kraus\textsuperscript{161,782,996} by the reaction of $\text{R}_3\text{SnX}$ with $\text{R}_3\text{MNa}$ (formed by the action of Na on $\text{R}_3\text{MX}$). In 1933, Kraus and Eatough\textsuperscript{995} obtained $\text{Ph}_3\text{SnSiMe}_3$ by the reaction of $\text{Ph}_3\text{SnLi}$ with $\text{Me}_3\text{SiCl}$. Afterward, Gilman and Rosenberg\textsuperscript{767} synthesized $\text{Ph}_3\text{SnSiPh}_3$ by the reaction of $\text{Ph}_3\text{SnLi}$ with $\text{Ph}_3\text{SiCl}$ in 1952. In 1961, Blake and coworkers\textsuperscript{960} obtained $\text{Bu}_3\text{SnSiMe}_3$ by the reaction of $\text{Bu}_3\text{SnLi}$ and $\text{Me}_3\text{SiCl}$. Analogously, Gilman and Gerow\textsuperscript{217} synthesized $\text{Ph}_3\text{SnGePh}_3$ by the reaction of $\text{Ph}_3\text{SnCl}$ with $\text{Ph}_3\text{GeK}$ in 1957. The attempt of Buckton\textsuperscript{604} to obtain a compound containing a Sn–Pb bond failed in 1859, but three quarters of a century later the synthesis of $\text{Me}_3\text{SnPbPh}_3$ was patented\textsuperscript{982}. In all the studies mentioned above it was demonstrated that the Sn–Sn bond is more reactive than the Si–Si and the Ge–Ge bonds and is closer in reactivity to the Pb–Pb bond.

Chemical transformations of organotin compounds containing the Sn–Sn bond started to develop in the 19th century by Cahours\textsuperscript{575} (1860) and Ladenburg\textsuperscript{900} (1870). They found that halogens cleaved this bond easily in ($\text{R}_2\text{Sn}$)\textsubscript{n} and $\text{R}_3\text{SnSnR}_3$ to form $\text{R}_2\text{SnX}_2$ and $\text{R}_3\text{SnX}$, respectively. In the last century the reaction of halogens with $\text{R}_2\text{Sn}$ and $\text{R}_3\text{SnSnR}_3$ was carried out in the laboratories of Krause\textsuperscript{647,769,781,831} (1918–1929), Böeseken\textsuperscript{677} (1923), Kraus\textsuperscript{161,782,995} (1925, 1927, 1933), Law\textsuperscript{676} (1926), Kochemshkov\textsuperscript{665} (1938) and Gilman\textsuperscript{217} (1957).

Kraus and Session\textsuperscript{782} (1925), Kraus and Bullard\textsuperscript{996} (1926), Harada\textsuperscript{641} (1939) and Brown and Fowbes\textsuperscript{1008} (1958) observed that $\text{R}_3\text{SnSnR}_3$ is slowly oxidized by the air oxygen to $\text{R}_3\text{SnOSnR}_3$.

In 1925, Kraus and Session\textsuperscript{782} showed that elementary sulfur reacted easily with the Sn–Sn bond of hexaalkyldistannanes to form hexaalkyldistannathianes.

In 1908, Rügheimer\textsuperscript{993} observed that hexaalkyldistannanes were slowly oxidized by air to $\text{R}_3\text{SnOSnR}_3$ under exposure to air. In 1870, Ladenburg\textsuperscript{778} showed that $\text{Et}_3\text{SnSnEt}_3$ was cleaved by $\text{H}_2\text{SO}_4$ with the formation of inflammable gas and an oil-like product, which crystallized on cooling and was probably $\text{Et}_2\text{SnSO}_4$. When the latter was recrystallized from the hot HCl, $\text{Et}_2\text{SnCl}_2$ was isolated. Ladenburg obtained $\text{Et}_3\text{SnCl}$ and Sn by the reaction of $\text{Et}_3\text{SnSnEt}_3$ with $\text{SnCl}_4$. Therefore, he was the first to discover that hexaalkyldistannanes possess reductive properties. In 1871, Ladenburg was also the first to cleave the Sn–Sn bond by organic halides. The reaction of $\text{Et}_3\text{SnSnEt}_3$ with EtI at 220°C led to $\text{Et}_3\text{SnI}$ and butane, but with CICH\textsubscript{2}COOH it led to $\text{Et}_2\text{SnCl}_2$, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{4}H\textsubscript{10} and CO\textsubscript{2}768. Continuing this research, Ladenburg\textsuperscript{606} cleaved $\text{Et}_3\text{SnSnEt}_3$ by MeI (at 220°C) and CICH\textsubscript{2}COOEt. In 1917, Grütter\textsuperscript{994} followed these studies and showed that hexaalkyldistannanes were cleaved by EtI at 180°C to $\text{R}_3\text{SnI}$ and EtSnR\textsubscript{3} (R = Et, Pr, i-Bu). He also reported that hexaalkyldistannanes were slowly oxidized by air to $\text{R}_3\text{SnOSnR}_3$. Krause and Pohland\textsuperscript{709} and Kraus and Bullard\textsuperscript{996} found an unusual reaction of hexamethyldistannane with CaCl\textsubscript{2} in the presence of air, which led to trimethylchlorostannane. In 1917, Grütter\textsuperscript{994} first showed that hexaethylidistannane was cleaved by HgCl\textsubscript{2} to give $\text{Et}_3\text{SnCl}$ and mercury. Then Kraus and Session\textsuperscript{782} (1925) and Kocheshkov, Nesmeyanov and Puzyreva\textsuperscript{1009} (1937) carried out an analogous reaction. In 1936, the latter authors\textsuperscript{820} found that the Sn–Sn bond in hexaethyldistannane was cleaved by aromatic organomercury compounds $\text{Ar}_2\text{Hg}$ and ArHgCl, with the formation of $\text{Et}_3\text{SnAr}$ and metallic mercury (with ArHgCl, $\text{Et}_3\text{SnCl}$ was also formed). The products $\text{Et}_2\text{SnAr}_2$ and Hg were obtained in the reaction of $\text{Ar}_2\text{Hg}$ with $\text{Et}_3\text{Sn}$. The reactions of HgCl\textsubscript{2} with $\text{Et}_3\text{SnSnEt}_3$ and Et2Sn gave Hg as well as $\text{Et}_3\text{SnCl}$ and Et2SnCl\textsubscript{2}, respectively.

During 1917–1957 it was found that the Sn–Sn bond was also cleaved by AgNO\textsubscript{3}, BiBr\textsubscript{3}, sodium amide, and organolithium compounds.
The ability of the Sn–Sn bond to be cleaved by alkali metals was first established by Kraus and Session\(^{782}\) in 1925. They found that hexaorganyldistannanes were cleaved by sodium in liquid ammonia to give triorganylstannylsodium\(^ {148,227,782}\). Subsequently, Gilman and Marrs\(^ {246}\) showed that lithium could also cleave hexaphenyldistannane in THF. The Sn–Sn bond in \( \text{R}_2\text{Sn} \) was as reactive as that in \( \text{R}_3\text{SnNR}_3 \) and was similarly cleaved by the reagents mentioned above. For example, in 1911 Pfeiffer and coworkers\(^ {618}\) reported that reactions of \( \text{Et}_2\text{Sn} \) with oxygen and halogens resulted in the formation of \( \text{Et}_2\text{SnO} \) and \( \text{Et}_2\text{SnX}_2 \) (\( X = \text{Cl}, \text{Br}, \text{I} \)), respectively. In 1958, Bähr and Gelius discovered an unusual reaction of \( \text{R}_2\text{Sn} \) (\( R = 2-, 3- \) and \( 4-\text{PhC}_6\text{H}_4 \)) with \( \text{SnCl}_2 \), which led to \( \text{Sn} \) and \( \text{R}_3\text{SnNR}_3 \). The latter product with \( R = 2-\text{PhC}_6\text{H}_4 \) was isolated in two crystal modifications. The precursor (\( 2-\text{PhC}_6\text{H}_4 \))\(_2\)\( \text{Sn} \) was the cyclic trimer, since its molecular weight determined in 1,2-dibromoethane after careful purification is 1300\(^ {1010}\).

I. Compounds of Nontetracoordinated Tin

Already in 1862 Cahours\(^ {596} \) obtained adducts with the composition \( \text{R}_3\text{SnI} \cdot 2\text{B} \) (\( R = \text{Me}, \text{Et}, \text{Pr} \); \( \text{B} = \text{NH}_3, \text{i}-\text{C}_5\text{H}_11\text{NH}_2, \text{PhNH}_2 \)) and for the first time he drew attention to the tendency of organotin compounds to complex with organic bases and ammonia. One quarter of a century later, Werner and Pfeiffer\(^ {585} \) reproduced these data and obtained complexes \( \text{Et}_3\text{SnI} \cdot 2\text{B} \). They also obtained complexes with the composition \( \text{Et}_2\text{SnX}_2 \cdot 2\text{B} \) (\( X = \text{Cl}, \text{Br}, \text{I} \); \( \text{B} = \text{NH}_3, \text{Py} \)) and considered their structure according to Werner’s coordination theory\(^ {1011}\). Richardson and Adams\(^ {1012} \) reported adducts with the composition \( \text{SnX}_4 \cdot 4[\text{PhNH}_2 \cdot \text{HX}] \) (\( X = \text{Cl}, \text{Br} \)). Werner assigned to the latter complex the \( [\text{SnX}_2(\text{HX} \cdot \text{PhNH}_2)_4]\text{X}_2 \) structure, and the Richardson complexes were probably mixtures of \( [\text{PhNH}_3]_2^+\text{[SnX}_6]^{2-} \) and \( 2\text{PhNH}_2 \cdot \text{HX} \). Twenty-seven years later Pfeiffer and coworkers\(^ {309,618,620} \) continued the research of his teacher. He obtained and studied many complexes of organotin halides with amines which contained a hexacoordinated Sn atom, namely \( \text{Me}_2\text{SnI} \cdot 2\text{Py} \) (1903)\(^ {309} \); \( \text{R}_2\text{SnX}_2 \cdot 2\text{Py} \) (\( R = \text{Me}, \text{Et}, \text{Pr}, \text{Bu}, \text{Ph}, 4-\text{MeC}_6\text{H}_4; X = \text{Cl}, \text{Br}, \text{I}) \); \( \text{MeSnX}_3 \cdot 2\text{Py} \) (\( X = \text{Cl}, \text{Br} \)) (1911)\(^ {618} \); \( \text{R}_2\text{SnX}_2 \cdot 2\text{B} \) (\( R = \text{Me}, \text{Et}, \text{Pr} ; X = \text{Cl}, \text{Br}, \text{I} ; B = \text{PhNH}_2, \text{Py} \) quinoline) (1924)\(^ {620} \). At that time he and then others described the adducts \( \text{Pr}_4-n\text{SnX}_n \cdot 2\text{B} \) (\( B = \text{Py}; n = 1–3 \)) containing hexacoordinated tin \( ^{616–618,1013–1015} \). In 1911 he obtained the \( \text{R} \text{SnX}_3 \cdot 2\text{Py} \)\(^ {618} \) complexes. Pfeiffer and coworkers\(^ {309,618} \) also synthesized the first complexes of the type \( \text{R}_4-n\text{SnX}_n \cdot 2\text{B} \cdot 2\text{HX} \) (\( R = \text{Me}, \text{Et}, \text{Pr}, \text{Ph} ; X = \text{Cl}, \text{Br} ; B = \text{Py}, \text{quinoline, PhNHMe, PhNH}_2 \); \( \text{PhNH}_2; n = 1–3 \)). It may be assumed that the structure of these complexes corresponded to the \( [\text{BH}^+]_2[\text{R}_4-n\text{SnX}_n+2]^{2-} \) formula with a hexacoordinated Sn atom. Ten years later Druce\(^ {850,851,868,1016} \) obtained the similar adducts \( \text{RSnX}_3 \cdot 2\text{B} \cdot 2\text{HX} \). It can now be stated that these complexes corresponded to the general formula \( [\text{BH}^+]_2[\text{R}_3\text{SnCl}_5]^{2-} \) (\( R = \text{Me}, \text{Et}, \text{i}-\text{Pr} ; B = \text{Py}, \text{PhNH}_2, \text{PhMeNH} \), as well as to \( [(\text{PhH})_2^+\text{(i}-\text{PrSnBr}_3)_2^{2-}]^{851,868,1016} \).

In 1923, Kraus and Greer\(^ {777} \) obtained the 1 : 2 complexes of \( \text{Me}_2\text{SnX} \) (\( X = \text{Cl}, \text{I} \)) and \( \text{Me}_2\text{SnCl}_2 \) with \( \text{NH}_3, \text{PhNH}_2 \) and pyridine. Within a year Krause and Pohland\(^ {769} \) obtained the adduct \( (c-\text{C}_6\text{H}_11)_2\text{SnCl} \cdot \text{NH}_3 \), which was prepared despite the presence of three bulky substituents at the tin atom. In 1937, Karantassis and Basillides\(^ {624} \) described a series of complexes of the composition \( \text{Me}_2\text{SnI} \cdot 2\text{B} \) (\( B = \text{Py}, \text{PhNH}_2, 2-\text{MeC}_6\text{H}_4\text{NH}_2, \text{PhN} \text{Et}_2, 4-\text{MePy}, 2\)-methylquinoline). In 1934, Kocheshkov\(^ {1014} \) obtained the adducts \( \text{R}_4-n\text{SnX}_n \cdot 2\text{Py} \) (\( R = \text{Me}, \text{Et}; X = \text{Cl}, \text{Br} \)) and, in 1936, the \( \text{Et}_3\text{SnBr} \cdot \text{NH}_3 \) adduct\(^ {820} \). One such complex, namely \( (\text{Me}_2\text{SnCl}_2 \cdot 2\text{Py}) \), was obtained in the Rochow laboratory in 1957\(^ {1015} \). In 1934–1935, Kocheshkov and coworkers\(^ {799,803,1014} \) prepared the complexes of \( \text{Py} \) and aryltrihalostannanes \( \text{ArSnX}_3 \cdot 2\text{Py} \). In 1958, Reutov and coworkers\(^ {1017} \)
1. Genesis and evolution in the organic chemistry of Ge, Sn, and Pb compounds

synthesized a series of coordinated compounds of the composition [ArN₂]₂⁺[MeSnCl₅]⁻ and [ArN₂]₂⁺[Et₂SnCl₄]⁻. In 1959, Nesmeyanov, Reutov and coworkers obtained the unusual complexes [Ph₂I⁺][SnCl₄Y₂]⁻, containing hexacoordinated tin atom, by the reaction of diphenylhaloiodides Ph₂IY with SnCl₄. Reaction of these complexes with tin powder gave Ph₃SnCl₂.

Almost all these complexes had a hexacoordinated tin atom in octahedral environment. It is remarkable that only five intermolecular coordination compounds Me₃SnX·B(Cl, Br, I; B = NH₃, Py, PhNH₂) containing pentacoordinated tin atom were obtained in 1923–1934. In 1901, Kehrmann described an unusual 1 : 1 complex of triphenylchloromethane with tetrachlorostannane. The formula [Ph₃C][SnCl₅] could describe its structure. Unlike it and according to Gustavson, methyl iodide (as well as H₂Cl₂ and HCl₃) did not form the addition products in the reaction with SnCl₄, but the reactants were involved in a very slow exchange reaction between the iodine and chlorine atoms. The tin atom in the 1 : 1 complexes is placed in the center of a trigonal bipyramid or have the ionic tetrahedral structure [Me₂SnX]. These simple statistics mentioned above indicate that the complexes of the pentacoordinated tin atom were less stable thermodynamically, and consequently they were easily converted into their analogs having the hexacoordinated Sn atom.

In 1924, Pfeiffer and coworkers reported the existence of the sole adduct Et₂SnCl₂·3NH₃, in which the tin atom was heptacoordinated. In the fourteen years 1910–1924, Pfeiffer had shown that intermolecular complexes, having octacoordinated tin atom, are not rarities. He obtained Ph₂SnBr₂·4Py, MeSnI₃·4Py, Ph₂SnCl₂·4Py, Me₂SnCl₂·4NH₃, Et₂SnCl₂·4NH₃ and Et₂SnBr₂·4NH₃. It could not be stated unequivocally that the tin atom in these complexes was octacoordinated. However, it is probable that their structure corresponded to the formula [R₄SnX₄]ⁿ⁺ⁿ⁻ in which the Sn atom was hexacoordinated and the complexes are salts or ion pairs. As a whole, according to Gol’dshtein and coworkers the tendency of organylchlorostannanes for complexing decreased in the following series: PhSnCl₃ > Bu₂SnCl₃ > Ph₂SnCl₂ > Ph₃SnCl > Bu₃SnCl, i.e. with the decreasing number of chlorine atoms at the central Sn atom.

Alkylhalostannanes form stable complexes with oxygen-containing ligands. First, the aliphatic organotin bases having an Sn–X or Sn–O bond in which the oxygen atom has a strong nucleophilic reactivity belong to such ligands. The first complex of such a type, Et₂SnO·Et₂SnI₂, was obtained by Strecher in 1858. From 1914 complexes of the compositions (R₃SnO)n·R₂SnX₂, (R₃SnO)₃H·R₃SnX₂, (R₃SnO)₂·R₃SnX, (R₃SnOH)·R₃SnX, and R₃SnOH·R₂SnX were described. This series can be supplemented with the Me₂SnO·Me₂Sn(OH)I adduct. Such complexes often appeared as by-products when the syntheses of organotin compounds having a Sn–X or Sn–O bond were carried out. It is noteworthy that many solid organotin compounds having the stannoxane bond were found to be coordinated polymers rather than monomers, as hitherto considered, because their molecules were bonded by donor–acceptor (bridge) Sn–O → Sn bonds.

Hypervalent intramolecular organotin compounds are stannatranes RSn(OCH₂CH₂)₃N and dragonoides Y(CH₂)₃SnX₃ (Y = an atom having at least one lone electron pair, e.g. N, O, Cl), which appeared only in the 1970s and hence do not yet belong to history.

The first attempt of Zelinskii and Kravin to prove the ionization of alkylhalostannanes was undertaken in 1896. By electroconductive investigations of methanolic solutions of Et₃Sn and Et₂SnI₂ they established that these compounds behaved similarly to weak electrolytes in the aqueous medium, i.e. according to the dilution law. From the second quarter of the 20th century the possible existence of organotin cations...
R$_3$Sn$^+$ and R$_2$Sn$^{2+}$ in solutions was raised. In the Kraus$^{1013,1033,1034}$ (1923–1924) and Rochow$^{915,924,1035}$ (1952–1957) laboratories the dissociation of alkylchlorostannanes in water and in organic solvents was studied extensively. The solutions of ethyl- and methylhalostannanes in water, in lower alcohols, in acetone and in pyridine displayed comparatively efficient electrolytic conduction, but their conductivity in ether, nitrobenzene and nitromethane was insignificant$^{1013,1033,1034,1036}$. The ionization constant of Me$_3$SnCl in EtOH was $10^{-5}$ at 25$^\circ$C$^{1034}$. Rochow and coworkers$^{915,924}$ found that Me$_2$SnCl$_2$ was dissociated in water into Me$_2$Sn$^{2+}$ and Cl$^-$. The solutions were acidic, indicating that partial hydrolysis (ca 10% in very dilute solutions)$^{1037}$ took place. According to the conductometric titration data of solutions of the organylhalostannanes Me$_3$SnCl, Me$_2$SnCl$_2$, Ph$_3$SnCl, Ph$_3$SnF (as well as Ph$_3$MCl, where M = Si, Ge, Pb) they did not dissociate into ions$^{1035}$ in such an aprotic solvent as pure DMF.

Dissociation of Me$_3$SnCl$_2$ and Me$_3$SnCl and their analogs in H$_2$O enable the displacement of the halogen atoms in organylhalostannanes by other atoms and groups present in the aqueous medium.

The Rügheimer’s$^{993}$ ebullioscopic molecular weight measurements (1908) of Et$_3$SnSnEt$_3$ in ether indicated the possibility of the generation of a free organotin radical R$_3$Sn$^*$ (Section III.H). These measurements showed that the apparent molecular weight of hexaethyldistannane decreased on decreasing its concentration in ether solvent. In 1925, Kraus and Session$^{782}$ achieved similar results when they found that Me$_2$SnMe$_3$ was almost completely dissociated in dilute solutions into free Me$_3$Sn$^*$ radicals. Bullard, in his doctoral dissertation (1925), found that Me$_3$SnSnEt$_3$ was formed from an equimolecular mixture of Me$_3$SnSnMe$_3$ and Et$_3$SnSnEt$_3$ in boiling benzene solution. In his opinion this indicated the intermediacy of Me$_3$Sn$^*$ and Et$_3$Sn$^*$ free radicals. Stable free radicals R$_3$Sn$^*$ with R = CH(Me$_3$Si)$_2$ were first obtained by Lappert$^{514,1038}$ by photochemical disproportionation of [(Me$_3$Si)$_2$CH]$_2$Sn at the end of the last century.

The history of organic hypovalent (divalent) tin derivatives R$_2$Sn seemed as old as the rest of the chemistry of organotin compounds, but this is not so because almost all compounds with the structure R$_2$Sn synthesized for over 100 years were the cyclic oligomers or polymers of tetravalent tin (see Section III.H), but not the monomers as originally thought. Old arguments which supported the monomeric structures of these compounds, such as the facile addition reactions of halogens, hydrohalic acids, oxygen and sulfur to R$_2$Sn, were in fact due to Sn–Sn bond cleavage. Nevertheless, many investigators in the past encountered monomeric diorganylstannylenes R$_2$Sn, which were the intermediates in reactions developed by them. Organotin compounds R$_2$Sn=Y (Y = SnR$_2^{516}$, CR$_2$, OS, Se$^{523}$ etc.), having three-coordinated Sn atom, bonded by a double bond atom or to another Sn element, can be considered as the hypovalent tin derivatives. However, they also appeared only at the end of the past century and their historical development lies beyond the scope of this chapter. In 1926 Chambers and Scherer$^{662}$, and then Schmitz-DuMont and Bungard$^{1039}$ observed the formation of the first representative of these labile compounds, i.e. diphenylstannylenne Ph$_2$Sn, in the thermal dissociation of diphenylstannane Ph$_2$SnH$_2$. However, Krause and Becker$^{781}$ were the first who had Ph$_2$Sn in their hands in 1920. In 1943, Jensen and Clauson-Kaass$^{984}$ confirmed this fact when they showed that freshly prepared (according to the Krause) diphenylstannylene was monomeric and that it slowly polymerized on storing to give the pentamer (Ph$_2$Sn)$_5$, hexamer and higher oligomers. Diphenylstannylene, which was diamagnetic in all the polymerization stages, maintained a constant value of its dipole moment (1.0 D). This gave rise to the suggestion that, when formed as intermediates, the oligomers were biradicals obtained according to equation 19.
1. Genesis and evolution in the organic chemistry of Ge, Sn, and Pb compounds

The synthesis of stable diorganylstannylenes, the true divalent organotin derivatives, was carried out only in the second half of the 20th century,\textsuperscript{68,97,105,508,514,1038,1040–1043}. The first stable diorganylstannylene (named ‘homoleptic’\textsuperscript{1040}) [(Me₃Si)₂CH]₂Sn appeared in the Lappert laboratory\textsuperscript{1044,1045} after 1975. However, these investigations\textsuperscript{1040} and those about stable free radicals R₃Sn\textsuperscript{58,516} lie beyond the scope of this chapter.

\section*{J. Biological Activity}

Among investigations into the biological activities of organometallic compounds, those of organotin derivatives are highly important\textsuperscript{91,99,1046–1049}, being comparable only with those on the biological activity of mercury and lead compounds. The majority of investigations into the organotin compounds were related to their toxicity that influenced the working process and the experimentalist’s health. In 1951 there were four cases of poisoning with Me₄Sn and Et₄Sn which were reported to result from careless treatment of these substances in the laboratory\textsuperscript{1050}.

Already in 1853, Frankland\textsuperscript{45} paid attention to the toxicity of organotin compounds. But the first experimental investigations of their toxicity were conducted by White\textsuperscript{1051,1052} in 1881 and 1886. He found that, unlike inorganic tin salts, triethylacetoxystannane was highly toxic for frogs, rabbits and dogs. In 1886, Ungar and Bodländer\textsuperscript{1053} studied the toxicity of some organotin compounds on mammalians.

Only forty years later did the investigations on toxicity and biological activity of organotin compounds restart in 1926 due to Hunt\textsuperscript{1054}. Collier\textsuperscript{1055} found in 1929 that the toxicity of aromatic organotin compounds increased in the order: Ph₄Sn < Ph₃SnPh₃ < Ph₃SnPr < Ph₃SnBr. According to Lesbre and coworkers\textsuperscript{1056} aliphatic tin derivatives are more toxic than the aromatic ones, and R₃SnX is more toxic than R₂SnX₂ and R₄Sn (R = alkyl). In 1954–1955 the toxic action of the organotin compounds on warm-blooded animals was determined\textsuperscript{1056,1057}. It was found that in the Et₄₋ₙSnXₙ series the toxicity of the compounds with \( n = 1 \), i.e. Et₃SnX (LD\textsubscript{50} = 5–10 mg kg\textsuperscript{−1}), was the highest. The Et₃SnX\textsubscript{2} poisoning was reduced by 2,3-dimercaptopropanol (dimercaptol-BAL), demonstrating an equal toxic action of R₂SnX₂ to that of organic mercury and lead compounds. At the same time, antagonists for Et₃SnX were not found. Seifert\textsuperscript{1058} (1939), Gilman\textsuperscript{1059} (1942), Glass and coworkers\textsuperscript{1060} (1942) and McCombie and Saunders\textsuperscript{971} (1947) were involved in the search of organotin compounds as war poisoning substances during World War II. As a result of their investigations the structure–toxicity relationship of organotin compounds was established. Trialkylstannane derivatives R₃SnX, R = Me, Et stimulated progress of the momentum reversible paralysis and retarded encephalopathy. These compounds and also R₂SnX₂ derivatives, R = Me, Et, Pr, Bu possessed dermato-vesical, lachrymatorial and skin-irritating influence. However, none of them was employed as war poisoning agents. In 1940–1942, toxicological studies of the organotin compounds started at the Medical Research Council in Great Britain and in Toulouse University. In 1955 Stoner, Barnes and Duff\textsuperscript{1057} studied the toxicity and biological activity of the R₄₋ₙSnXₙ (R = Alk; \( n = 0–3 \)) series. They found that the influence of Et₃SnX and Et₂SnX₂ was quite different and that only the toxic effect of the latter compound was suppressed by 2,3-dimercaptopropanol. The results of investigations of the influence of tetraalkylstannane under intravenous, intramuscular, oral and intraperitoneal infusion\textsuperscript{125} were summarized in
Meynier’s doctoral dissertation (1955) and published in 1956. In 1955–1959 a series of physiological investigations of organotin compounds and a mechanistic study of their influence on laboratory animals were carried out. In 1950 in Utrecht intensive investigations of toxicity and fungicidal activities of organotin compounds begun under van der Kerk supervision. First, the fungicide activities of Et₄₋ₙSnXₙ (n = 0–4) were investigated and it was found that Et₃SnCl (n = 1) possessed the maximal fungicidal action. Compounds R₄Sn, R₂SnX₂ and RSnX₃, having different R and X substituents, were less active in comparison with R₃SnX.

Further studies of the fungicidal activities of compounds R₃SnX showed that the activity was almost independent of the type of the substituent X. This led to the conclusion that toxicity of R₃SnX was conditioned by the R₃Sn⁺ ion or probably by the undissociated R₃SnOH. In contrast, the R substituents affected strongly the fungicidal properties of the R₃SnX (X = OCOMe) series. This effect was maximal at R = Pr, Bu. Further investigation of R'R₂SnX (R = Me, Et; R' = CₙH₂ₙ₊₁; n = 2–12) derivatives showed that the fungicidal activity was dependent only on the total number of carbon atoms in the three-alkyl groups bonded to the tin atom. The maximal activity was achieved when this number was 9–12.

In 1938 it was found that organotin derivatives of proteins and nucleoproteins and the products of their hydrolysis could be used to treat some skin and blood diseases. Kerr and Walde found that Bu₂Sn(OCOC₁₁H₂₃)₂ was a very effective medication against some intestinal worm infections of chickens. Later, this medication was patented.

Physicians called attention to the effective antimicrobial action of organotin compounds in the middle of the last century. In 1958, ‘Stalinon’, a medical preparation consisting of diethyldiiodostannane and isolinolenic acid esters, was produced in France for the treatment of staphylococcus infections. Hexabutyldistannoxane in combination with formaldehyde was used as a remedy against Staphylococcus aureus.

The insecticide action of organotin compounds attracted attention in the first half of the 20th century. In 1929 and 1930 a great number of compounds R₄₋ₙSnXₙ were patented as a remedy against moth. In 1952 a patent on the application of trialkylchlorostannanes as insecticides was issued. In 1946, some organotin compounds were patented as the active components of anti-overgrowing coatings. Somewhat later the stable bioprotective organotin coatings were developed on the basis of monomers of the R₃SnS(CH₂)ₙSi(OR')₃ type.

K. Practical Use

In the second half of the 20th century organotin compounds found extensive applications in different technological fields and in agriculture. In 1980 the annual world production of organotin compounds was 35,000 tons and 28,000 tons of metallic tin were used as the precursor. The practical application of the organotin compounds started with the fundamental investigations of Yngve, who found that several organotin compounds were excellent photo- and thermo-stabilizers of polyvinyl chloride and other chlorinated polymers, and received a patent in 1940. For the next several years, many other organotin compounds were patented. Compounds of the types Bu₂Sn(OCOR)₂ and Bu₂Sn(OCO)₂R' (R' = divalent organic radical, preferably unsaturated) were found to be the best stabilizers. Just up to 1960, 82 patents, cited in reviews and in several articles, were devoted to PVC organotin stabilizers. In 1953, Kenyon first started to investigate the mechanism governing the influence of the organotin stabilizers.
organotin compounds were offered as stabilizers for liquid chlorinated dielectrics, chloro-containing dye stuffs for rubber, and polystyrene and as inhibitors of corrosion. In 1949, based on Hart’s investigations, a patent for the use of tribenzylalkylstannanes as antioxidants for protecting rubbers from cracking was issued. In 1954–1959 a series of different R₂SnX₂ and R₃SnX compounds which were identical to already known polyvinyl chloride stabilizers were patented for similar use.

Patents dealing with possible practical use of organotin compounds as components for catalytic systems for polymerization of olefins appeared during the same period of time. The investigations of chemists and biologists from Utrecht proposed the practical use of organotin compounds as biocides (fungicides, insecticides) and biocide coatings and impregnations. Compounds Et₃SnX (X = OH, OCOMe) were found to effectively suppress ordinary types of fungus which damaged wood. Consequently, they recommended these compounds for practical use, for example, to protect timber in mines from biodegradation, and against fabric damage (cotton, jute) by insects and fungus. Further, the R₃SnX compounds were proposed as highly effective means against plant diseases (pesticides), for the bioprotection of hemp, sisal ropes, and paper, as insecticides and as fungistatic agents for dyes.

IV. ORGANOLEAD COMPOUNDS

A. Introduction

Organolead compounds came into the world in 1852–1853, i.e. at the same time as organotin chemistry was born. The Swedish chemist Löwig, mentioned extensively in section III as one of the founders of organotin chemistry, is also the father of organolead compounds. He had in his hands for the first time simple representatives of organolead compounds such as Et₃PbPbEt₃ and the triethylplumbane derivatives Et₃PbX (X = I, Br, Cl, OH, NO₃, 0.5SO₄) . In the 19th century and at the beginning of the 20th century, the development of the chemistry of organolead compounds was not intensive, although its basis was founded at this period. Only in the years 1915–1925 did organolead chemistry start to develop more quickly due to the efforts of Grüttners and Krause and coworkers. The systematic investigations showed that organolead compounds could be divided into two main classes: derivatives of tetravalent lead (R₄ₕ-NPbXₙ) and divalent lead (R₂Pb). Gilman’s investigations carried out in 1937–1952 (for reviews see References) contributed significantly to the chemistry of organolead compounds. His investigations led to the development of metalloorganic lead derivatives, such as Ph₃PbLi, which turned out to be an important synthon for the synthesis of different organolead compounds. The studies of Kocheshkov and coworkers, who were the first to study the possible existence of aryltriacyloxyplumbanes Rₚb(OCOR’), were unknown until 1950.

What had Löwig done and what would follow from his work? Among the organic derivatives of the heavy elements of Group 14 only the organolead compounds attracted the least attention. This is evident by the number of publications in this field, which totaled up to the middle of the 20th century (of which only 20 appeared in the 19th century) and 420 publications appeared up to 1963. Due to their high toxicity, low thermal and chemical stability, and the similarity of the methods for their synthesis and chemical properties with those of their isostructura tin compounds, there was in general less interest in the organolead compounds. In addition, there was a dominant opinion that the fundamental investigations of organolead compounds could not lead to new developments in comparison with organotins. Nevertheless, the chemistry of tetraalkylplumbanes led to two important discoveries in the 1920s, namely the
thermal generation of free radicals by Paneth and Lautsch in 1929–1931 \cite{1137-1139} and the
discovery of antiknock additives for motor fuels by Midgley and coworkers in 1923 \cite{1140}.

**B. Synthesis from Metallic Lead and its Alloys**

In 1852, Löwig \cite{1107} obtained hexaethylidiplumbane \( \text{Et}_3\text{PbPbEt}_3 \), initially confused with
\( \text{Et}_4\text{Pb} \), by heating ethyl iodide with a lead–sodium alloy. In the 20th century this became
the predecessor of the industrial synthesis of \( \text{Et}_4\text{Pb} \). Following Löwig, Polis \cite{1141} (1887),
Ghira \cite{1142,1143} (1893, 1894), Tafel \cite{1144} (1911), Calingaert \cite{1145} (1925), Fichter and Stein
\cite{1146} (1931), Goldach \cite{1147} (1931) and others \cite{47,54,110,1129} studied the reaction of lead–sodium
alloy with organic halides. Tafel \cite{1144} and Ghira \cite{1142,1143} established the correct structure
of the substance obtained by Löwig \cite{42,43,1107}. Kraus and Callis \cite{643} found the optimal
conditions for the industrial production of \( \text{Et}_4\text{Pb} \), namely the reaction of \( \text{Pb}–\text{Na} \) alloy
with \( \text{EtCl} \), which was cheaper and more readily available than \( \text{EtI} \), which proceeded
according to equation 20.

\[
4\text{NaPb} + 4\text{EtCl} \rightarrow \text{Et}_4\text{Pb} + 3\text{Pb} + 4\text{NaCl}
\]  

(20)

Consequently, 3/4 of the lead was recovered and could be used further. In the laboratory
this method had only limited use. In particular, it was used by Calingaert and
coworkers \cite{1148} and Saunders and coworkers \cite{1149,1150} to obtain \( \text{R}_4\text{Pb} \) with \( \text{R} = \text{Me}, \text{Et}, \text{Pr}, \text{i-Bu} \) in 1948 and 1949, respectively. From 1927 \cite{1151,1152} many dozens of patents appeared
following the investigations of Kraus and Callis, to protect the method for preparing the
\( \text{R}_4\text{Pb} \) (\( \text{R} = \text{Me}, \text{Et} \), Mg, Ca) with \( \text{RCl}, \text{RBr} \) and \( (\text{EtO})_2\text{SO}_2 \) under different conditions \cite{47,109,110}. It is impossible
to demonstrate all of them here, but we point out that one of the first patents for
the preparation of \( \text{Et}_4\text{Pb} \) was granted to Kraus in 1928 \cite{1153}. Even in 1950 patents for
the preparation of \( \text{Et}_2\text{Pb} \) from lead alloys with \( \text{Mg} \), \( \text{Ca} \) were published.

Hence the reaction of alkyl halides with lead–sodium alloy, discovered by Löwig \cite{42,43,1107}.
Kraus and Callis \cite{643} found the optimal conditions for the industrial production of \( \text{Et}_4\text{Pb} \), namely the reaction of \( \text{Pb}–\text{Na} \) alloy
with \( \text{EtCl} \), which was cheaper and more readily available than \( \text{EtI} \), which proceeded
according to equation 20.

Already in 1887, Polis \cite{1141} obtained tetraphenylplumbane \( \text{Ph}_4\text{Pb} \) by the reaction of \( \text{PhBr} \) with
\( \text{Pb}–\text{Na} \) alloy in the presence of ethyl acetate. Calingaert \cite{1145} found that the reaction of
alkyl halides with \( \text{Pb}–\text{Na} \) alloy was promoted also by water and by the other compounds,
and hydrogen was formed in the reaction with the alloy. We note that in 1853 Cahours \cite{1158}
found that metallic lead reacted at a low rate with \( \text{EtI} \) on heating to give unidentified
organolead compounds. Although this was not of any practical interest, metallic lead, but
not its alloy, was used successfully for the synthesis of \( \text{R}_4\text{Pb} \). In 1911, Tafel \cite{1144} showed
that the electrochemical reduction of acetone on lead cathode in sulfuric acid solution led
to formation of \( \text{i-Pr}_4\text{Pb} \). In 1925, the electrochemical synthesis of tetraalkyplumbanes
from alkyl bromides and iodides by using a lead cathode was patented \cite{1159,1160}. The
intermediate in this process was dialkylplumbylene, which was rapidly transformed into
tetraalkyplumbane at the high temperature of the cathode electrolyte. In 1942, Nad’ and
Kocheshkov \cite{1161} found that the reaction of \( \text{Ar}_2\text{PbCl}_2 \) with metallic lead or \( \text{Pb}–\text{Na} \) alloy
in boiling xylene led to \( \text{Ar}_3\text{PbCl}_2 \) and \( \text{PbCl}_2 \).

**C. Metalloorganic Approaches to Organolead Compounds**

Historically, the first metalloorganic method for the synthesis of organolead compounds
was based on the use of zinc dialkyls. It was not surprising that the method was first
used by Frankland and Lawrence\textsuperscript{591,1162}, who used zinc dialkyl in other reactions. In 1859 they synthesized $\text{R}_2\text{PbCl}_2$ by the reaction of $\text{PbCl}_2$ with $\text{R}_2\text{Zn}$ ($\text{R} = \text{Me}$, Et). In 1859 Buckton\textsuperscript{603,604,1163} obtained $\text{R}_4\text{Pb}$ by the reaction of $\text{PbCl}_2$ with $\text{R}_2\text{Zn}$ ($\text{R} = \text{Me}$, Et). The effort of Tafel\textsuperscript{1144} to synthesize (i-Pr)$_4\text{Pb}$ in 1911 failed. In 1925, Meyer\textsuperscript{1164} described the organozinc synthesis of Et$_4\text{Pb}$ from $\text{PbCl}_2$.

The reactions of lead dihalides with organomagnesium compounds then became widely used and a convenient laboratory method. Unlike organic derivatives of silicon, germanium and tin, which were usually prepared from $\text{MHal}_4$ ($\text{M} = \text{Si, Ge, Sn}$) according to the Grignard method, the lead tetrahalides $\text{PbHal}_4$ could not be used for this purpose because of their extraordinary instability. The organomagnesium synthesis of organolead compounds was first applied by Pfeiffer and Trüskier\textsuperscript{1165} in 1904 and then by Möller and Pfeiffer in 1916\textsuperscript{1166}. They obtained both a tetraalkyl- and a tetraarylstannane $\text{R}_4\text{Pb}$ ($\text{R} = \text{Et, Ph}$) by the reaction of organylmagnesium halides $\text{RMgX}$ with $\text{PbCl}_2$. Metallic lead was the by-product of the reaction. Later, Ph$_4\text{Pb}$ was similarly synthesized in the laboratories of Krause\textsuperscript{1124} (1925), Gilman\textsuperscript{1167,1168} (1927 and then 1939), Kocheshkov\textsuperscript{1169} (1937) and others. This method was not suitable for the preparation of some other tetraarylplumbanes; e.g. $\text{Ar}_3\text{PbPbAr}_3$\textsuperscript{1120,1170,1171} was the main product of the reaction of $\text{ArMgX}$ with $\text{PbCl}_2$. Krause and Reissaus\textsuperscript{1122} managed to carry out the reaction of $\text{PhMgBr}$ with $\text{PbCl}_2$ in such a way that the main reaction product was $\text{P}_3\text{PbPbPh}_3$. In 1914, Grüttnert and Krause\textsuperscript{674,1121} succeeded in obtaining tetraacetylcyclohexylplumbane according to the Grignard method. In 1916–1918, Grüttnert and Krause\textsuperscript{1110,1114,1115,1117} used Grignard reagents for the synthesis of $\text{R}_4\text{Pb}$ with $\text{R} = \text{Me}$, Et, Pr, i-Pr, i-Bu, i-Am. In 1916, Möller and Pfeiffer\textsuperscript{1166} were the first to use organylhaloplumbanes in the Grignard reaction. They obtained $\text{Ph}_2\text{PbEt}_2$ by the reaction of $\text{Ph}_2\text{PbBr}_2$ with $\text{EtMgBr}$. In 1919, Krause and Schmitz\textsuperscript{814} synthesized mixed tetraorganoplumbanes ($\text{1-C}_{10}\text{H}_7$)$_2\text{PbR}_2$ ($\text{R} = \text{Et, Ph}$) by the Grignard method. It was also found that in the reaction of $\text{2,5-Me}_2\text{C}_6\text{H}_3\text{MgBr}$ with $\text{PbCl}_2$ only ($\text{2,5-Me}_2\text{C}_6\text{H}_3$)$_3\text{PbPb}$($\text{C}_6\text{H}_3\text{Me}_2-2,5$ $\text{C}_6\text{H}_3-2,3$ $\text{Me}_2$)$_3$ was obtained, but not tetra-p-xylylplumbane. The reaction of $\text{PbCl}_2$ with $\text{2-MeC}_6\text{H}_4\text{MgBr}$ proceeded analogously\textsuperscript{1122}. There were no doubts that such a result was due to the steric hindrances. In 1928 the organomagnesium method of the synthesis of Et$_4\text{Pb}$ was patented\textsuperscript{1172–1175}. The use of the Grignard reagent enabled one to obtain compounds of the types $\text{R}_3\text{PbPbR}_3$, $\text{R}_2\text{Pb}$, $\text{R}_4\text{Pb}$ ($n = 0$–3) and $\text{R}_2\text{R}'/\text{R''Pb}$\textsuperscript{1129} from $\text{PbX}_2$. Compounds such as 1,1-diorganylplumbacycloalkanes belong to this group, and the first representative 1,1-diethylplumbacyclohexane $\text{Et}_2\text{Pb}(\text{CH}_2)_{5-c}$ was obtained by the reaction of $\text{Et}_2\text{PbCl}_2$ with $\text{BrMg}(\text{CH}_2)_2\text{MgBr}$ by Grüttnert and Krause\textsuperscript{1112} in 1916. Tetraphenylplumbane, which is extremely easily oxidized by air (sometimes with inflammation), was first synthesized by Hardtmann and Backes\textsuperscript{710} by the Grignard method and two years later by Krause and Schlöttig\textsuperscript{833} and then by Lesbre\textsuperscript{1176}. Unstable tetravinylplumbane was first synthesized by the action of the Norman reagent $\text{CH}_2=\text{CHMgX}$ ($\text{X} = \text{Cl, Br}$) on $\text{PbCl}_2$ or on $\text{Pb(OCOME)}_2$ by Juenge and Cook\textsuperscript{1177} in 1959. As early as in 1916, Grüttnert and Krause\textsuperscript{1110} and Möller and Pfeiffer\textsuperscript{1166} observed that in the reaction of the Grignard reagent with $\text{PbCl}_2$ the reaction mixture became red. This was explained by the intermediate formation of colored diorganylplumbylbenzenes $\text{R}_2\text{Pb}$. However, all attempts to isolate dialkylplumbylbenzenes from the solutions failed\textsuperscript{1145}. In contrast, several publications\textsuperscript{984,1122,1178,1179} were devoted to diarylplumbylbenzenes $\text{Ar}_2\text{Pb}$, before 1961. In 1922, Krause and Reissaus\textsuperscript{1122} isolated the red powder-like $\text{Ar}_2\text{Pb}$ together with $\text{Ar}_3\text{PbPbAr}_3$ from the reaction products of $\text{PbCl}_2$ with $\text{ArMgBr}$ ($\text{Ar} = \text{Ph}$, 4-$\text{MeC}_6\text{H}_4$) at $0{\degree}\text{C}$.

In 1932, Austin\textsuperscript{680} used for the first time organolithium compounds for the synthesis of organoleads. He reported that the reaction of $\text{ArLi}$ with $\text{PbCl}_2$ led to $\text{Ar}_2\text{Pb}$. Further heating of the latter led to products such as $\text{Ar}_4\text{Pb}$, $\text{Ar}_3\text{PbPbAr}_3$ and $\text{Pb}$\textsuperscript{680,1180,1181}.
However, in 1941 Bindschadler and Gilman\textsuperscript{1182} concluded that the reaction proceeded in another way. The reaction mixture of PbCl\textsubscript{2} with PhLi at $-5\,^\circ\mathrm{C}$ was not red colored due to Ph\textsubscript{2}Pb, and free lead was not isolated. In addition, boiling of Pb\textsubscript{3}PbPbPh\textsubscript{3} in an ether–toluene mixture did not result in the formation of Ph\textsubscript{4}Pb. Based on these facts they concluded that Pb\textsubscript{3}PbPbPh\textsubscript{3}, Pb\textsubscript{3}PbLi and, finally, Ph\textsubscript{4}Pb\textsuperscript{1182} were consequently formed in the reaction. Austin\textsuperscript{680,1180} obtained R\textsubscript{3}PbAr and R\textsubscript{2}PbAr\textsubscript{2} (R = Ar) by the reaction of ArLi with R\textsubscript{3}PbCl and R\textsubscript{2}PbCl\textsubscript{2}, respectively. In 1940, Gilman and Moore\textsuperscript{1183} used the reaction of ArLi with R\textsubscript{4-n}PbX\textsubscript{n} (n = 1, 2) for the synthesis of R\textsubscript{3}PbAr and R\textsubscript{2}PbAr\textsubscript{2}. Austin\textsuperscript{680,1180} in 1932 obtained optically active PrPh\textsubscript{2}(2-MeC\textsubscript{6}H\textsubscript{4})Pb(C\textsubscript{6}H\textsubscript{4}OOct-\textit{i}) by the reaction of (i-OctOC\textsubscript{6}H\textsubscript{4})\textit{Li} with optically active PrPh(2-MeC\textsubscript{6}H\textsubscript{4})PbX. Talalaeva and Kocheshkov\textsuperscript{666,667} were the first to describe the reaction of PhLi with lead powder which resulted in low yield of Ph\textsubscript{4}Pb and metallic Li. Replacement of lead with its amalgam increased the output of the products and reduced the time of the reaction\textsuperscript{667}. In 1950, Gilman and Jones\textsuperscript{1184} found that the reaction of MeLi with PbI\textsubscript{2} and MeI resulted in Me\textsubscript{4}Pb formation. Metallic lead and Me\textsubscript{2}PbI\textsubscript{2} were the intermediate products of the reaction. The reaction of PbCl\textsubscript{2} with ArLi and with the appropriate aryl iodide was carried out analogously and led to Ar\textsubscript{4}Pb (Ar = Ph, 4-Me\textsubscript{2}NC\textsubscript{6}H\textsubscript{4})\textsuperscript{239,1185}.

In 1941, in the Gilman laboratory, triphenylplumbyllithium was first synthesized by the addition of excess PhLi to PbCl\textsubscript{2} in ether at $-10\,^\circ\mathrm{C}$\textsuperscript{1182}. In 1951, Gilman and Leeper\textsuperscript{316} developed another synthesis of triphenylplumbyllithium Pb\textsubscript{3}PbLi by the reaction of Pb\textsubscript{3}PbPbPh\textsubscript{3} with metallic Li. In 1917, Schlenk and Holtz\textsuperscript{1186} and later Hein and Nebe\textsuperscript{1187} (1942) found that metallic Na cleaved R\textsubscript{4}Pb in ether solvent. In 1938, Calingaert and Soroos\textsuperscript{1188} found that alkylhaloplumbanes reacted with a stoichiometric amount of Na in liquid ammonia to give hexaalkyldiplumbanes R\textsubscript{3}PbPbR\textsubscript{3} (R = Me, Et). Gilman and Bailie\textsuperscript{791,1170}, Foster and coworkers\textsuperscript{1189} and Bindschadler\textsuperscript{1190} observed that R\textsubscript{3}PbPbR\textsubscript{3} was formed by the reaction of Na with R\textsubscript{3}PbX (R = Alk, Ph; X = Cl, Br) in ammonia, and that the dark-red solution of R\textsubscript{3}PbNa was formed. In 1941, Bindschadler\textsuperscript{1190} succeeded in obtaining R\textsubscript{3}PbNa by the cleavage of R\textsubscript{4}Pb by sodium in liquid ammonia. The ease of the R–Pb bond cleavage was found to decrease in the following order for R : CH\textsubscript{2}CH\textsubscript{2} > i-Bu > Bu > Et > Me > Ph > 4-Me\textsubscript{2}NC\textsubscript{6}H\textsubscript{4}. Thus, for example, Et\textsubscript{3}PbPbNa\textsuperscript{1190} was formed from the reaction of sodium with Et\textsubscript{3}PbPh in the liquid ammonia. However, the best way for obtaining Et\textsubscript{3}PbNa became the cleavage of Et\textsubscript{4}Pb by sodium in liquid ammonia. Ph\textsubscript{3}PbNa was prepared similarly from Ph\textsubscript{3}PbPbPh\textsubscript{3}\textsuperscript{1190}. In 1951, Gilman and Leeper\textsuperscript{316} found that Ph\textsubscript{3}PbPbPh\textsubscript{3} was cleaved by K, Rb, Ca, Sr, Ba in liquid ammonia. In 1926, Hardmann and Backes\textsuperscript{710} patented the method of tetraalkylplumbane preparation by the reaction of PbCl\textsubscript{2} and RX with Na in toluene.

The transformations of compounds Ph\textsubscript{3}PbM (M = Li, Na) and their possible use for synthetic purposes started to develop in 1939, but the basic investigations in this field were carried out after 1960. In 1939, Gilman and Bailie\textsuperscript{791,1170} demonstrated that the reaction of Ar\textsubscript{3}PbNa with PhCH\textsubscript{2}Cl or Ph\textsubscript{3}CCl led to Ar\textsubscript{3}PbR (R = CH\textsubscript{2}Ph, CPh\textsubscript{3}). In 1950 in Gilman’s laboratory\textsuperscript{1191} Et\textsubscript{3}PbNa, which turned out to be more reactive than Ph\textsubscript{3}PbNa, was introduced as a reagent in the reaction with organic halides. The reaction of Et\textsubscript{3}PbNa with PhCH\textsubscript{2}Cl was ‘abnormal’ and led mainly to formation of stilbene. In 1959, Et\textsubscript{3}PbNa was used for the synthesis of Et\textsubscript{3}PbCH\textsubscript{2}=CHPh by Glockling and Kingston\textsuperscript{1192}.

Triphenylplumbyllithium was introduced into synthetic practice by Gilman and Summers\textsuperscript{239,1193} only in 1952. In 1952, D’Ans and coworkers\textsuperscript{986} used Ph\textsubscript{3}PbLi to obtain fluorenllithium. In 1932, Shurov and Razuvaev\textsuperscript{1194} studied the transfer of phenyl radicals, formed by the thermolysis of Ph\textsubscript{3}M (M = metal) to another metal atom, which formed...
more thermally stable phenyl derivatives. They found that the reaction of Ph₄Pb with Sn led to the formation of Ph₂Sn and Pb at 300–375 °C.

Shurov and Razuvaev tried, but failed to prepare phenyl derivatives of lead by the reaction of metallic lead with Ph₃Hg, as well as with Ph₃Bi. Aromatic mercury compounds were first used for the synthesis of organolead compounds in 1932 when Austin obtained Ph₃PbCl by the reaction of Ph₂Hg with Ph₂PbCl₂, but he failed when synthesizing Ph₄Pb and (p-MeC₆H₄)₂PbCl₂ by this method. In 1934, Nesmeyanov and Kocheshkov reported that the reaction of Ph₃Pb with HgCl₂ led to Ph₂PbCl or Ph₃PbCl₂ along with PhHgCl. In 1942, Nad’ and Kocheshkov found that the reaction of Ar₂Hg with tetraacetoxyplumbane Pb(OCOMe)₄ proceeds easily at room temperature in CHCl₃, to give Ar₂Pb(OCOMe)₂. The same reaction with Et₂Hg took three months. These authors first used this reagent for the synthesis of organolead compounds. This reaction enabled one to obtain otherwise almost inaccessible compounds, like Ar₂PbX₂ having reactive substituents in the aromatic ring. The reaction of tetraacetoxyplumbane with (ClCH=CH)₂Hg was used by Nesmeyanov and coworkers for the preparation of (ClCH=CH)₂Pb(OCOMe)₂ in 1948. In 1956–1964, the reaction of Ar₂Hg with Pb(OCOR)₄ was used extensively for the synthesis of ArPb(OCOR)₃ in Kocheshkov’s laboratory.

Hein and Klein obtained hexaethylplumbane by the reaction of an alkaline solution of Et₃PbCl with aluminum powder. In 1959, Razuvaev, Vyazankin and coworkers showed that Et₃Pb was formed in this reaction along with Et₃PbPbEt₃. This reaction was a usual reduction process and organoaluminum compounds were not its intermediate products. The use of the reaction for the synthesis of organolead compounds began only in 1957. Its use was complicated by the fact that both aluminum alkyls and AlCl₃, which are obtained by the reaction of the organoaluminum compounds with PbCl₂, cleaved the C–Pb bond in the formed organolead compounds. Therefore, the reaction of R₃Al with PbCl₂ had to be carried out in the presence of alkali metals halides, which reacted with AlCl₃ or when PbCl₂ was replaced by Pb(OCOMe)₂ or PbF₂ (when the inert AlF₃ was formed). In 1957, Jenker used this method. In 1957–1958, the methods for the preparation of tetraalkylplumbanes by the reaction of PbCl₂ with LiAlEt₄ or with equivalent amounts of R₃Al and RI were patented.

D. Nonorganometallic Approaches to the Formation of a C–Pb Bond

The Nesmeyanov reaction based on a decomposition of double aryldiazonium salts by the powdered metals had little importance for the synthesis of organolead compounds because of the low yields of the products. In 1936 Kocheshkov, Nesmeyanov and Gipp prepared Ph₃PbCl by the decomposition of PhN₂Cl·PbCl₂ with zinc powder in ether medium. Ph₂PbCl₂ was prepared when copper powder and acetone were used in the reaction. In both cases the yields of phenylchloroplumbanes were small. In 1945 Nesmeyanov, Kocheshkov and Nad succeeded in obtaining Ph₄Pb in 16.5% yield by the decomposition of PhN₂BF₄ by powdered pure lead at 6 °C. When the alloy of lead with 10% Na was used instead, the yield of Ph₄Pb increased to 30%.

Tetra-p-xylplumbane (4-MeC₆H₄)₄Pb was synthesized analogously in 18% yield. Aliphatic diazo compounds were originally used for the synthesis of organotin compounds by Yakubovich in his laboratory in 1950 and 1952. He showed that Et₃PbCl and Et₂PbCl₂ reacted with diazomethane in the presence of powdered bronze to give Et₃PbCH₂Cl and Et₂Pb(CH₂Cl)Cl or Et₂Pb(CH₂Cl)₂, respectively.

In 1960, Becker and Cook found that the reaction of trialkylplumbanes R₃PbH (R = Me, Et) with diazoethane at −80 °C in ether led to R₃PbEt in a low yield.
The hydroplumbylation reaction (addition of organolead hydrides to multiple bonds) was first carried out by Becker and Cook. They showed that Me₃PbH added to ethylene in diglyme at 0°C under pressure of 17–35 atm to give Me₃PbEt in 92% yield. Further investigations were performed by Neumann and Kühllein and by Leusink and van der Kerk in 1965. The addition of R₃PbOH or R₃PbOCOR to ketene, which was studied only in 1965, was of specific interest.

In 1958, Panov and Kocheshkov found another route to the formation of the C–Pb bond, namely the interaction of tetraacyloxyplumbanes with aromatic and heteroaromatic compounds (the plumbylation reaction). They showed that the reaction of thiophene with Pb(OCOPr-i)₄ at room temperature during 10 days led to unstable RPb(OCOR)₃ (R = 2-thienyl; R′ = i-Pr), which was disproportionated to R₂Pb(OCOR)₂ and Pb(OCOR)₄.

Alkylhaloplumbanes Et₃PbX (X = Cl, Br, I) were synthesized by Löwig in 1852–1853. He found that the evaporation of an alcoholic solution of Et₃PbPbEt₃ (formed from EtI and a Pb–Na alloy) resulted in the formation of bis(triethylplumbyl)carbonate (Et₃Pb)₂CO₃ and Et₃PbOH. Treatment of the products with hydrohalic acids gave Et₃PbX, X = Cl, Br, I. Analogously, the treatment of the above products with HNO₃ and H₂SO₄ resulted in the formation of Et₃PbNO₃ and (Et₃Pb)₂SO₄, respectively.

In 1860, Klippel obtained a series of triethylacyloxyplumbanes Et₃PbOCOR with R = H, Me, Pr, Ph, as well as the corresponding oxalates, tartrates, cyanides and cyanates.

E. Cleavage of the C–Pb and Pb–Pb Bond

Among the C–Pb bond cleavage reactions, thermo- and photo-induced homolytic cleavage is of special theoretical and practical interest.

As early as 1887 Polis observed that Ph₄Pb decomposed at 300°C to free metallic lead. In 1927, Zechmeister and Csabay showed that the reaction occurred even at 270°C to give biphenyl. Thermal decomposition of Ph₄Pb was studied thoroughly by Razuvaev, Bogdanov and Koton in 1929–1934. It was also shown that the thermolysis of tetraphenylplumbane at 200°C under normal pressure or at 175°C in ethanol under autogenic pressure resulted in metallic lead and biphenyl. The process was catalyzed by metals, which decreased the initial decomposition temperature to 150°C. The catalysis by the metal decreased in the order: Pd > Au > Ag > Ni. Dull and Simons (1933) found that the thermolysis of Ph₄Pb gave benzene, biphenyl and terphenyl. The ratio of the products was temperature-dependent. In 1933, Dull and Simons found that the thermolysis of Ph₄Pb in the presence of evaporated mercury involved the formation of Ph₂ and Ph₂Hg, indicating the intermediate formation of phenyl radicals. Krause and Schmitz in 1919 found that the thermal decomposition of Ph₃PbEt gave lead at 235°C i.e. at a lower temperature than that for Ph₄Pb. The data indicated that replacement of the aryl with an alkyl substituent decreased the thermolysis temperature of tetraorganylplumbanes.

From 1929, the Paneth discovery, was published, that the thermal decomposition of lower tetraalkylplumbanes R₄Pb (R = Me, Et) at ca 400°C led to metallic lead and free CH₃⁺ or C₂H₅⁺ radicals, respectively. These free radicals transformed the smooth surface of the metals Pb, Zn, Cd, As and Sb into the corresponding metal alkyls. This prominent discovery corroborated the existence of the free radicals and made a name for Paneth. Later, Calingaert (1925), Taylor and Jones (1930), Simons, McNamee, and Hurd (1932), Meinert (1933), Cramer (1934) and Garzuly (1935) studied the thermal decomposition of tetraalkylplumbanes. Taylor and Jones found that the thermal decomposition of Et₄Pb at 250–300°C led to metallic lead and a mixture of gaseous and liquid hydrocarbons (C₂H₄, C₂H₆, C₄H₈, C₆H₁₂), formed by the ethyl radicals generated in this process. According to Calingaert,
the thermolysis of tetraethylplumbane over pumice gave a mixture of butane (40%),
ethane and ethylene. Simons, McNamee and Hurd\textsuperscript{1230} identified the gaseous hydrocarbons \( \text{HC} = \text{CH}, \text{CH}_2 = \text{CH}_2, \text{MeCH} = \text{CH}_2, \text{Me}_2\text{C} = \text{CH}_2, \text{CH}_4, \text{C}_2\text{H}_6 \), and small amounts of liquid hydrocarbons as well as \( \text{H}_2 \) among the products of \( \text{Me}_4\text{Pb} \) thermolysis. Razuvaev, Vyzazkin and Vyshinskii\textsuperscript{1234} (1959) showed that the thermal decomposition of \( \text{Et}_4\text{Pb} \) was a multiple chain process involving the consequent cleavage of \( \text{Et}_3\text{Pb}^* \) and the intermediate formation of \( \text{Et}_3\text{PbPbEt}_3 \) and \( \text{Et}_2\text{Pb} \) which terminated with lead precipitation. A year later these authors studied the kinetics of the thermolysis of \( \text{Et}_4\text{Pb} \) and its mixtures with \( \text{Et}_3\text{PbPbEt}_3 \text{.} \) The catalytic effect of the formed metallic lead on this process was also established. The investigations of Razuvaev and coworkers demonstrated for the first time that during the homolytic cleavage of the C–Pb bonds in \( \text{R}_4\text{Pb} \) an intermediate formation of a Pb–Pb bond took place. The easy decomposition of the intermediates \( \text{R}_3\text{PbPbR}_3 \) and \( \text{R}_2\text{Pb} \) resulted finally in metallic lead. As a consequence of the homolytic C–Pb and Pb–Pb bond cleavages we deal with their reaction in this section in spite of the fact that Section IV. J is devoted to organolead compounds containing Pb–Pb bonds. The dissociation of tetraalkylplumbanes into free radicals was carried out photochemically under UV irradiation. In 1936, Leighton and Mortensen\textsuperscript{1235} showed that the photolysis of gaseous \( \text{Me}_4\text{Pb} \) resulted in lead and ethane. Photolytic decomposition of \( \text{Ph}_4\text{Pb} \) in aromatic hydrocarbons was investigated in McDonald’s\textsuperscript{1236} (1959) and Razuvaev’s\textsuperscript{1237} (1963) laboratories. The formation of metallic lead and biphenyl in benzene solution\textsuperscript{1237} as well as the formation of 2- or 3-isopropylbiphenyl in cumene medium\textsuperscript{1236} was observed. The use of a \(^{14}\text{C}\)-labelled benzene and cumene solvents showed that, on photolysis of \( \text{Ph}_4\text{Pb} \), the formed phenyl radicals reacted with the solvent. Hexaphenyldiplumbane \( \text{Ph}_3\text{PbPbPh}_3 \) was apparently the intermediate decomposition product. It confirmed that Pb-centered free radicals \( \text{R}_3\text{Pb}^* \) were the first products of the \( \text{R}_4\text{Pb} \) thermolysis.

In 1918, Grüttner\textsuperscript{1118} was the first who called attention to the thermal decomposition of organylhaloplumbanes and found that \( \text{Ph}_3\text{PbBr} \) was decomposed to give \( \text{PbBr}_2 \) even at its melting point (166°C). In 1925, Calingaert\textsuperscript{1145} started to investigate in detail the thermolysis of organylhaloplumbanes. He found that during thermal decomposition of \( \text{Et}_3\text{PbX} \ (X = \text{Cl, Br}) \), \( \text{Et}_4\text{Pb} \) and \( \text{Et}_2\text{PbX}_2 \) were formed. This observation initiated a study of the thermal disproportionation (dismutation) reactions of organylhaloplumbanes. Twenty-three years later Calingaert and coworkers\textsuperscript{1148} found that \( \text{Et}_3\text{PbBr} \) was spontaneously decomposed at room temperature with formation of \( \text{Et}_2\text{PbBr}_2 \) within 50 hours. In 1932, Austin\textsuperscript{1136} showed that \( \text{Ph}_3\text{PbCl} \) was transformed to \( \text{Ph}_4\text{Pb} \) and \( \text{Ph}_2\text{PbCl}_2 \) in boiling butanol. The products of the disproportionation reaction of \( \text{Et}_3\text{PbCl} \) were \( \text{Et}_4\text{Pb} \) and \( \text{PbCl}_2 \). In 1938, Evans\textsuperscript{1238} pointed out that \( \text{Bu}_4\text{PbCl} \), \( \text{PbCl}_2 \) and \( \text{BuCl} \) were the products of the thermal decomposition of \( \text{Bu}_2\text{PbCl}_2 \). In 1939, Gilman and Apperson\textsuperscript{1239} found that the thermolysis of \( \text{Et}_2\text{PbCl}_2 \) behaved analogously. In 1948, Calingaert and coworkers\textsuperscript{1148} studied the hydrothermal decomposition of \( \text{Et}_3\text{PbX} \) and \( \text{Et}_2\text{PbX}_2 \) (\( X = \text{Cl, Br} \)) during steam distillation: \( \text{Et}_3\text{PbX} \) was transformed to \( \text{Et}_2\text{PbX}_2 \) and \( \text{Et}_4\text{Pb} \) and \( \text{Et}_2\text{PbX}_2 \) to \( \text{Et}_3\text{PbX}, \text{PbX}_2 \) and \( \text{C}_4\text{H}_{10} \), respectively. The authors assumed that the extremely unstable \( \text{EtPbX}_3 \) was the intermediate product of this reaction. As a summary: the decomposition products of \( \text{Et}_3\text{PbX} \) and \( \text{Et}_2\text{PbX}_2 \) were identical, but their ratios were different. Hydrothermal decomposition of \( \text{Et}_2\text{PbBr}_2 \) occurred instantly, and for \( \text{Et}_2\text{PbCl}_2 \) it happened over a period of two minutes. In contrast, \( \text{Et}_3\text{PbX} \) rather slowly decomposed by steam, but \( \text{Et}_3\text{PbBr} \) decomposed faster than \( \text{Et}_3\text{PbCl} \). The thermolysis of \( \text{Et}_3\text{PbOH} \) and \( \text{Et}_3\text{Pb(OH)}_2 \),\textsuperscript{1148,1239,1240} and organylacyloxyplobumane \( \text{R}_4\text{–}_n\text{Pb(OCOR)}_n \)\textsuperscript{1241} was also studied in 1939–1962 (see Section IV. F).

The hydrogenolysis of the C–Pb bond in \( \text{R}_4\text{Pb} \ (R = \text{Me, Et, Ph}) \) was first studied in the Ipatiev\textsuperscript{741–743,1220–1224} laboratory. Since 1929, his coworkers Razuvaev and
Bogdanov\textsuperscript{1220–1222} as well as Koton\textsuperscript{1222,1224} illustrated that Ph\textsubscript{4}Pb was decomposed under a pressure of 60 atm hydrogen at 175–225 °C to metallic lead and benzene. Tetraalkylplumbanes R\textsubscript{4}Pb (R = Me, Et) under such conditions precipitated a metallic lead even at 125°C and 100°C, respectively\textsuperscript{1220,1221}. In 1930–1932, Adkins and coworkers\textsuperscript{1242–1245} followed the Russian scientists in studying the hydrogenation of tetraorganylplumbanes. They found that R\textsubscript{4}Pb (R = Alk) was cleaved by hydrogen with formation of the corresponding alkanes RH and Pb\textsuperscript{1242}. Hydrogenolysis of tetraarylplumbanes Ar\textsubscript{4}Pb (Ar = Ph, 4-MeC\textsubscript{6}H\textsubscript{4}) led to a quantitative formation of the corresponding diaryl and metallic lead at 200°C under H\textsubscript{2} pressure of 125 atm. Tetraheptylplumbane under these conditions was transformed to tetradecane in only 62% yield. In 1931, Adkins and Covert\textsuperscript{1243} found that Ni catalyzed the cleavage of tetraalkyl- and tetraarylplumbanes. In 1932, Zartmann and Adkins\textsuperscript{1245} found that catalytically active Ni significantly decreased the thermolysis temperature of R\textsubscript{4}Pb (R = Alk, Ar) to 200 °C under H\textsubscript{2} pressure. The hydrocarbons R–R were formed in a high yield as the recombination products of the R radicals. In the absence of Ni the precursor Ph\textsubscript{4}Pb did not change under the experimental conditions, and under nitrogen pressure at 200 °C it did not change with or without Ni. These data contradicted the results gained by Ipatiev and his coworkers\textsuperscript{1220,1223}. In 1933, Razuvaev and Koton\textsuperscript{743,1222} studied a catalytic effect of Cu, Ag, Au, Ni and Pd on the destruction of Ph\textsubscript{4}Pb by hydrogen under pressure. In the presence of these metals (except Pd) its decomposition proceeded at low temperatures and led to Pb and C\textsubscript{6}H\textsubscript{6}. Palladium catalyzed only the thermal decomposition of Ph\textsubscript{4}Pb (but not the hydrogenolysis process) to form biphenyl, but not benzene. It cannot be believed that Ipatiev remembered in the twilight of his life the investigations on hydrogenolysis of metalloorganic compounds carried out during his Soviet period. In the article of Gershbein and Ipatiev\textsuperscript{744} published already after Ipatiev’s death, the hydrogenolysis results of Ph\textsubscript{4}M (M = Pb, Sn) obtained at the Ipatiev laboratory in the USSR were confirmed without using new experiments. It was reported that, at 200 °C and under an initial H\textsubscript{2} pressure of 60 atm, Ph\textsubscript{4}Pb was decomposed to Pb, C\textsubscript{6}H\textsubscript{6} and a trace amount of Ph\textsubscript{2} (i.e. nothing new). The composition of the products remained unchanged when copper powder was added to the reaction (as was known earlier). The appearance of this article was unfortunate.

The heterolytic cleavage of the C–Pb bond was especially easy in a series of organometallic compounds of the silicon subgroup. In 1887, Polis\textsuperscript{1246} was the first to find C–Pb bond cleavage in tetraalkylplumbanes with halogens. He demonstrated that by bubbling chlorine through a CS\textsubscript{2} solution of Ph\textsubscript{4}Pb, the Ph\textsubscript{2}PbCl\textsubscript{2} was the product formed. Similarly, Ph\textsubscript{4}Pb with bromine in CS\textsubscript{2} or in CHCl\textsubscript{3} media was transformed to Ph\textsubscript{2}PbBr\textsubscript{2}. A year later Polis\textsuperscript{1247} synthesized (4-MeC\textsubscript{6}H\textsubscript{4})\textsubscript{2}PbX\textsubscript{2} (X = Cl, Br, I) by the action of chlorine, bromine and iodine on (4-MeC\textsubscript{6}H\textsubscript{4})\textsubscript{4}Pb. In 1904, Pfeiffer and Trüskier\textsuperscript{1165} prepared Et\textsubscript{3}PbCl by chlorination of Et\textsubscript{4}Pb with strong cooling. Following him in 1916, Grütter and Krause\textsuperscript{1110} showed that halogens cleaved only one of the R–Pb bonds in tetraalkylplumbanes with formation of R\textsubscript{3}PbX only at low temperatures (−70 °C). The reaction of gaseous chlorine with R\textsubscript{4}Pb (R = Me, Et) at −70 °C in ethyl acetate solution led to R\textsubscript{3}PbCl in a quantitative yield. The chlorination of Me\textsubscript{3}PbCl at −10 °C also resulted in a quantitative formation of Me\textsubscript{2}PbCl\textsubscript{2}. Later, R\textsubscript{3}PbX or R\textsubscript{2}PbX\textsubscript{2} were synthesized similarly by the reaction of chlorine or bromine with R\textsubscript{4}Pb (R = Me, Et, Pr, i-Bu, i-Am, c-C\textsubscript{6}H\textsubscript{11}) at an appropriate temperature\textsuperscript{1108,1110,1114,1188}. In 1921, Grütter and Krause\textsuperscript{1108} succeeded in synthesizing (c-C\textsubscript{6}H\textsubscript{11})\textsubscript{3}PbI and (c-C\textsubscript{6}H\textsubscript{11})\textsubscript{2}Pbl\textsubscript{2} by cleavage of (c-C\textsubscript{6}H\textsubscript{11})\textsubscript{4}Pb with iodine. Only in 1938, by the reaction of iodine with Me\textsubscript{4}Pb in ether at 60 °C, did Calingaert and Soroos\textsuperscript{1188} prepare Me\textsubscript{3}PbI in 60% yield. The realization of the reaction of iodine with Et\textsubscript{4}Pb at −65 °C allowed Juenge and Cook\textsuperscript{1177} (1959) to synthesize Et\textsubscript{3}PbI (in 73% yield). The reaction of halogens with Ar\textsubscript{4}Pb even at...
–75 °C resulted in cleavage of two aryl groups with the formation of \( \text{Ar}_2\text{PbX}_2 \). Gerchard and Gertruda Grüttnern succeeded in obtaining \( \text{Ar}_3\text{PbBr} \) by the reaction of bromine in pyridine solution with \( \text{Ar}_4\text{Pb} \) at \(-15^\circ\text{C}\), i.e. with the \( \text{Py} \cdot \text{Br}_2 \) complex. In 1939, Gilman and Bailie used this method to synthesize \( (3\text{-MeC}_6\text{H}_4)_3\text{PbBr} \). They also obtained 88% of \( \text{Ph}_3\text{PbI} \) by the reaction of iodine with \( \text{Ph}_4\text{Pb} \) in \( \text{CHCl}_3 \) at room temperature. Investigations of Grüttnern and Krause (1917) and later Calingaert and Soroos (1938) demonstrated that, during the action of halogens on mixed tetraalkylplumbanes, the smaller alkyl group could be eliminated more easily. A phenyl group, \( \text{Ph}_3\text{PbI} \), still cleaved easily from a \( \text{Pb} \) atom and a cyclohexyl group was eliminated with more difficulty. When \( \text{Me}_3\text{PbEt} \) was brominated at \(-70^\circ\text{C}\), \( \text{Me}_2\text{EtPbBr} \) was formed, and at \(-10^\circ\text{C}\), \( \text{MeEtPbBr}_2 \) was the product. By the reaction of bromine with \( i\text{-Am(Pr)PbMe}_2 \), \( i\text{-Am(Pr)MePbBr} \) (the latter compound with an asymmetric lead atom) and \( \text{AmPrPbBr}_2 \) were subsequently obtained.

A series of organolead dihalides \( \text{RR}^'\text{PbX}_2 \) (\( \text{R} = \text{Et}, \text{Pr}, \text{Bu}; \text{R}^' = \text{Bu}, \text{i-Bu}, \text{i-Am}; \text{X} = \text{Cl}, \text{Br} \)) was prepared by the detachment of the low alkyl radicals from mixed tetraalkylplumbanes with bromine or chlorine. Juenge and Cook prepared \( (\text{CH}_2=\text{CH})_2\text{PbCl}_2 \) by chlorination of \( (\text{CH}_2=\text{CH})_4\text{Pb} \) in acetic acid solution at room temperature in 1959. It was remarkable that chlorine cleaved the \( \text{C} \cdot \text{Pb} \) bond more easily than it was added to the double bond. In 1921, Krause demonstrated that \( (c\text{-C}_6\text{H}_{11})_4\text{PbX}_n \) (\( \text{X} = \text{Br}, \text{I}; \text{n} = 1, 2 \)) was obtained preferably by the \( (c\text{-C}_6\text{H}_{11})_3\text{PbPb}(c\text{-C}_6\text{H}_{11})_3 \) cleavage with bromine or iodine. In 1917, Grüttnern and Krause found that cleavage of \( (\text{i-Bu})_3\text{PbCl} \) by bromine gave \( (\text{i-Bu})_2\text{PbClBr} \) and \( \text{i-BuBr} \). When Flood and Horvitz (1933) studied the cleavage of \( \text{R}_3\text{MX} \) (\( \text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}; \text{X} = \text{Hal} \)) with halogens, they found that \( \text{Ph}_3\text{PbX} \) (\( \text{X} = \text{Cl}, \text{I} \)) reacted with iodine in \( \text{CCl}_4 \) to form \( \text{PhI}, \text{Ph}_2\text{PbCl} \) and \( \text{Ph}_2\text{PbI}_2 \), respectively.

The ability of the \( \text{C} \cdot \text{Pb} \) bond to be cleaved with proton acids was shown in the 19th century. In 1859, Buckton was the first to introduce the cleavage reaction of alkyl radical from the \( \text{Pb} \) atom by the action of gaseous \( \text{HCl} \) on \( \text{Et}_4\text{Pb} \) with the formation of \( \text{Et}_3\text{PbCl} \). Others followed the procedure. Cahours (1862) and Pfeiffer and Truskier repeated the reaction. Pfeiffer and coworkers obtained organylhaloplumbanes by bubbling dry \( \text{HCl} \) or \( \text{HBr} \) through an ethereal \( \text{R}_4\text{Pb} \) solution. Browne and Reid (1927), Gilman and Robinson (1930) and Catlin (1935) found that the reaction of saturated \( \text{HCl} \) solution with \( \text{Et}_4\text{Pb} \) led to \( \text{Et}_3\text{PbCl} \). Gilman and Robinson showed that the reaction of \( \text{HCl} \) with \( \text{Et}_4\text{Pb} \) could lead to \( \text{Et}_3\text{PbCl} \) and \( \text{Et}_2\text{PbCl}_2 \), depending on the reaction conditions. In 1939, Gilman and Bailie obtained \( \text{Et}_3\text{PbBr} \) when gaseous \( \text{HBr} \) reacted with \( \text{Et}_4\text{Pb} \). Austin (1931), Gilman and coworkers (1939, 1950), Bähr (1947) and Juenge and Koch (1959) also described the \( \text{Ar}_3\text{Pb} \) cleavage by \( \text{HCl} \). Möller and Pfeiffer (1916), Hurd and Austin (1931, 1933), Gilman and coworkers (1933), Calingaert, Soroos and Shapiro (1940), Stuckwisch (1943), Calingaert and coworkers (1945), Heap and coworkers (1951) and Koton and coworkers (1960) studied the relative order of elimination of organic substituents from the lead atom in mixed tetraorganylplumbanes. In 1931, Austin showed that the reaction of gaseous \( \text{HCl} \) with \( \text{PhPbEt}_3 \) led to \( \text{Et}_3\text{PbCl} \) and \( \text{C}_6\text{H}_6 \). Two years later, he found that the more electronegative group (according to the ‘Kharasch row’) was the first to cleave when \( \text{HCl} \) acted on mixed tetraarylplumbanes. Thus, for example, \( \text{Ph}_3\text{PbCl} \) was formed from \( 4\text{-MeC}_6\text{H}_4\text{PbPh}_3 \), \( \text{PrPb}_2\text{PbCl} \) from \( \text{PrPbPh}_3 \) and \( \text{PrPh}(2\text{-MeC}_6\text{H}_4)_2\text{PbCl} \) from \( \text{Pr}(2\text{-MeC}_6\text{H}_4)_2\text{PbPh} \). According to Gilman and coworkers (1932, 1936) and other investigators mentioned above, the ease of eliminating the substituents from lead
atom decreased in the following order: 2-Thi > 2-Fu > 1-C10H7 > All > CH=CHPh. Alkyl groups, as well as CH2Ph, CH2CH2CH=CH2 and 4-MeOC6H4 were bonded more strongly to the lead atom than Ph. Delhaye and coworkers found a second order kinetics for the cleavage of Me3PbPh with HCl in methanol. In 1935, Yakubovich and Petrov obtained both Et3PbCl and Et2PbCl2 by the reaction of gaseous HCl with Et4Pb. In the second quarter of the 20th century (1945) numerous methods for the preparation of organolead compounds were used in the Calingaert laboratory. It was found that R3PbBr and R2PbCl2 prepared by the reaction of R4Pb (R = Alk) with HBr and HCl in ether were contaminated with PbBr2 and PbCl2. However, pure R3PbCl was obtained in a high yield by bubbling HCl through a 5–10% solution of R4Pb in hexane. This method surpassed the methods described previously for the preparation of R3PbCl, which used concentrated hydrochloric acid. In 1945, Calingaert and coworkers prepared Me3PbCl when cleaving Me4Pb with hydrogen chloride. Later, R3PbCl with R = Pr, i-Bu, CH2=C6H5 and 4-MeOC6H4 were prepared analogously. In 1951, Saunders and coworkers prepared Et4PbCl2 in 80% yield when bubbling dry HCl through an Et4Pb solution in toluene at 90°C. Under long-time boiling, all ethyl groups were cleaved off to give PbCl2. Earlier, in 1949, they considered the reaction of R4Pb with saturated HCl in ether solution to be the best method for the synthesis of trialkylchloroplumbanes.

In 1887–1888, Polis showed that the C–Pb bonds in Ar4Pb (Ar = Ph, 4-MeC6H4) were cleaved by inorganic and organic acids (HNO3, HCOOH, MeCOOH) with the formation of appropriate salts Ar2PbX2 (X = NO3, OOCMe). In the following century the reaction of tetraarylplumbane with organic acids was carried out (see Section IV.F) by Goddard and coworkers (1922), Gilman and Robinson (1930) and Koton (1939, 1941). In 1916, Möller and Pfeiffer found that aryI groups were cleaved off more easily than alkyls from lead atom of Ph2PbEt2 with inorganic acids. In 1925, Krause and Schlöttig reached the same conclusion when they cleaved Ph2PbR2 (R = Me, Et, c-C6H11), while Calingaert (1925) and Hurd and Austin (1931) concluded likewise when conducting the cleavage of PhPbEt3. In 1931–1932, Austin demonstrated that the (2-MeC6H4)–Pb and (4-MeC6H4)–Pb bonds cleaved more easily than the Ph–Pb bond. According to Austin (1931) and McCleary and Degering (1938), two ethyl groups are usually cleaved off from Et4Pb in the reaction with nitric acid with the formation of Et2Pb(NO3)2. The reaction of Et4Pb with H2SO4 proceeds in the same way. Jones and coworkers carried out the reaction of HNO3, H2SO4 and HCl with R4Pb (R = Pr, Bu, Am) which led to R2PbX2.

In 1930, Gilman and Robinson showed that HSO3Ph cleaved Et4Pb to form Et3PbSO3Ph. Gilman and Robinson (1929) obtained selectively Ph3PbCl or Ph2PbCl2 by the reaction of gaseous HCl with Ph4Pb.

Remarkably, according to Krause and Schlöttig (1925) even NH4Cl cleaved at 170–180°C the C–Pb bond of Et4Pb with formation of Et3PbCl. Analogously, in 1948, Koton prepared Ph3PbCl by heating a mixture of Ph4Pb and Me3N·HCl at 130°C. In the early part of the last century it was established that tetraorganylplumbanes R4Pb (R = Alk, Ar) were cleaved by some metal and nonmetal halides with the formation of R3PbX and R2PbX2. So triethylchloroplumbane, as well as the products of ethylation of the corresponding element chlorides were formed during the reaction of Et4Pb with H2Cl2, AlCl3, SiCl4, TiCl4, PCl5, BiCl3, FeCl3 and also RCOCl (R = Me, Ph) in particular, Gilman and Apperson found in 1939 that the first reaction product of Et4Pb with AlCl3 was Et2PbCl2. The further process could be described by equations 21a and 21b.

\[
2\text{Et}_2\text{PbCl}_2 \rightarrow \text{Et}_3\text{PbCl} + \text{PbCl}_2 + \text{EtCl} \quad (21a)
\]
1. Genesis and evolution in the organic chemistry of Ge, Sn, and Pb compounds

Et₂PbCl₂ \rightarrow PbCl₂ + C₄H₁₀ \quad (21b)

In 1934 Kocheshkov and Nesmeyanov \cite{813,1279} and in 1949 Hein and Schneiter \cite{1280}
carried out the dearylation reaction of Ph₄Pb by mercury dihalides, which led to Ph₃PbX
and Ph₂PbX₂ (X = Cl, Br). According to Panov and Kocheshkov \cite{1281–1283} (1952, 1955)
Hg(OOCR)₂ smoothly cleaved off phenyl groups from Ph₄Pb in the corresponding
carboxylic acid medium to consequently form Ph₄₋ₙPb(OCOR)ₙ with \( n = 1–4 \). In the
case of tetraalkyplumbane R₄’Pb (R’ = Alk) such reaction resulted in R₄’Pb(OCOR)₂
formation. In 1949–1959 the possible dearylation process of Ph₄Pb with TlCl \cite{3728},
PCl₃ \cite{1284–1286}, AsCl₃ \cite{1284,1285}, SbCl₃ and SbCl₅ \cite{1285} was shown to result in the formation
of Ph₂PbCl₂ and Ph₂TlCl, Ph₂PCl, Ph₂AsCl, Ph₂SbCl and Ph₂SbCl₃, respectively. The
results mentioned above showed that tetraorganylplumbanes could be used as specific
alkylating and arylating agents. In 1919, Krause and Schmitz \cite{814} showed the possibility
of C–Pb bond cleavage by silver nitrate in the case of Ph₄Pb. The reaction products
were Ph₂Pb(NO₃)₂ and metastable PhAg, which easily decomposed to Ph₂ and Ag. The
R₄Pb (R = Alk, Ar) cleavage by silver nitrate was further used by many investigators \cite{54},
as shown by the 13 publications devoted to the reaction.

The coproportionation reaction (‘komproportionierung’), which was so well developed
in organotin chemistry, did not attract attention in organolead chemistry for a
long time. This was because PbCl₄, which should be used in this reaction, was
both unstable and has a chlorination action. In 1932, Austin \cite{1136} showed that the
interaction of Ph₄Pb and Pb₂PbCl₂ led to Ph₃PbX. In 1968, Willemens and van
der Kerk \cite{1287} replaced PbCl₄ with the more stable Pb(OOCMe)₄ in the presence
of catalytic amounts of mercury diacetate (Section IV.F). The processes of radical
rearrangement in a mixture of two tetraorganylplumbanes (which could be attributed
tocoproportionation) in the presence of Lewis acids (such as BF₃, AlCl₃, SnCl₄,
EtPbX) as catalysts were studied in detail by Calingaert and coworkers \cite{1276,1288–1291}.

When carried out at relatively low temperatures \cite{1276,1288–1291} these processes led to
a mixture of tetraorganylplumbanes including all possible combinations of substituents
present in the starting reagents. However, isomerization of alkyl groups was not
observed. For example, during the coproportionation of an equimolecular mixture of
Me₄Pb and Et₄Pb (mol%): Me₃PbEt (25%), Et₃PbMe (25%) and Me₂PbEt₂ (37.5%)
were formed together with only about 6.25% of the unreacted precursors Me₄Pb and
Et₄Pb. Calingaert and coworkers \cite{1258,1260} (1940–1945) called attention to the dealkylation
reaction of nonsymmetric tetraalkylplumbanes with HCl, which was often accompanied
by disproportionation of the formed trialkylchloroplumbanes that led to several reaction
products.

Further disproportionation reaction is important in organolead chemistry. As reported in
Section III. C, tetraorganylplumbanes were obtained by reacting PbCl₂ with organometal-
lic compounds via the intermediates :PbR₂. The processes were accompanied by cleavage
and formation of C–Pb and Pb–Pb bonds as described by equations 22 and 23.

\[ 3R₂Pb \rightarrow R₃PbPbR₃ + Pb \quad (22) \]
\[ R₃PbPbR₃ \rightarrow R₄Pb + Pb \quad (23) \]

The results of these reactions depended essentially on the nature of the substituent
(mainly on steric factors). The first reaction of aliphatic organometallic compounds with
PbCl₂ was so fast that it was impossible to stop it at the stage of R₂Pb formation.
However, Ar₂Pb, Ar = Ph, 4-MeC₆H₄ was proved to be rather stable and it was possible
to synthesize it by the organomagnesium method at a low temperature. Even at 20 °C
the reaction resulted in Ar₃PbPbAr₃, and at the temperature of boiling ether it led
to Ar₄Pb. It might be emphasized that these reactions depended considerably on the
nasc of the substituent at the lead atom. The studies of Krause and Reissaus\textsuperscript{1122,1292} (1921, 1922), Austin\textsuperscript{1262} (1931), Calingaert and Soroos\textsuperscript{1188} (1938) and Gilman and Bailie\textsuperscript{1170} (1939) clearly demonstrated that the steric factor in the disproportionation reaction of R\textsubscript{3}PbPbR\textsubscript{3} played a very essential role. When R = Ph and 4-MeC\textsubscript{6}H\textsubscript{4} the reaction led easily to R\textsubscript{4}Pb\textsuperscript{1122,1170,1292}. If R = 2-MeC\textsubscript{6}H\textsubscript{4} the disproportionation became difficult \textsuperscript{1122,1170,1262,1292} and when R = 2,4,6-Me\textsubscript{3}C\textsubscript{6}H\textsubscript{2}, 2,4-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{4} and c-C\textsubscript{6}H\textsubscript{11} the process did not proceed. According to Calingaert and Soroos\textsuperscript{1188} and Gilman and Bailie\textsuperscript{1170} the tendency to disproportionate increased in the following order: 2,4,6-Me\textsubscript{3}C\textsubscript{6}H\textsubscript{2} < c-C\textsubscript{6}H\textsubscript{11} < 1-C\textsubscript{10}H\textsubscript{7} < 2-ROC\textsubscript{6}H\textsubscript{4} < 2-MeC\textsubscript{6}H\textsubscript{4} < 4-ROC\textsubscript{6}H\textsubscript{4} < 4-MeC\textsubscript{6}H\textsubscript{4} < 3-MeC\textsubscript{6}H\textsubscript{4} < Ph < Et < Me. Calingaert\textsuperscript{1145} (1925) was the first to observe the disproportionation of alkylchloroplumbanes. Later, together with coworkers he found that a mixture of Me\textsubscript{4}nPbEt\textsubscript{n} (n = 0–4) as well as of MeEt\textsubscript{2}PbCl and Et\textsubscript{3}PbCl\textsuperscript{1258} was formed by boiling EtMe\textsubscript{2}PbCl. In 1932, Austin\textsuperscript{1136} reported the transformation of Ph\textsubscript{3}PbCl into Ph\textsubscript{4}Pb and Ph\textsubscript{2}PbCl\textsubscript{2}. In 1960, Razuvaev and coworkers\textsuperscript{1293} found out that thermal decomposition of Et\textsubscript{3}PbBr at 70°C led to Et\textsubscript{4}Pb and Et\textsubscript{2}PbBr\textsubscript{2}. Reducing agents\textsuperscript{1161,1294} promoted the disproportionation of organylhaloplumbanes, and Gilman and Barnett\textsuperscript{1294} showed that Ph\textsubscript{3}PbCl was transformed into Ph\textsubscript{4}Pb in 70% yield in the presence of hydrazine\textsuperscript{1294}. In analogous conditions Ph\textsubscript{4}Pb was also obtained from Ph\textsubscript{2}PbCl\textsubscript{2}. In 1942, Nad' and Kocheshkov\textsuperscript{1161} observed the transformation of Ar\textsubscript{2}PbCl\textsubscript{2} (Ar = Ph, 2-MeC\textsubscript{6}H\textsubscript{4}) into Ar\textsubscript{3}PbCl in the presence of metallic lead powder or its alloys with Na. In 1959–1961 investigations, carried out in the Razuvaev\textsuperscript{1202,1293,1295–1297} laboratory, showed that the disproportionation reactions of organolead compounds should be divided into thermal and catalytic reactions. It was established that Et\textsubscript{3}PbPbEt\textsubscript{3}, which was usually stable in the absence of air at room temperature, was easily disproportionated with the formation of Et\textsubscript{4}Pb and Pb\textsuperscript{1293,1295,1296} in the presence of a catalytic amount of H\textsubscript{2}X\textsubscript{2}, EtH\textsubscript{2}X (X = Cl, Br), AlX\textsubscript{3} (X = Cl, Br), Et\textsubscript{3}SnCl, Et\textsubscript{3}PbBr\textsuperscript{1296} or Et\textsubscript{2}PbBr\textsubscript{2} and BrCH\textsubscript{2}CH\textsubscript{2}Br\textsuperscript{1293}. All these catalytic reactions were not accompanied by evolution of gaseous products. According to the patent literature, silica or activated carbon\textsuperscript{1298,1299} could be used for the catalytic disproportionation. Free Et* radicals stimulated the formation of gaseous products and were generated along with the formation of Et\textsubscript{4}Pb and Pb in the thermal disproportionation of Et\textsubscript{3}PbPbEt\textsubscript{3}. The intermediate product of this process was PbEt\textsubscript{2}\textsuperscript{1202,1203,1297,1300}.

Thermal disproportionation of Et\textsubscript{3}PbOH at 150°C and its kinetics were studied by Alexandrov and coworkers in 1959\textsuperscript{1240}. The thermolysis reaction products were Et\textsubscript{4}Pb, Et\textsubscript{2}Pb(OH)\textsubscript{2} as well as H\textsubscript{2}O, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6} and C\textsubscript{4}H\textsubscript{10}. In 1961, Alexandrov and Makeeva\textsuperscript{1301} showed that Et\textsubscript{2}Pb(OOCMe)\textsubscript{2} disproportionated into Et\textsubscript{3}PbOOCMe and EtPb(OOCMe)\textsubscript{3}, but the latter immediately decomposed to Pb(OOCMe)\textsubscript{2} and MeCOOEt. Analogously, Et\textsubscript{2}Pb(OOCCH\textsubscript{2}Cl)\textsubscript{2} disproportionated\textsuperscript{971,1241}.

\section*{F. Compounds having a Pb-O Bond}

The majority of organolead compounds having the Pb-O bond have the following formulas: R\textsubscript{4–n}Pb(OH)\textsubscript{n} (n = 1–3), R\textsubscript{3}PbOPbR\textsubscript{3}, (R\textsubscript{2}PbO)\textsubscript{n}, (RPbOOH)\textsubscript{n}, R\textsubscript{4–n}Pb(OR\textsuperscript{'})\textsubscript{n} (n = 1, 2) and R\textsubscript{4–n}Pb(OOCR\textsuperscript{'})\textsubscript{n} (n = 1–3). They were studied less intensively than their organogermanium and organotin analogs. Nevertheless, the number of known organolead compounds with a Pb-O bond reached 200 by 1953. In 1853, Löwig\textsuperscript{42} obtained the first representative of trialkylplumbanols Et\textsubscript{3}PbOH by the reaction of Et\textsubscript{3}PbI or (Et\textsubscript{3}Pb)\textsubscript{2}CO\textsubscript{3} with moist silver oxide or with aqueous alkali in ether medium. He showed that the compound was a typical base, which was neutralized by inorganic acids HX (X = Cl, Br, I, NO\textsubscript{3}, 0.5SO\textsubscript{4}) with the formation of the corresponding salts Et\textsubscript{3}PbX. In 1860,
Klippel\textsuperscript{1217,1218}, following Löwig\textsuperscript{42} synthesized Et\textsubscript{3}PbOH (which he considered to be a monohydrate of hexaethylplumbane) by the reaction of Et\textsubscript{3}PbI with moist Ag\textsubscript{2}O, followed by water treatment. He found also that Et\textsubscript{3}PbOH was formed in the reaction of Et\textsubscript{3}PbNO\textsubscript{3} with alcoholic KOH solution. However, Klippel\textsuperscript{1217,1218} found this method less convenient. He synthesized a series of triethylacyloxyplumbanes Et\textsubscript{3}PbOOOCR (R = H, Me, Pr, Ph) as well as triethylplumbyl derivatives of oxalic, tartaric, hydrocyanic and cyanic acids by the neutralization of Et\textsubscript{3}PbOH with the corresponding acids. In the 19th century Buckton\textsuperscript{604} (1859) and Cahours\textsuperscript{596} (1862) also synthesized trialkylplumbanols. In the 20th century Pfeiffer and Trüskier\textsuperscript{1249} (1916), Krause and Pohland\textsuperscript{123} (1922), Calingaert and coworkers\textsuperscript{1140} (1923), Browne and Reid\textsuperscript{1250} (1927), Bähr\textsuperscript{1255} (1947) and Saunders and Stacey\textsuperscript{1150} (1949) used the methods mentioned above for the synthesis of R\textsubscript{3}PbOH. Calingaert and coworkers\textsuperscript{1260} (1945) found that the reaction of Et\textsubscript{3}PbX (X = Cl, Br, I) with aqueous alkali in ether did not lead to pure Et\textsubscript{3}PbOH due to contamination by the starting Et\textsubscript{3}PbX. They showed that pure Et\textsubscript{3}PbOH could be obtained by modification of two methods described earlier. The ether was replaced by benzene during the alkaline hydrolysis of Et\textsubscript{3}PbX, and an aqueous solution of Et\textsubscript{3}PbCl was used during the Ag\textsubscript{2}O hydrolysis. The yield of triethylplumbanol then reached 93%. It was also established that the reaction of an aqueous solution of Et\textsubscript{3}PbOH with CO\textsubscript{2} led to (Et\textsubscript{3}Pb)\textsubscript{2}CO\textsubscript{3}, a compound which was previously unknown. A hydrolytic method for the synthesis of Ar\textsubscript{3}PbOH (mainly Ph\textsubscript{3}PbOH) from Ar\textsubscript{3}PbX was described by Grüttnert\textsuperscript{1118} (1918) and Krause and Pohland\textsuperscript{1123,1302} (1922, 1938). In 1921, Krause\textsuperscript{121} obtained the first tricyclohexylplumbanol by the reaction of (c-C\textsubscript{6}H\textsubscript{11})\textsubscript{3}Pb with 30% KOH.

Another method for the preparation of R\textsubscript{3}PbOH was based on the oxidation of R\textsubscript{3}PbPbR\textsubscript{3} by potassium permanganate in acetone. Austin\textsuperscript{1262} (1931) and Bähr\textsuperscript{1255} (1947) obtained Ar\textsubscript{3}PbOH (Ar = Ph, 2,4-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3}) in the same way. In 1959, Razuvaev and coworkers\textsuperscript{1303} isolated Et\textsubscript{3}PbOH when Et\textsubscript{3}PbPbEt\textsubscript{3} was oxidized by organic peroxides.

Jones and coworkers\textsuperscript{1271} (1935), Schmidt\textsuperscript{1304} (1938), Calingaert and coworkers\textsuperscript{1148,1260} (1945, 1948), Saunders and coworkers\textsuperscript{1241} (1951) and Alexandrov and coworkers\textsuperscript{1240} (1959) synthesized diorganylplumbanediols R\textsubscript{2}Pb(OH)\textsubscript{2} (R = Alk, Ar). In 1935 and 1940, Lesbre\textsuperscript{1176,1305} reported the synthesis of organylplumbanetriols by the reaction of alkyl iodides with an alkaline solution of lead oxide (i.e. NaPb(OH)\textsubscript{3}) at 5 °C. These compounds were regarded as hydrated alkylplumbane acids.

Trialkylplumbanols as well as triorganylstannanol have no tendency to undergo the reaction of anhydrocondensation and that is their main difference from R\textsubscript{3}MOH with M = Si, Ge. Only in 1960–1962 did Brilkind and coworkers\textsuperscript{1306,1307} succeed in transforming R\textsubscript{3}PbOH to R\textsubscript{3}PbOPbR\textsubscript{3} by the action of metallic sodium, which did not form R\textsubscript{3}PbONa. Up to 1964\textsuperscript{109} only three hexaorganyldiplumbanoxanes R\textsubscript{3}PbOPbR\textsubscript{3} with R = Et\textsuperscript{143,1217,1218,1306–1311}, i-Am\textsuperscript{1217,1218} and Ph\textsuperscript{1118,1254,1256,1306} appeared in the literature. Löwig\textsuperscript{45} (1853) reported the first representative of hexaalkyldiplumbanoxanes Et\textsubscript{3}PbOPbEt\textsubscript{3}, which was obtained by alkaline hydrolysis of Et\textsubscript{3}PbI. In 1860, Klippel\textsuperscript{1217,1218} synthesized R\textsubscript{3}PbOPbR\textsubscript{3} with R = i-Am by the reaction of i-Am\textsubscript{3}PbI with moist silver oxide, followed by water treatment.

Et\textsubscript{3}PbOH (‘methplumbâthyloxydhydrat’) was obtained analogously from Et\textsubscript{3}PbI. The reaction of the latter with CO\textsubscript{2} led to (Et\textsubscript{3}Pb)\textsubscript{2}CO\textsubscript{3}. Although Löwig\textsuperscript{45} and other authors reported that they had obtained Et\textsubscript{3}PbOPbEt\textsubscript{3} by different methods involving water or even air moisture, it could not be true because this compound is extremely unstable hydrolytically. Apparently they dealt with Et\textsubscript{3}PbOH. In 1918, Grüttnert\textsuperscript{1118} mentioned for the first time hexaphenyldiplumbanoxane Ph\textsubscript{3}PbOPbPh\textsubscript{3}. He assumed that it was obtained by the reaction of Ph\textsubscript{3}PbBr with hot alcoholic KOH or NaOH solution, followed by
treatment with water or by shaking of \( \text{Ph}_3\text{PbBr} \) with 10\% aqueous alkali in the cold. Actually, it was \( \text{Ph}_3\text{PbOH} \). Up to 1960 hexaorganyldiplumboxanes were neither isolated nor characterized. The compounds with \( R = \text{Et, Ph} \) were hardly formed because their syntheses were conducted in aqueous or water–alcohol media, in which they were very easily hydrolyzed with the formation of \( \text{R}_3\text{PbOH} \). Austin\textsuperscript{1253,1262} (1931) and Bähr\textsuperscript{1255} (1947) assumed that the labile \( \text{Ph}_3\text{PbOPbPh}_3 \), the isolation and characterization of which had failed, was apparently the intermediate in the oxidation reaction of \( \text{Ph}_3\text{PbPbPh}_3 \) which led to \( \text{Ph}_3\text{PbOH} \). At the beginning of the 1960s Russian chemists\textsuperscript{1306,1307} developed the most convenient preparative method of hexaorganyldiplumboxane. It was based on the reaction of triorganylplumbanols with dispersed Na in benzene. Compounds \( \text{R}_3\text{PbOPbR}_3 \) with \( R = \text{Et, Ph} \)\textsuperscript{1307,1309} and \( \text{Ph} \)\textsuperscript{1306} were obtained by this method and characterized.

In 1856, Klippel\textsuperscript{1217,1218} obtained and then published in 1860 the data which indicated the ease of Pb–O–Pb group protolysis by water and acids. Particularly, he showed that during the synthesis of \( \text{Et}_3\text{PbOPbEt}_3 \) its monohydrate, i.e. \( \text{Et}_3\text{PbOH} \), was formed upon contact with water. He also cleaved \( \text{R}_3\text{PbOPbR}_3 \) with \( R = \text{i-Am} \) by hydrochloric and sulfuric acids. In 1960–1961, Alexandrov and coworkers\textsuperscript{1307,1309} showed that \( \text{R}_3\text{PbOPbR}_3 \) with \( R = \text{Et, Ph} \) was easily protolyzed not only by water with formation of \( \text{R}_3\text{PbOH} \) (especially in aqueous methanol or dioxane), but also by alcohols already at \(-10^\circ \text{C}\). By the way, \( \text{Et}_3\text{PbOH} \) (in 95–100\% yield) and \( \text{Et}_3\text{PbOR} \)\textsuperscript{1309} (\( R = \text{Me, Et, CH}_2\text{Ph, CMe}_2\text{Ph} \)) were formed from \( \text{Et}_3\text{PbOPbEt}_3 \). Analogously, \( \text{Et}_3\text{PbOPbEt}_3 \) was cleaved by organic hydroperoxides ROOH with the formation of \( \text{Et}_3\text{PbOH} \) in 95–100\% yield and \( \text{Et}_3\text{PbOR} \) (\( R = \text{Me}_3\text{C, Me}_2\text{Ph} \)). Hexaethyl diplumboxane decomposed with formation of \( \text{Et}_4\text{Pb} \), \( \text{(Et}_2\text{PbO})_n \), ethylene and ethane\textsuperscript{1309} even at 70–90\°C. Hexaphenyldiplumboxane disproportionated with the formation of \( \text{Ph}_4\text{Pb} \) and \( \text{(Ph}_2\text{PbO})_n \) in xylene at 100\°C\textsuperscript{1306}.

The first dialkylplumbanediols \( \text{R}_2\text{Pb(OH)}_2 \) were synthesized only in the middle of the 20th century. All were synthesized from \( \text{R}_2\text{PbX}_2 \) by alkaline hydrolysis or by the reaction with moist silver oxide\textsuperscript{1148,1240,1241,1260,1271,1304}. The first \( \text{R}_2\text{Pb(OH)}_2 \) with \( R = \text{Bu, Am} \) were prepared by Jones and coworkers\textsuperscript{1271} in 1935. Later, \( \text{Et}_2\text{Pb(OH)}_2 \) was synthesized in the laboratory of Calingaert\textsuperscript{1260} by the reaction of \( \text{Et}_2\text{PbCl}_2 \) with \( \text{Ag}_2\text{O} \) in water. \( \text{Et}_2\text{Pb(OH)}_2 \) was isolated as hexahydrate, which transformed into polymeric \( \text{[Et}_2\text{PbO}]_n \), losing water even at room temperature. It was shown that \( \text{Et}_2\text{Pb(OH)}_2 \) was a rather weak base, like \( \text{NH}_4\text{OH} \). Its aqueous solutions were neutralized by strong acids (\( \text{HX} \)) with the formation of the corresponding salts \( \text{Et}_2\text{PbX}_2 \), and by saturating with \( \text{CO}_2 \) it led to \( \text{Et}_2\text{PbCO}_3 \). Calingaert and coworkers studied the decomposition of \( \text{Et}_3\text{PbOH} \) and \( \text{Et}_2\text{Pb(OH)}_2 \) during their contact with water steam at 100\°C\textsuperscript{1260}. It was found that \( \text{Et}_2\text{Pb(OH)}_2 \) was more stable than \( \text{Et}_3\text{PbOH} \). The initial products of the hydrothermal disproportionation of the latter were \( \text{Et}_4\text{Pb} \) and \( \text{Et}_2\text{Pb(OH)}_2 \), which in turn decomposed into \( \text{Pb(OH)}_2 \) and gaseous hydrocarbons. In 1951, Heap and coworkers\textsuperscript{1241} found also that \( \text{Et}_2\text{Pb(OH)}_2 \) was easily dehydrated in vacuum at room temperature, and the \( \text{(Et}_2\text{PbO})_n \) formed slowly decomposed with isolation of \( \text{PbO} \) at 100\°C. Shushunov, Brilkina and Alexandrov\textsuperscript{1312} (1959) found that high yield of \( \text{Et}_2\text{Pb(OH)}_2 \) and insignificant yield of \( \text{Et}_3\text{PbOH} \) were formed as intermediate products during the oxidation of \( \text{Et}_4\text{Pb} \) by oxygen in nonane or in trichlorobenzene.

In 1959, Alexandrov and coworkers\textsuperscript{1240} reported that \( \text{Et}_2\text{Pb(OH)}_2 \) decomposed on heating with explosion. The thermal decomposition of both \( \text{Et}_2\text{Pb(OH)}_2 \) and \( \text{Et}_3\text{PbOH} \) was studied in nonane medium at 40–120\°C and \( \text{PbO} \), \( \text{Et}_4\text{Pb} \), ethylene, ethane and butane were isolated. The intermediate decomposition product of \( \text{Et}_3\text{PbOH} \) under mild conditions was \( \text{Et}_2\text{Pb(OH)}_2 \), and thermal decomposition of the latter led back to \( \text{Et}_3\text{PbOH} \). In 1938, Schmidt\textsuperscript{1304} reported the formation \( \text{Ar}_2\text{Pb(OH)}_2 \). Unlike triarylplumbanols, these compounds were extremely unstable and easily transformed into polydiarylplumboxanes \( \text{(Ar}_2\text{PbO})_n \).
As early as in the 19th century the polymeric diorganylplumboxanes \((\text{Et}_2\text{PbO})_n\) were first synthesized. Already in 1853, Löwig\(^{43}\) was the first to obtain polydialkylplumboxane \((\text{Et}_2\text{PbO})_n\) in the reaction of alkali with \(\text{Et}_2\text{PbI}_2\). In 1916, Grütter and Krause\(^{1110}\) synthesized first \((\text{Me}_2\text{PbO})_n\). In 1887, Polis\(^{1246}\) obtained \((\text{Ph}_2\text{PbO})_n\) by the reaction of alkali with \(\text{Ph}_2\text{PbI}_2\). In 1927, Zechmeister and Csabay\(^{1219}\) had reproduced this synthesis. In 1955, Kocheshkov and Panov\(^{1313}\) demonstrated that \((\text{Ar}_2\text{PbO})_n\) with \(\text{Ar} = \text{4-MeC}_6\text{H}_4\) could be prepared by the reaction of \(\text{Ar}_2\text{Pb(NO}_3)_2\) with KOH. According to them, diaryldiacyloxyplumbanes were hydrolyzed with formation of \((\text{Ar}_2\text{PbO})_n\) much more easily than the corresponding diaryldihaloplumbanes. In 1943, Hein and coworkers\(^{1314}\) obtained the first polydicyclohexylplumboxane. Polydiorganylplumboxanes did not receive the special attention of investigators and the number of publications dealing with them did not exceed 10 until 1960. The polymers, corresponding to the \(\text{RPbOOH}\) formula, i.e. the so-called organylplumbane acids, were described in more detail. Such compounds with \(\text{R} = \text{Me, Et, Pr, i-Pr, Bu, CH}_2\text{CHCH}_2\) and \(\text{PhCH}_2\) were first obtained by Lesbre\(^{1305}\) (1935) by the reaction of the corresponding organic iodides \(\text{RI}\) with alkaline \(\text{PbO}\) solution at \(5^\circ\text{C}\)\(^{1176,1305}\) according to equation 24.

\[
\text{RI} + \text{NaPb(OH)}_3 \underset{-\text{NaI}}{\longrightarrow} \text{RPb(OH)}_3 \longrightarrow \text{RPbOOH} + \text{H}_2\text{O} \quad (24)
\]

Lesbre assumed that organylplumbanetriols were intermediates of this reaction. Arylplumbane acids \(\text{ArPbOOH}\) were first obtained at the Koshechkov laboratory\(^{1198,1283,1313,1315}\) by the hydrolysis of \(\text{RPb(OCOR)}_3\) with aqueous alcoholic ammonia solution. These polymeric compounds (‘acids’) turned out to be bases which were easily dissolved in mineral and organic acids. They could not be neutralized by aqueous \(\text{Na}_2\text{CO}_3\) or \(\text{NH}_3\) solution but dissolved with difficulty only in 15–20% KOH\(^{1315}\). On long-time drying \(\text{ArPbOOH}\) converted into polyarylplumbsesquioxanes \((\text{ArPbO}_{1.5})_n\)\(^{1198,1315}\).

Organylacyloxyplumbanes \(\text{R}_4-n\text{Pb(OOCR)}_n\), organolead carbonates \((\text{R}_3\text{Pb})_2\text{CO}_3\), \(\text{R}_2\text{PbCO}_3\) and organylorganoxyplumbanes \(\text{R}_4-n\text{Pb(OR)}_n\) are classified as organoleads containing the \(\text{Pb}–\text{O}–\text{C}\) group. The latter were unknown until the second half of the last century. For the first time they appeared in Gilman and coworkers\(^{1308}\) article. In 1962, the formation of \(\text{Et}_3\text{PbOR}\) by the reaction of \(\text{Et}_3\text{PbPbEt}_3\) with ROH was reported\(^{1311}\). In 1964, Rieche and Dahlmann\(^{1316}\) developed three methods for the synthesis of organolead peroxides described in equations 25–27.

\[
\begin{align*}
\text{R}_3\text{PbX} + \text{NaOOR}' & \longrightarrow \text{R}_3\text{PbOOR}' + \text{NaX} \quad (25) \\
\text{Ph}_3\text{PbBr} + \text{HOOR}' + \text{NaNH}_2 & \longrightarrow \text{Ph}_3\text{PbOOR}' + \text{NaBr} + \text{NH}_3 \quad (26) \\
\text{R}_3\text{PbOR}'' + \text{HOOR}' & \longrightarrow \text{R}_3\text{PbOOR}' + \text{R}''\text{OH} \quad (27)
\end{align*}
\]

\(\text{X} = \text{Cl, Br; R} = \text{Alk, Ar; R}' = \text{Alk, ArAlk; R}'' = \text{Alk}\)

The triorganyl(organylperoxy)plumbanes proved to be hydrolytically very unstable and were easily transformed into the corresponding triorganylplumbanols even under the action of air moisture. Only in 1963–1967 was a simple method for the synthesis of \(\text{R}_3\text{PbOR}'\) found: by the reaction of \(\text{R}_3\text{PbX} (\text{X} = \text{Cl, Br})\) with \(\text{R}'\text{ONa}\)\(^{1310,1311,1316–1319}\) under conditions which completely excluded any contact with air moisture. Trialkylalkoxyplumbanes \(\text{R}_3\text{PbOR}'\) attained importance only in 1966, when Davies and Puddephatt\(^{1318}\) studied their reactions with RNCO, PhNCS, CS₂, \(\text{Cl}_3\text{CCH}=\text{O}\), \((\text{Cl}_3\text{C})_2\text{C}=\text{O}\), \(\text{Cl}_3\text{CC}=\text{N}\) and other compounds.

The first organylacyloxyplumbanes were synthesized in the 19th century. Klippel\(^{1217,1218}\) (1860) synthesized triethylacyloxyplumbanes \(\text{Et}_3\text{PbOOCR}\) with \(\text{R} = \text{H},\)
Me, Pr, Ph by the reaction of the corresponding acids with Et$_3$PbOH (he thought that they were monohydrates of hexaethyldiplumboxane) or with (Et$_3$Pb)$_2$CO$_3$ (the product of Et$_3$PbH with CO$_2$). Browne and Reid$^{1250}$ applied this method for the synthesis of triethyldiacloxyplumbane in 1927. In 1952, Panov and Kocheshkov$^{1281}$ used the cleavage reaction of (Ar$_2$PbO)$_n$ by carboxylic RCOOH (R = Me, i-Pr) acids for synthesis of Ar$_2$Pb(OOCR)$_2$. Polis$^{1246,1247}$ prepared in 1887 Ar$_2$Pb(OOCR)$_2$ (Ar = Ph, 4-MeC$_6$H$_4$; R = H, Me) by heating Ar$_4$Pb with RCOOH. In addition, he demonstrated that diaryldiacloxyplumbanes were involved in an exchange reaction with NH$_4$SCN, K$_2$Cr$_2$O$_7$ and H$_2$S. In 1927, Browne and Reid$^{1250}$ used for the first time the cleavage reaction of Et$_4$Pb by eight different carboxylic acids (from acetic to pelargonic) in the presence of silica as catalyst for the synthesis of trialkyldiacloxyplumbanes. Analogously, five diethyl(haloacetoxy)plumbanes Et$_2$PbOOCCH$_3$/X$_n$ with X = Cl, Br; $n = 1–3$ were synthesized. By the same method he obtained Et$_3$Pb(OOCEt)$_2$, i.e. he showed the possibility of the cleavage of two ethyl groups from Et$_4$Pb by acetic acid. An attempt at synthesis of Pb(OOCEt)$_4$ by the same method was unsuccessful. Browne and Reid$^{1250}$ also found that on heating Et$_4$Pb with acetic acid at over 90°C, Et$_2$Pb(OOCEt)$_2$ was formed. Later, other experiments confirmed these data$^{971,1150,1308}$. For instance, on heating Et$_4$Pb with PhCOOH at 100°C, Et$_2$Pb(OOCPh)$_2$ was prepared. In 1922, Goddard, Ashley and Evans$^{728}$ found that on heating Ph$_4$Pb with aliphatic or aromatic carboxylic acids, two phenyl groups were easily eliminated with the formation of Ph$_2$Pb(OOCR)$_2$. This method for synthesis of diaryldiacloxyplumbanes was used later by Koton$^{1268,1269}$ (1939, 1941) and by Panov and Kocheshkov$^{1282,1283,1313}$ (1952, 1955). These experiments had established that the reaction rate of the acidolysis of tetraalkyplumbanes decreased as the lengths of the alkyl radicals increased.

Goddard, Ashley and Evans$^{728}$ (1922), Gilman and Robinson$^{1248}$ (1930), Koton$^{1268,1269}$ (1939, 1941) and Calingaert and coworkers$^{1260}$ (1945) also used this method to prepare triethyldiacloxyplumbane. The latter authors$^{1260}$ showed that the use of silica for the Me$_3$PbOOCEt synthesis was optional. Browne and Reid$^{1250}$ (1927) developed another synthesis of triethyldiacloxyplumbanes based on the reaction of Et$_3$PbOOCEt with RCOOK (R = Bu, Ph) in aqueous media. They carried out a similar reaction with KCN which resulted in Et$_3$PbCN$^{1250}$. In 1930 and 1953 Gilman and Robinson$^{1248,1308}$ used this method. Thereafter, Calingaert and coworkers$^{1260}$ (1945), Saunders and coworkers$^{971,1149,1150,1241,1320}$ (1947–1951) and Gilman and coworkers$^{1308}$ (1953) obtained R$_3$PbOOCR from R$_4$Pb.

In 1934, Kocheshkov and Alexandrov$^{1321}$ found a method for the preparation of triphenyldiacloxyplumbanes based on the reaction of Ph$_3$PbCl with potassium salts of carboxylic acids. They first synthesized Ph$_3$PbOOCH$_2$COOEt by this method. Thermal decomposition of the latter at 160–165°C resulted in Ph$_3$PbCH$_2$COOEt and CO$_2$. Analogously, Ph$_3$PbOOCH$_2$COOEt was obtained and its thermolysis led to Ph$_3$PbCH$_2$(Ph)COOEt. Another method for the preparation of triorganyldiacloxyplumbanes, based on the neutralization reaction of triorganylplumbanols by carboxylic acids, was used by Gilman and coworkers$^{1308}$ in 1953. They observed that sometimes the reaction of triethylplumbanol with some carboxylic acids was accompanied by cleavage of one ethyl group that led to diethyldiacloxyplumbanes. The reaction of carboxylic acids with triarylplumbanols, developed by Koton$^{1322,1323}$, was of special synthetic interest.

Nad' and Kocheshkov$^{1161}$ first established the possibility of reacylation of organylacicloxyplumbanes by high carboxylic acids in 1942. This reaction was used at the laboratories of Kocheshkov$^{1197–1199,1216,1282,1283,1315}$, Nesmeyanov$^{1195}$ (1948) and Saunders$^{1241}$ (1951). In 1947, McCombie and Saunders$^{971}$ showed that trialkylacicloxyplumbanes could be obtained by reacylation of triethylplumbylcarbonate by carboxylic acids.
1. Genesis and evolution in the organic chemistry of Ge, Sn, and Pb compounds

In 1953, Gilman and coworkers\textsuperscript{1308} proposed an unusual method for reacylation of triethylacetoxylplumbane. They found that insoluble Et$_3$PbOOCR was immediately precipitated when an aqueous solution of triethylacetoxylplumbane was mixed with the sodium salts of higher carboxylic acids RCOONa.

In 1952, Panov and Kocheshkov\textsuperscript{1281} employed the reaction of trialkylacyloxyplumbane cleavage by mercury salts of carboxylic acids Hg(OOCR)$_2$ for the synthesis of R$_2$Pb(OOCR)$_2$. Triethylacetoxylplumbane was also obtained by Razuvaev and coworkers\textsuperscript{903} using Et$_3$PbPbEt$_3$ cleavage of Pb(OOCMe)$_4$ in benzene media.

In 1942, Nad’ and Kocheshkov\textsuperscript{1161} studied in detail the reaction of Pb(OOCMe)$_4$ with diarylmercury in CHCl$_3$ at room temperature. This appeared to be a useful method for the preparation of diaryldiacetoxyplumbane. In 1948, Nesmeyanov and coworkers\textsuperscript{1195,1196} used it for the synthesis of (CIC=CH)$_2$Pb(OOCMe)$_2$.

Organolead compounds of the RPbX$_3$ series (R = organic substituent) were unknown up to 1952. However, in 1935–1940, Lesbre\textsuperscript{1176,1305,1324,1325} reported the synthesis of alkyltriiodoplumbanes RPbI$_3$ (but their physical constants were not given) by the reaction of alkyl iodides with CsPbCl$_3$. However, Capinjola at the Calingaert laboratory\textsuperscript{1148} could not reproduce Lesbre’s data. In accordance with that, Druce in 1922\textsuperscript{1326} and Gilman and Apperson in 1939\textsuperscript{1239} pointed out the high instability of RPbX$_3$ (X = halogen).

The first stable representatives of organolead compounds of type RPbX$_3$ turned out to be arylacyloxyplumbanes ArPb(OOCR)$_3$, which were obtained in a high yield by Kocheshkov, Panov and Lodochnikova\textsuperscript{1197–1199,1281,1283} by the reaction of Hg(OOCR)$_2$ with Ar$_2$Pb(OOCR)$_2$\textsuperscript{1281} in RCOOH media or by the reaction of Ar$_2$Hg with Pb(OOCR)$_4$ (R = Me, Et, i-Pr) in CHCl$_3$ in 1956–1959. Aryltriaacyloxyplumbanes were transformed into Ar$_2$Pb(OOCR)$_2$\textsuperscript{1199} by the action of Ar$_2$Hg. In 1952, Panov and Kocheshkov\textsuperscript{1281} first prepared arylacyloxylplumbanes (ArPbOOH)$_n$ by the reaction of ArPb(OOCR)$_3$ with weak alkali solution or aqueous ammonia. They also carried out re-esterification of aryltriaacyloxyplumbanes with carboxylic acids having higher boiling temperatures than MeCOOH (e.g. PhCOOH or CH$_2$=CMeCOOH). By the same method the labile Et$_2$Pb(OOCMe)$_2$ was transformed into the more stable Et$_3$Pb(OOCCH$_2$Cl)$_2$.

In 1930 the first organolead sulfonates were obtained by Gilman and Robinson\textsuperscript{1248} by heating Et$_4$Pb with 4-MeC$_6$H$_4$SO$_2$OH in the presence of silica to form Et$_3$PbOSO$_2$C$_6$H$_4$Me-4. In 1953, Gilman and coworkers\textsuperscript{1308} synthesized triethylplumbylsulfonates and sulfinites Et$_3$PbOSO$_2$R, Et$_3$PbOSOR from Et$_3$PbOOCMe and the sodium salts of the corresponding acids. In 1936, Schmidt\textsuperscript{1304} prepared them by the reaction of Ph$_2$PbO with sodium pyrocatecholdisulfonate.

Triorganylplumbane and diorganylplumbane esters of oxygen-containing inorganic acids R$_3$PbX and R$_2$PbX$_2$, where X were the acid anions, could be considered as organolead compounds formally having the plumboxon bond. However, not all of them had a Pb—O—M group with a covalent Pb—O bond and so they were properly salts. Particularly, this concerns the derivatives of oxygen-containing strong inorganic acids in which the M atom is highly electronegative (Cl, S, N etc.). For example, organolead ethers of H$_2$SO$_4$ and HNO$_3$ were typical salts. The compounds of this type, i.e. Et$_3$PbNO$_3$\textsuperscript{43,1217,1218}, (Et$_3$Pb)$_2$SO$_4$\textsuperscript{43,1163,1217,1218} and [(i-Am)$_3$Pb]$_2$SO$_4$\textsuperscript{1217,1218}, were first obtained by L"owig\textsuperscript{43} (1853), Buckton\textsuperscript{1163} (1859) and Klippel\textsuperscript{1217,1218} (1860). In 1887, Polis\textsuperscript{1246,1247} first obtained Pb$_2$Pb(NO$_3$)$_2$ by the reaction of Pb$_2$PbCl$_2$ with AgNO$_3$. Compounds such as Ph$_2$Pb[(OH)CO$_2$]$_2$, (Ph$_2$Pb)$_2$(PO$_4$)$_2$, Ph$_2$PbCrO$_4$, Ph$_2$Pb(OH)CN and Ph$_2$PbBr$_2$ were synthesized by the exchange reactions of Ph$_2$Pb(NO$_3$)$_2$ with Na$_2$CO$_3$, Na$_3$PO$_4$, K$_2$Cr$_2$O$_7$, KCN and KBr, respectively. In 1930, Gilman and Robinson\textsuperscript{1248} synthesized Et$_3$PbOPO(OH)$_2$ by heating Et$_4$Pb with H$_3$PO$_4$. The reaction of aqueous or alcoholic solution of R$_3$PbOH or R$_2$Pb(OH)$_2$ with the corresponding acids was the
basic method for synthesis of $R_3PbA$ and $R_2PbA_2$ ($A =$ acid anion). In the past century Tafel$^{1144}$ (1911), Pfeiffer and Truskier$^{1249}$ (1916), Goddard and coworkers$^{728}$ (1922), Vorlander$^{1327}$ (1925), Buck and Kumro$^{1328}$ (1930), Austin and Hurd$^{1256,1262}$ (1931), Challenger and Rothstein$^{1329}$ (1934), Jones and coworkers$^{1271}$ (1935), Gilman, Woods and Leeper$^{1116,1330}$ (1943, 1951), McCombie and Saunders$^{971}$ (1947), Nesmeyanov and coworkers$^{1329}$ (1951) synthesized a series of $R_3PbA$ and $R_2PbA_2$ by this method. In addition, arylsulfonates$^{1149}$ and iodates$^{728}$ were among the anions in the series given above along with sulfates and nitrates.

G. Compounds having a Pb$–S$, Pb$–Se$ and Pb$–Te$ Bond

As indicated in Section III. G, according to the Goldschmidt geochemical classification lead as well as tin belong to the chalcophile elements, i.e. they have high affinity to sulfur. Consequently, numerous organolead compounds possessing the plumbathiane Pb$–S$ bond have been easily formed in many reactions involving hydrogen sulfide, alkaline metal sulfides, sulfur and some other sulfurizing agents with various organolead derivatives.

The main organolead derivatives of this type have the following general formulas: $R_3PbSPbR_3$, $(R_2PbS)_n$, $(RPbS)_n$, $R_4Pb(SR')_n$, $R_2PbSMe$ (n = 1, 2). Compounds containing the Pb$–S$–H bond do not appear in this list, due to their extreme instability. In contrast with isostructural compounds of tin, organolead compounds containing the Pb$–S$ bond attracted only a little attention of researchers and industrial chemists. The number of known compounds of this type, which was less than 50$^{1331}$ by 1967, bears witness to this fact. On the one hand this was due to their unacceptability to be used as synthons and reagents, and, on the other hand, due to the seemingly absence of any future practical use. Only a few patents dealing with the application of $Me_3PbSMe^{1332,1333}$, $R_3PbSCH_2CONH_2^{1334}$ and $Me_3PbSPbMe_3^{1332}$ as potential motor engine antiknocks and the use of compounds $R_3PbSCH_2CONH_2^{1334}$ and $Me_3PbSCH_2COOMe^{1335}$ as potential pesticides were issued.

Organolead compounds containing sulfur appeared in chemical circles in the 19th century. The first one was hexaethylplumbathiane $Et_3PbSPbEt_3$, which was prepared by Klippel$^{1217,1218}$ employing the reaction of $Et_3PbCl$ with an aqueous solution of $Na_2S$ in 1860. Significantly later, in 1945 the above reaction was repeated at the Calingaert laboratory at 0°C$^{1260}$. It was found during the reaction that $Et_3PbSPbEt_3$ was slowly oxidized by air oxygen to $(Et_3Pb)_2SO_4$. In 1887, Polis$^{1246}$ synthesized $(Ar_2PbS)_3$, $Ar = Ph$, 4-MeC$_6$H$_4$ by the reaction of $Ar_2Pb(OOCMe)_2$ with $H_2S$. Only in the second half of the 20th century,$^{1336–1338}$ $(Ph_3PbS)_3$ was synthesized again, and it was proved that it was a trimer. Other compounds of the series of $R_3PbSPbR_3$ were obtained in 1911–1917. In 1911, Tafel$^{1144}$ synthesized its representative with $R = i$-Pr, and its analogs with $R = c$-C$_6$H$_{11}$ and $Me$ were synthesized by Grütter and Krause$^{674,1110}$. In 1917, Grütter and Krause$^{1113}$ obtained $MeEtPbS$, $Pr(i-Bu)PbS$ and $Pr(i-Am)PbS$. At last, in 1918, Grütter synthesized $Ph_3PbSPbPh_3$ for the first time. After this pioneer research no organolead compound having the Pb$–S$–Pb group was obtained up to 1945. Henry and Krebs$^{443,1337}$ (1963) found that the reaction of $Ph_3PbCl$ with $Na_2S$ proceeded in a different direction with formation of $Ph_3PbSn$. The latter interacted with RI ($R = Me$, $Et$) to give $Ph_3PbSr$. In 1965, Davidson and coworkers$^{437}$ obtained $Ph_3PbSPbPh_3$ in a quantitative yield by the reaction of $Ph_3PbX$ ($X =$ Cl, Br) with $H_2S$ in the presence of $Et_3N$ or pyridine. Organyl(organythio)plumbanes $R_4-nPb(SR')_n$ were prepared by the reaction of the corresponding organylhaloplumbanes with mercaptides or thiophenolates of alkali metals or of silver or lead. Saunders and coworkers$^{971,1149,1150}$ first described this type of compound $(Et_3PbSEt$, $Et_3PbSPh)$ in 1947 and 1949. They were synthesized
by the reaction of Et₃PbOH with RSH or Et₃PbCl with NaSR. These compounds slowly hydrolyze by water and they turned out to be effective sternutators. A convenient method for the synthesis of Ph₃PbSR (R = Me, Et, Pr, Bu, Ph, CH₃Ph, COMe, COPh) based on the use of Pb(SR)₂ was elaborated by Krebs and Henry (1963) and later applied by Davidson and coworkers (1965). This method proved to be unsuitable for the preparation of Ph₂Pb(SR)₂. These authors also attempted to obtain Ph₃PbSN by the cleavage of R₄Pb by thiols, but they were unsuccessful. Compounds of the Ph₃PbSR series turned out to be hydrolytically stable, but it was impossible to distill them without decomposition. This research demonstrated that the thermal stability of the M−SR bond in R₃MSR (M = Si, Ge, Sn, Pb; R = Alk, Ar) is diminished on increasing the atomic number of M, but their hydrolytic stability had increased. Abel and Brady obtained Me₃PbSEt (in 53% yield) by the reaction of Me₃PbCl with EtSH in aqueous NaOH solution in 1965. In 1951, Saunders and coworkers illustrated that the reaction of Et₄Pb with MeCOSH resulted in Et₃PbSCOMe and in the presence of silica, in Et₂Pb(SCOMe)₂, indicating that thiols were capable of cleaving the C−Pb bond. Davidson and coworkers synthesized diphenyl(diorganylthio)plumbanes Ph₂Pb(SR)₂ by condensation of Ph₂PbX₂ (X = Cl, Br) with RSH (R = Alk, Ar) in benzene in the presence of Et₃N or Py as an acceptor of the hydrohalic acids. These compounds appeared to be unstable and decomposed by heating according to equation 28.

\[
3\text{Ph}_2\text{Pb} (\text{SPh})_2 \rightarrow \text{2Ph}_3\text{PbSPh} + \text{Ph} (\text{SPh})_2 + \text{PhSSPh}
\]  

By the reaction of Ph₂PbCl₂ with HSCH₂CH₂SH in the presence of Et₃N, 2,2-diphenyl-1,3-dithio-2-plumbacyclopentane was obtained. Finally, Davidson and coworkers synthesized a series of carbofunctional triphenyl(organylthio)plumbanes Ph₃PbS(CH₃)ₙX, where X = COOMe, CONH₂ (n = 1); OH, NH₂ (n = 2); Ph₃PbSC₆H₄X-4 (X = Cl, NH₂, NO₂) and Ph₃PbSC₆F₅. They also prepared the first organolead derivative of a natural hormone, i.e. Ph₃PbS-17-β-mercaptotestosterone. The Pb−S bond in trialkylthiocyanatoplumbanes R₃PbSCN was definitely ionic. Klippel obtained the first compound of the Et₃PbSCN series by the reaction of Et₃PbCl with AgSCN in alcoholic media as early as 1860. However, Saunders and coworkers could not repeat this reaction. They synthesized the same compound by the reaction of Et₃PbCl with KSCN in alcohol, and Gilman and coworkers obtained it by the reaction of Et₃PbOOCMe with KSCN; it could also be regarded as a compound containing a Pb−Se bond.

In 1961, R₃PbSPbR₃ (R = Alk) were proposed as motor fuel antiknocks.

H. Compounds having a Pb−N Bond

Compounds with a Pb−N bond are the least studied in organolead chemistry. By 1953 there were only less than 10 of them. The syntheses of the first representatives of this class were published by McCombie and Saunders in 1947–1950, but preliminary
reports on their syntheses were given in 1940. These were \( N \)-trialkyplumbylarene sulfonamides \( R_3PbNR_0SO_2Ar \), -phthalimides \( R_3PbN(CO)_2C_6H_4-o \) (\( R = Et, Pr \)) and -phthalhydrazides \( R_3PbNHN(CO)_2C_6H_4-o \). They were synthesized by the reaction of the corresponding sodium derivatives with \( R_3PbCl \) or by the reaction of the free acids or phthalimide with \( R_3PbOH \). In 1953, Gilman and his coworkers\(^{1308} \) synthesized analogous compounds by reaction of organolead bases \( R_3PbOH \) or \((R_3Pb)_2\) with \( NH \) acids such as sulfonamides or imides.

Willemsens and van der Kerk\(^{110} \) applied this method for the synthesis of \( N \)-trialkyplumbyl-substituted heterocycles containing the endocyclic \( NH \) group in 1965. In some cases trialkylhaloplumbanes were also used to synthesize organolead compounds containing the \( Pb-N \) bond using reagents containing an \( N-H \) bond. In this process an excess of a nitrogen base served as an acceptor of the hydrogen halide\(^{456,471} \).

In the 1950s, some patents were granted for the use of \( N \)-trialkyplumbyl phthalimide and -phthalhydrazide as fungicides\(^{1344,1345} \) and of \( Et_3PbNHCHMeEt \) as a herbicide\(^{1346} \). The latter was obtained by the reaction of \( Et_3PbCl \) with \( NaNHCHMeEt \). It is remarkable that the preparation of triorganyl(dialkylamino)plumbanes \( R_3PbNR_0_2 \) (\( R = Me, Et \)) (as well as that of their organotin analogs)\(^{1347} \) from \( R_3PbX \) (\( X = Cl, Br \)) was successful only when lithium dialkylamides \( LiNR_0_2 \) were used as the aminating agents. This was caused by the ability of triorganylhaloplumbanes (as well as \( R_3SnX \)) to form adducts (less stable than the corresponding tin complexes) during the reaction with ammonia and amines but not to substitute the halogen atom by an amino group. Neumann and Kuhlne\(^{1348,1349} \) first used this method of synthesis in their laboratory in 1966.

The \( Pb-N \) bond turned out to be rather active. For example, trialkyl(dialkylamino)plumbanes hydrolyzed extremely rapidly by water, whereas \( N \)-trialkyplumbyl derivatives of sulfonamides, amides and imides of carboxylic acids as well as their nitrogen heterocycles were hydrolytically rather stable. In the 1960s, the cleavage reactions of the \( Pb-N \) bond in \( R_3PbNR_0_2 \) by inorganic and organic acids, alcohols and \( NH \) acids (e.g. re-amination by organometallic hydrides) were developed\(^{1350} \). We shall not consider them here since this period is not yet regarded as historical.

In the 1960s at the Schmidt laboratory\(^{456,471} \), organometallic compounds containing \( Pb-N-M \) (\( M = Si, Ge \)) bonds were synthesized\(^{1350} \). In 1964, Sherer and Schmidt\(^{456} \) obtained trimethylbis(trialkylsilylamino)plumbanes \( Me_3PbN(SiR_3)_2 \), \( R = Me, Et \) by the reaction of \( Me_3PbCl \) with \( NaN(SiR_3)_2 \)\(^{456,1351} \). Schmidt and Ruidish\(^{471} \) (1964) prepared analogously \( Me_3PbN(GeMe_3)_2 \) from \( LiN(GeMe_3)_2 \).

One year later Sherer and Schmidt\(^{1352} \) carried out the reaction of \( Me_3PbCl \) with \( LiN(SiMe_3)Me \), which led to \( Me_3PbN(SiMe_3)Me \). In 1961 and 1963 Lieber and coworkers\(^{1353,1354} \) synthesized phenylazidoplumbanes \( Ph_4-nPb(N_3)_n \) \((n = 1, 2)\) from \( Ph_4-nPb(OH)_n \) with \( HN_3 \). In 1964, Reichle\(^{465} \) reported that, contrary to expectations, \( Ph_3PbN_3 \) proved to be rather thermostable and decomposed with formation of \( Ph_2Pb \) and \( N_2 \) under thermolysis.

The number of organolead compounds having a \( Pb-N \) bond reached fifty by 1968\(^{1350} \). Pfeiffer and Tröskier\(^{1249} \) obtained the first organic compounds of hypervalent lead, having coordinated \( N!Pb \) bonds in 1916. They were isolated during recrystallization of \( Ph_2PbX_2 \) (\( X = Br, Cl, NO_3 \)) from pyridine and corresponded to the formula \( Ph_2PbX_2 \cdot 4Py \). These complexes were stable only under pyridine atmosphere. In the absence of the latter they lost two molecules of pyridine and transformed into hexacoordinated lead complexes \( Ph_2PbX_2 \cdot 2Py \). In ammonia atmosphere \( Ph_2PbBr_2 \) formed the unstable complex \( Ph_2PbBr_2 \cdot 2NH_3 \), which easily lost ammonia\(^{1355} \). Even these limited data showed that the complexes of organylhaloplumbanes \( Ph_3PbX \) and \( Ph_2PbX_2 \) with nitrogen bases were unstable and they were not studied further. The preparation of complexes of amines
with RPbX$_3$ and PbX$_4$ failed, apparently due to their redox reaction with the addend. Nevertheless, the stable complexes [Me$_3$PbPy]$^+\text{ClO}_4^-$, and [Me$_2$PbPy$_2$]$^{2+}\text{2ClO}_4^-$ and [Me$_3$Pb(OP(NMe$_2$)$_3$)$_2$]$^+\text{ClO}_4^-$ were described in 1966. However, they had an ammonium structure, i.e. the lead atom was tetracoordinated but not hypervalent$^{1356}$. One should note that, with respect to DMSO, organylhaloplumbanes served as rather strong Lewis acids. In 1966 the stable complexes Ph$_2$PbX$_2$·2OSMe$_2$ (X = Cl, Br) containing hexacoordinated lead atom because of the presence of two O·Pb bonds$^{1357}$ were synthesized. They were so stable that they could be synthesized even in aqueous medium. The melting point of Ph$_2$PbCl$_2$·2OSMe$_2$, 171°C, witnessed its thermal stability. In 1964, Matviyov and Drago$^{1358}$ prepared the complexes of R$_3$PbCl (R = Me, Et) with tetramethylenesulfoxide (B) of compositions R$_3$PbCl·B and R$_3$PbCl·2B, Me$_2$PbCl$_2$·2B and R$_3$PbCl$_2$·4B. Me$_3$PbCl·B had a trigonal-bipyramidal structure, i.e. its lead atom was pentacoordinated. The second and third complexes were apparently of octahedral structure and in Me$_2$PbCl$_2$·4B the lead atom was octacoordinated. Later, the analogous complex [Me$_2$Pb(OSMe$_2$)$_4$](ClO$_4$)$_2$ was obtained. In 1961, Duffy and Holliday$^{1359}$ showed that the reaction of Me$_3$PbCl with KBH$_4$ in liquid NH$_3$ at −70°C led to an adduct of Me$_3$Pb(BH$_4$)$_n$·nNH$_3$ composition with $n \geq 2$ (probably, it was a mixture of Me$_3$PbH·NH$_3$ and H$_3$N·BH$_3$). The product obtained at −5°C to +20°C decomposed with the formation of Me$_3$PbH, NH$_3$ and H$_3$N·BH$_3$. The Me$_3$PbH obtained reacted instantly with liquid ammonia at −78°C with the formation of an unstable green adduct, which evidently was Me$_3$PbH·NH$_3$. Based on the $^1$H NMR data, the authors ascribed to the product the very unlikely structure of ammonium trimethylplumbate Me$_3$PbNH$_4$ containing the Me$_3$Pb$^-$ anion. This complex evolved CH$_4$ and NH$_3$ at −78°C and was slowly transformed into Me$_3$PbPbHMe$_2$·NH$_3$, which in the authors’ opinion provided the red color of the reaction mixture. However, it was most probably Me$_2$Pb:, which provided the red color according to equations 29 and 30.

$$\text{Me}_3\text{PbH} \cdot \text{NH}_3 \rightarrow \text{Me}_2\text{Pb} + \text{CH}_4 + \text{NH}_3 \quad (29)$$

$$\text{Me}_3\text{PbH} \cdot \text{NH}_3 + \text{Me}_2\text{Pb} \rightarrow \text{Me}_3\text{PbPbHMe}_2 \cdot \text{NH}_3 \quad (30)$$

Pentamethyldiplumbane ammoniate decomposed to Me$_4$Pb, Me$_3$PbPbMe$_3$, CH$_4$, H$_2$ and Pb at −45°C. The solution of Me$_3$PbH in Me$_3$N was less stable than its solution in liquid ammonia.

I. Organolead Hydrides

The first investigations of organolead hydrides R$_4$−$n$PbH$_n$ (n = 1, 2) were conducted only in the 1960s. The reason for their late appearance was their extreme instability due to the presence of the Pb−H bond. Early attempts to obtain organolead hydrides R$_3$PbH by the reaction of R$_3$PbNa (R = Et, Ph) with NH$_4$Br in liquid ammonia$^{1170,1360}$ or by catalytic hydrogenation of Ph$_3$PbPbPh$_3$ had failed. In 1958, Holliday and Jeffers$^{1361}$ were the first to report the preparation of Me$_3$PbH, when they found that it was formed by decomposition of Me$_3$PbBH$_4$ in liquid ammonia. Later, Duffy and Holliday$^{1359,1362,1363}$ used the reduction reaction of R$_3$PbCl by KBH$_4$ in liquid ammonia to prepare R$_3$PbH (R = Me, Et). An intermediate of this reaction was R$_3$PbBH$_4$, which eliminated R$_3$PbH at −5°C. In 1960, Amberger$^{1364}$ synthesized R$_3$PbH and R$_2$PbH$_2$ (R = Me, Et) by the reduction of the appropriate organolead chlorides by LiAlH$_4$ in Me$_2$O. Becker and Cook$^{1212}$ (1960) used for this purpose the reaction of R$_3$PbX (X = Cl, Br) with KBH$_4$ in liquid ammonia or with LiAlH$_4$ in Me$_2$O at −78°C. Dickson and West$^{1365}$ succeeded in obtaining some amount of Et$_3$PbH by the decomposition of Et$_3$PbNa by ammonium bromide in liquid ammonia in 1962.
Neumann and Kühlein\textsuperscript{1213,1366} used the reduction of \( \text{R}_3\text{PbCl} \) by \( \text{LiAlH}_4 \) for the synthesis of \( \text{R}_3\text{PbH} \), \( \text{R} = \text{Pr}, \text{Bu}, \text{i-Bu}, \text{c-C}_6\text{H}_{11} \) in 1965. They also synthesized \( \text{Bu}_2\text{PbH}_2 \) from \( \text{Bu}_3\text{PbCl} \). Such solvents as \( \text{Me}_2\text{O}, \text{Et}_2\text{O}, \text{THF} \) or diglyme, which interacted with the \( \text{AlCl}_3 \) formed, were used for this purpose since the \( \text{AlCl}_3 \) caused decomposition of the \( \text{R}_3\text{PbH} \)\textsuperscript{1212,1317,1366}. In 1965, Neumann and Kühlein\textsuperscript{1213,1366} demonstrated that trialkylmethoxyplumbanes \( \text{R}_3\text{PbOMe} \) reacted with \( \text{B}_2\text{H}_6 \) at \( 15^\circ \text{C} \) to form \( \text{R}_3\text{PbBH}_4 \). Further treatment at \(-78^\circ \text{C} \) by \( \text{MeOH} \) resulted in \( \text{R}_3\text{PbH} \) with \( \text{R} = \text{Me}, \text{Et}, \text{Pr}, \text{Bu} \). Even without methanolysis, \( \text{Me}_3\text{PbBH}_4 \) slowly decomposed in ether with formation of \( \text{Me}_3\text{PbH} \) at \(-78^\circ \text{C} \)\textsuperscript{1362}. In 1965, Neumann and Kühlein\textsuperscript{1213,1366} showed that \( \text{Et}_3\text{PbCl} \) could be reduced by \( \text{Bu}_3\text{PbH} \) to \( \text{Et}_3\text{PbH} \), which was removed from the reaction mixture by distillation. High-boiling organotin hydrides \( \text{R}_3\text{SnH} \) and \( \text{R}_2\text{SnHCl} \) (\( \text{R} = \text{Bu}, \text{Ph} \)) were employed as reductants of \( \text{Et}_3\text{PbX} \). Thus, within the period from 1960 till 1965, 10 organolead hydrides were synthesized. The low organolead hydrides \( \text{R}_4\text{PbH}_n \) (\( \text{R} = \text{Me}, \text{Et}; n = 1, 2 \)) were liquids, which decomposed at temperatures below \( 0^\circ \text{C} \)\textsuperscript{1212,1367}. Duffy and coworkers\textsuperscript{1363} (1962) identified methane as a gaseous product of the \( \text{Me}_3\text{PbH} \) decomposition. According to Amberger and Hönigschmid-Grossich\textsuperscript{1367} high trialkylplumbanes started to decompose to \( \text{R}_4\text{Pb}, \text{R}_3\text{PbPbR}_3, \text{Pb} \) and \( \text{H}_2 \)\textsuperscript{1367} without air in vacuum at \(-30 \) to \(-20^\circ \text{C} \). Neumann and Kühlein\textsuperscript{1213,1366} showed in 1965 that \( \text{Pr}_3\text{PbH} \) was completely decomposed (disproportionated) to \( \text{Pr}_4\text{Pb}, \text{Pr}_3\text{PbPbPr}_3, \text{Pb}, \text{C}_3\text{H}_8 \) and \( \text{H}_2 \)\textsuperscript{1366} within 24 hours. Propane appeared in the product of the hydrogen atom cleavage from \( \text{Pr}_3\text{PbH} \).

Becker and Cook\textsuperscript{1212} (1960) proposed a rather complicated scheme for the homolytic decomposition of \( \text{R}_3\text{PbH} \) (Scheme 1). It was possible that this process was simpler, involving the intermediate formation of \( \text{PbR}_2 \).

$$\begin{align*}
2\text{R}_3\text{PbH} \rightarrow h\nu & \rightarrow 2\text{R}_3\text{Pb}^* + \text{H}_2 \\
2\text{R}_3\text{Pb}^* & \rightarrow \text{R}_3\text{PbPbR}_3 \\
\text{R}_3\text{Pb}^* + \text{R}_3\text{PbPbR}_3 & \rightarrow \text{R}_4\text{Pb} + \text{R}_3\text{PbPbR}_2^* \\
\text{R}_3\text{PbPbR}_2^* & \rightarrow \text{R}_4\text{Pb} + \text{Pb} + \text{R}^* \\
\text{R}^* + \text{R}_3\text{PbH} & \rightarrow \text{R}_3\text{Pb}^* + \text{RH} \\
\text{R}^* + \text{R}_3\text{PbPbR}_3 & \rightarrow \text{R}_4\text{Pb} + \text{R}_3\text{Pb}^* \\
\end{align*}$$

SCHEME 1

In 1960, Becker and Cook\textsuperscript{1212} were the first to succeed in carrying out the reaction of hydroplumbylation (a term first suggested by Voronkov in 1964\textsuperscript{53}). They demonstrated that \( \text{Me}_3\text{PbH} \) was added to ethylene in diglyme at 35 atm and \( 0^\circ \text{C} \) with the formation of \( \text{Me}_3\text{PbEt} \) in 92\% yield. Unlike that, Duffy and coworkers\textsuperscript{1363} found that trialkylplumbanes did not add to ethylene in \( \text{Me}_2\text{O} \) media or without solvent at normal pressure. Neumann’s\textsuperscript{1366} attempts to carry out the hydroplumbylation reaction of \( \text{CH}_2=\text{CHR} \) (\( \text{R} = \text{C}_6\text{H}_{13}, \text{CH}_2\text{OH}, \text{CH}_2\text{OOCMe} \)) with \( \text{Bu}_3\text{PbH} \) at \( 0^\circ \text{C} \) or \( 20^\circ \text{C} \) were unsuccessful as well. Nevertheless, Blitzer and coworkers\textsuperscript{1368} patented a method of addition of organolead hydrides to terminal olefins and cyclohexene in 1964. In 1965, Neumann and Kühlein\textsuperscript{1213,1366} found that \( \text{Bu}_3\text{PbH} \) was added to compounds having terminal activated double bonds \( \text{CH}_2=\text{CHR} \) (\( \text{R} = \text{CN}, \text{COOMe}, \text{Ph} \)) at \( 0^\circ \text{C} \). In 1965, Leusink and van der Kerk\textsuperscript{1214} showed that \( \text{Me}_3\text{PbH} \) added easily to \( \text{HC}≡\text{C}−\text{CN} \) and \( \text{HC}≡\text{C}−\text{COOMe} \).
1. Genesis and evolution in the organic chemistry of Ge, Sn, and Pb compounds

The cis-adduct was the first product of the hydroplumbylation of cyanoacetylene and it was consequently converted into the trans-isomer at temperatures from −78 °C to 0 °C. At about the same time Neumann and Kühlein\textsuperscript{1213} carried out a similar reaction of Bu\textsubscript{3}PbH with HC≡CPh that led to the trans-adduct. They also showed that Bu\textsubscript{3}PbH did not add to the C=O bonds of aldehydes and ketones. In contrast, they showed that in the reaction of Bu\textsubscript{3}PbH with PhN≡C≡S the hydroplumbylation of thiocarbonyl group proceeded with the formation of Bu\textsubscript{3}PbS=CH=NPb. They also found that Bu\textsubscript{3}Pb(N(CH=O)Ph, the product of the N=C bond hydroplumbylation, was formed in the reaction of Bu\textsubscript{3}PbH with PhN≡C≡O at −70 °C. Phenylisocyanurate (PhNC=O)\textsubscript{3} and Bu\textsubscript{3}PbBu\textsubscript{3} were the final products of the reaction. In 1968, Neumann and Kühlein\textsuperscript{1369} investigated the mechanism of the hydroplumbylation reaction, which was found to proceed by both radical and ionic processes.

In 1960, Becker and Cook\textsuperscript{1212} pointed out that R\textsubscript{4−n}PbH\textsubscript{n} (R = Me, Et; n = 1, 2) reacted with diazoalkanes R′CHN\textsubscript{2} (R′ = H, Me) with the formation of both the products of hydrides disproportionation and the insertion of the R′CH group into the Pb-H bond from −80 to −0 °C.

Duffy and coworkers\textsuperscript{1359,1363} found that R\textsubscript{3}PbH (R = Me, Bu) were decomposed under ammonia and amines action. Trimethylplumbane reacted with liquid ammonia to give green and then red solutions (evidently connected with an intermediate formation of Me\textsubscript{3}Pb\textsuperscript{−} and Me\textsubscript{3}Pb) and Me\textsubscript{2}Pb and CH\textsubscript{4} were formed. Addition of PbCl\textsubscript{2} to an Me\textsubscript{3}PbH solution in NH\textsubscript{3} led to Me\textsubscript{3}PbPbMe\textsubscript{3} in almost a quantitative yield\textsuperscript{1359}. Organolead hydrides were extremely easily oxidized by air oxygen (Me\textsubscript{3}PbH was oxidized with an explosion)\textsuperscript{1212} and they turned out to be strong reductants (more effective than organic hydrides of Ge and Sn). In 1960, Neumann\textsuperscript{1370} found that trialkylplumbanes reacted with ethyl iodide even at temperatures from −60 up to −40 °C with the formation of ethane. Holliday and coworkers\textsuperscript{1363} (1962) found that Me\textsubscript{3}PbH reacted with HCl to give Me\textsubscript{3}PbCl and H\textsubscript{2} as well as some amount of Me\textsubscript{3}PbPbMe\textsubscript{3} at −112 °C. Along with them Me\textsubscript{2}PbCl\textsubscript{2} and CH\textsubscript{4} were identified at −78 °C.

In 1965, Neumann and Kühlein\textsuperscript{1213,1366} reduced aliphatic halogens, and carbonyl, nitro and nitroso compounds, and Et\textsubscript{3}SnCl as well, by tributylplumbane at 0 °C and 20 °C. A higher temperature was found unacceptable due to the decomposition of Bu\textsubscript{3}PbH.

J. Compounds Containing a Pb—Pb Bond

Almost all the known compounds having a Pb—Pb bond are hexaorganyldiplumbanes R\textsubscript{3}PbPbR\textsubscript{3} and only a few of them do not correspond to this formula. Hexaorganyldiplumbanes have been regarded for a long time as trivalent lead derivatives and it is a wonder that even such leaders of metalloorganic chemistry as Gilman (with Towne) in 1939\textsuperscript{1254} and Kocheshkov in 1947\textsuperscript{156} and with Panov even in 1955\textsuperscript{1313} gave the R\textsubscript{3}Pb formula to these compounds. Some historical aspects and data concerning the synthesis and transformations of hexaorganyldiplumbanes were given in Sections IV.B, IV.C and IV.E because they were connected with the quoted data. Herein we consider the historical developments of the investigations of compounds having the Pb—Pb bond in more detail.

As reported in Section IV.B, Löwig\textsuperscript{43} obtained hexaethylidiplumbane, the first organolead compound having the Pb—Pb bond, in 1953. It was difficult to decide whether this compound was Et\textsubscript{6}Pb\textsubscript{2} (Et\textsubscript{3}Pb radical by Löwig) or Et\textsubscript{4}Pb according to his data, which were based on the atomic weights known at that time. In 1859, Buckton\textsuperscript{1371} reported that the compound described by Löwig was apparently Et\textsubscript{4}Pb and this was confirmed by Ghira\textsuperscript{1372} in 1894. Moreover, he stated: 'At the present time no lead compounds of the type PbX\textsubscript{3} or Pb\textsubscript{2}X\textsubscript{6} have ever been reported, studied or isolated.'
In 1919, Krause and Schmitz\(^{1120}\) obtained for the first time hexaaryldiplumbane \(\text{Ar}_3\text{PbPbAr}_3\) (\(\text{Ar} = 2,5\text{-Me}_2\text{C}_6\text{H}_3\)) by the reaction of 2,5-Me\(_2\)C\(_6\)H\(_3\)MgBr with PbCl\(_2\). In 1921, Krause\(^{1121}\) synthesized hexacyclohexyldiplumbane analogously. He wrote that tetracyclohexylplumbane which was obtained by Grüttnert\(^{674}\) in 1914 was apparently nonpure. The synthesis of \(\text{R}_3\text{PbPbR}_3\) from \(\text{RMgX}\) and PbCl\(_2\) was further used by Krause and Reissaus\(^{1122,1292}\) (1921, 1922), Calingaert and coworkers\(^{1188,1373}\) (1938, 1942) and Gilman and Bailie\(^{1170}\) (1939). It was established that \(\text{R}_2\text{Pb}\) were the labile intermediates of this reaction, which is described by equations 31 and 32.

\[
2\text{RMgX} + \text{PbX}_2 \rightarrow \text{R}_2\text{Pb} + 2\text{MgX}_2 \quad (31)
\]

\[
3\text{R}_2\text{Pb} \rightarrow \text{R}_6\text{Pb}_2 + \text{Pb} \quad (32)
\]

Hexaethyldiplumbane, whose chemical composition and structure were unequivocally proved, was obtained by electrolysis of Et\(_3\)PbOH with lead cathode in alcoholic medium by Calingaert and coworkers\(^{1140}\) only in 1923. The electrochemical method for the \(\text{R}_3\text{PbPbR}_3\) synthesis was further developed by the Calingaert group\(^{1188,1373}\) in 1938–1942 and by Italian chemists\(^{1374}\) in 1960. In 1960, Vyazankin and coworkers\(^{1203}\) found that during the electrochemical synthesis of Et\(_3\)PbPbEt\(_3\) a new product, identified as Et\(_3\)Pb, was formed along with it. Hein and Klein\(^{1201}\) found that compounds \(\text{R}_3\text{PbPbR}_3\) (\(\text{R} = \text{Me}, \text{Et}\)) were easily formed by the reduction of \(\text{R}_3\text{PbCl}\) by Al, Zn or Pb in alkaline solution. In the years 1938 and 1939, the method for \(\text{R}_3\text{PbPbR}_3\) synthesis based on the reaction of \(\text{R}_3\text{PbX}\) (\(\text{R} = \text{Alk}, \text{Ar}; \text{X} = \text{Cl, Br, I}\)) with Na in liquid ammonia\(^{316}\) began to develop. This fact was more surprising since even in 1947 Kocheshkov related to the formation of \(\text{R}_3\text{PbPbR}_3\) from a reduction of \(\text{R}_3\text{PbX}\) to \(\text{R}_3\text{Pb}\). He referred to the magnetochemical evidence of this fact given by Preckel and Selwood in 1940\(^{1375}\).

Bright red tetrakis(triphenylplumbyl)plumbane (Ph\(_3\)Pb\(_4\)Pb) obtained by the simultaneous hydrolysis and oxidation of Ph\(_3\)PbLi or Ph\(_2\)Pb by H\(_2\)O\(_2\) at low temperature by Willemsens and van der Kerk\(^{109,1376,1377}\) turned out to be the first organolead compound having several Pb–Pb bonds. Tetrakis(triphenylplumbyl)plumbane was an unstable compound which decomposed into Ph\(_3\)PbPbPh\(_3\) and Pb at storage. This indicated that the Pb–Pb–Pb bond system was quite unstable.

Gilman and Woods\(^{1330}\) and Leeper\(^{1378}\) in 1943 and Gilman and Leeper in 1951\(^{316}\) described the condensation of diorganyldihaloplumbanes with lithium and calcium. Foster and coworkers\(^{1189}\) (1939) carried out the reaction of Ph\(_3\)PbCl with [Na\(_4\)Pb\(_3\)].

For the synthesis of hexaaryldiplumbanes Gilman and coworkers\(^{1170,1185}\) (1939, 1952) and Podall and coworkers\(^{1379}\) (1959) used lithium aryls. In 1941, Bindschadler\(^{1190}\) obtained hexaphenyldiplumbane by the reaction of Ph\(_3\)PbNa with BrCH\(_2\)CH\(_2\)Br. Hein and Nebe\(^{1187}\) synthesized hexacyclohexyldiplumbane by the reaction of (c-C\(_6\)H\(_{11}\))\(_3\)PbNa with mercury. In 1931, Goldach\(^{1147}\) found that hexaisopropylplumbane was formed by the reaction of acetone with an Na–Pb alloy in sulfuric acid. Hexamethylplumbane was isolated by the reaction of Me\(_3\)PbCl with the adduct Me\(_2\)PbH·NH\(_3\) in liquid ammonia by Duffy and Holliday\(^{1359}\). In 1962, the same authors\(^{1363}\) observed that Me\(_3\)PbPbMe\(_3\) was the product of the thermal dehydrocondensation of Me\(_3\)PbH. In the first half of the 20th century, twenty hexaorganyldiplumbanes were synthesized by the methods described above.

All hexaalkyldiplumbanes described in the literature turned out to be thermally unstable liquids which decomposed on distillation. In 1923, Calingaert and coworkers reported that Et\(_3\)PbPbEt\(_3\) dissociated into the Et\(_3\)Pb\(^*\) radicals in dilute solutions\(^{1140}\). However, in concentrated solutions Et\(_3\)PbPbEt\(_3\) was the main species. The molecular weights found for R\(_3\)PbPbR\(_3\) with R = Ph\(^{1336,1380,1381}\), 2,4,6-Me\(_2\)C\(_6\)H\(_2\)\(^{1382}\) and c-C\(_6\)H\(_{11}\)\(^{1380}\) showed that
all the compounds corresponded to the formula given above. In particular, the thermolysis data of $\text{Et}_3\text{PbPbEt}_3$ obtained by Razuvaev and coworkers$^{1202,1295,1300,1383}$ and other investigations$^{894,1239,1384}$ corroborated the structure.

In contrast, hexaaryldiplumbanes were crystalline substances and were successfully purified by recrystallization.

All the $\text{R}_3\text{PbPbR}_3$ disproportionated with the formation of $\text{R}_4\text{Pb}$ in up to 90% yields$^{1170}$ and to Pb during the thermolysis. The starting temperature for this process depended on the nature of R. As for hexaalkyldiplumbanes, Calingaert and coworkers$^{1373}$ (1942) reported that they similarly decomposed even on distillation. According to Krause and Reissaus$^{1122}$ (1922), hexaaryldiplumbanes decomposed around their melting points of $117\,^\circ\text{C}$ (R = 3-MeC$_6$H$_4$) and $255\,^\circ\text{C}$ (R = 1-C$_{10}$H$_7$, 2,4,6-Me$_3$C$_6$H$_2$). Gilman and Bailie$^{1170}$ (1939) found that the thermal stability of $\text{R}_3\text{PbPbR}_3$ increased in the following order for R: Me $<$ Et $<$ Ph $<$ 3-MeC$_6$H$_4$ $<$ 4-MeC$_6$H$_4$ $<$ 4-MeOC$_6$H$_4$ $<$ 4-EtOC$_6$H$_4$ $\ll$ 2-MeC$_6$H$_4$ $<$ 2-MeOC$_6$H$_4$ $<$ 2-EtOC$_6$H$_4$ $<$ c-C$_6$H$_{11}$, 2,4,6-Me$_3$C$_6$H$_2$ $<$ 1-C$_{10}$H$_7$.

In 1951–1963, a number of investigations established that the thermolysis of hexaorganyldiplumbanes is catalyzed by silica$^{1298}$ (1951), activated charcoal$^{1299}$ (1956), and AlCl$_3$$^{1295}$ (1960), as well as by lead, which is formed during the thermolysis process$^{1300}$ (autocatalysis) and also by UV irradiation$^{1237}$ (1963).

In 1960, Razuvaev, Vyaazankin and Chshepetkova$^{903}$ found that $\text{Et}_3\text{PbPbEt}_3$ decomposed with a Pb–Pb bond cleavage in the presence of a catalytic amount of free-radical initiators such as benzoyl peroxide or tetraacetoxyplumbane at room temperature.

In 1942, Calingaert and coworkers$^{1373}$ showed that the 1 : 1 $\text{Me}_3\text{PbPbMe}_3$–$\text{Et}_3\text{PbPbEt}_3$ system gave at 100 $^\circ\text{C}$ a mixture of tetraalkyldiplumbanes of the following composition (%): $\text{Me}_4\text{Pb}$ (18), $\text{Me}_3\text{PbEt}$ (15), $\text{Me}_2\text{PbEt}_2$ (23), $\text{MePbEt}_3$ (31), $\text{Et}_4\text{Pb}$ (13). The yield of lead was 5% of the theoretical calculated value. These data indicated that during the thermolysis of hexaalkyldiplumbanes, alkyl radicals, the corresponding Pb-centered free radicals as well as dialkylplumbylenes Alk$_2$Pb were formed. Indeed, in 1959 Razuvaev and coworkers$^{1202}$ established that the thermal decomposition of hexaethylidiplumbane proceeded in accordance with equations 33 and 34.

$$\text{Et}_3\text{PbPbEt}_3 \rightarrow \text{Et}_4\text{Pb} + \text{Et}_2\text{Pb} $$

$$\text{Et}_2\text{Pb} \rightarrow 2\text{Et}^* + \text{Pb} $$

One year later$^{1203}$ they also studied the kinetics of the thermolysis of mixtures of $\text{Et}_3\text{PbPbEt}_3$ with $\text{Et}_4\text{Pb}$ or with $\text{Et}_2\text{Pb}$ at 135 $^\circ\text{C}$. The data confirmed that the process proceeded according to equations 33 and 34. As a result of their investigations they concluded that the thermal decomposition of $\text{Et}_3\text{PbPbEt}_3$ was different from its disproportionation reaction, which occurred in the presence of catalysts.

In 1962, Razuvaev and coworkers$^{1383}$ studied the decomposition of $\text{Ph}_3\text{PbPbPh}_3$ in solutions and in the presence of metal salts. Krebs and Henry$^{1337}$ studied the same reaction in boiling MeCOOH. Belluco and Belluco$^{1385}$ used a radiochemical method to show that the intermediate of the thermolysis was diphenylplumbylene Ph$_2$Pb. As early as 1860 Klippel$^{1217,1218}$ observed the photochemical decomposition of hexaorganyldiplumbanes. He found that $\text{Et}_3\text{PbPbEt}_3$ decomposed under light and isolated metallic lead.

In 1919, Krause and Schmitz$^{1120}$ observed that the yellow color of the solution of $\text{R}_3\text{PbPbR}_3$ (R = 2,4-Me$_2$C$_6$H$_3$) quickly disappeared under sunlight to give a white precipitate. They concluded that the compound obtained decomposed under light irradiation. Two years later Krause$^{1121}$ reported that hexacyclohexyldiplumbane was also decomposed by light, but it was absolutely stable in the dark. According to Krause and Reissaus$^{1122,1292}$ its molecular weight was decreased when it was diluted in benzene. Analogously, the
molecular weights of $R_3PbPbR_3$ with $R = Ph$ and 4-MeC$_6$H$_4$ depended on the concentration of their solutions. In 1923, Calingaert and coworkers$^{1140}$ reached the same conclusion. Lesbre and coworkers$^{1171}$ determined cryoscopically the molecular weight of hexamesityldiplumbane. However, EPR data indicated that this compound did not dissociate into free radicals $R_3Pb^*$ in benzene. An EPR study of $R_3PbPbR_3$ in the crystal and in solutions in C$_6$H$_6$ and CHCl$_3$ also did not detect any dissociation into free radicals$^{1385}$. Willemsens$^{109}$ tried to ascribe the difference between the EPR and the cryoscopic data to the imperfection of the latter method. However, this explanation does not stand up to criticism because an analogous decrease of the molecular weight in dilute solutions of hexaorganyldistannanes $R_3SnSnR_3$ was established as well by ebullioscopy (see Section III.H). It must be assumed that the decrease of the molecular weight of hexaorganyldiplumbanes in dilute solutions was not caused by their dissociation into free radicals $R_3Pb^*$, but was caused by their decomposition into $R_4Pb$ and $R_2Pb$. In accordance with that, Razuvaev and coworkers$^{1202}$ observed that the concentration of Et$_4Pb$, which was usually presented in Et$_3PbPbEt_3$ increased with time.

A pale yellow or pink color$^{109}$ indicated the presence of $R_2Pb$ in the solution of $R_3PbPbR_3$ in organic solvents.

In 1943, Hein and coworkers$^{1314}$ studied the auto-oxidation process of hexacyclohexyldiplumbanes and found that it took place only under ultraviolet irradiation. Obviously, this observation allowed Peters$^{1386}$ to patent the use of this compound for the preparation of photosensitive films in 1961. In 1961–1963, Aleksandrov and coworkers$^{1310,1387,1388}$ investigated in detail the oxidation of Et$_3PbPbEt_3$ by oxygen at low temperatures. The final products of this reaction were Et$_3PbOH$, C$_2$H$_6$, C$_2$H$_4$ and PbO, and Et$_3PbOPbEt_3$ was the intermediate. Aleksandrov and coworkers$^{1303}$ (1959) studied the oxidation of Et$_3PbPbEt_3$ by $\alpha$-hydroperoxoisopropylbenzene HOOCMe$_2$Ph and 1,4-bis($\alpha$-hydroperoxoisopropyl)benzene 1,4-(HOOCMe$_2$)$_2$C$_6$H$_4$, which led to Et$_3PbOH$ formation. In the first case Et$_3PbOOCCMe$$_2$Ph and in the second (Et$_3PbOOCCMe$$_2$)$_2$C$_6$H$_4$ were formed. The two compounds were the first organolead peroxides. The reaction of Et$_3PbPbEt_3$ with Et$_3PbOOCCMe$$_2$Ph led to Et$_3PbOPbEt_3$ and Et$_3PbOCMe$$_2$Ph. The oxidation product of hexaethyldiplumbane by benzoyl peroxide was Et$_3PbOOCPb$. In 1960, Razuvaev and coworkers$^{903}$ found that the Pb—Pb bond in Et$_3PbPbEt_3$ was cleaved by MeCCOOOH to give Et$_3PbOOCE$. The reactions studied above were nonradical because they could not be initiated by AIBN. This suggested that a concerted cleavage of the Pb—Pb bond took place in the cyclic intermediate as shown in structure 1. According to Austin$^{1253}$ (1931) and Bähr$^{1255}$ (1947), the $R_3PbPbR_3$ oxidation by KMnO$_4$ led to $R_3PbOH$. In 1959, Podall and coworkers$^{1379}$ established that the hydrogenolysis of Ph$_3PbPbPh_3$ led to metallic lead formation, as well as to Ph$_4Pb$ or Ph$_2$ (depending on the reaction conditions and the catalyst used).
As early as in 1856, Klippe\textsuperscript{1217,1218} carried out the Pb–Pb bond cleavage by halogens. He found that hexaethyl- and hexaisoamyldiplumbane reacted easily with iodine in ether, to form R\textsubscript{3}PbI (R = Et, i-Am). In 1919, Krause and Schmitz\textsuperscript{1120}, by reacting R\textsubscript{3}PbPbR\textsubscript{3} (R = 2,5-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3}) with bromine, confirmed that hexaorganodiplumbanes decomposed by halogens. When pyridine was used as the solvent, R\textsubscript{3}PbBr was formed, but when chloroform was used the product was R\textsubscript{2}PbBr\textsubscript{2}. After 2–3 years, in the Krause laboratory, the cleavages of R\textsubscript{3}PbPbR\textsubscript{3} by bromine or iodine when R = c-C\textsubscript{6}H\textsubscript{11}\textsuperscript{1121}, Ph or 4-MeC\textsubscript{6}H\textsubscript{4}\textsuperscript{1122} were studied and the corresponding R\textsubscript{3}PbX (X = Br, I) were obtained in good yield. In the period 1931–1961, some reports had appeared about the halogenation of the R\textsubscript{3}PbPbR\textsubscript{3} series with R = Ar\textsuperscript{791,1170,1389}, PhCH\textsubscript{2}CH\textsubscript{2}\textsuperscript{833}, c-C\textsubscript{6}H\textsubscript{11}\textsuperscript{791,1187}. Depending on the reaction conditions R\textsubscript{3}PbX, R\textsubscript{2}PbX\textsubscript{2} and PbX\textsubscript{2} were prepared in different ratios.

In 1964, Willemsens and van der Kerk\textsuperscript{1377} found that reaction of (Ph\textsubscript{3}Pb)\textsubscript{4}Pb with iodine led to Ph\textsubscript{3}PbI and PbI\textsubscript{2}, thus confirming the branched structure of the compound. Remarkably, even in 1947 Kocheshkov\textsuperscript{156} considered the Pb–Pb bond cleavage in R\textsubscript{3}PbPbR\textsubscript{3} as an oxidation reaction of trivalent lead (R\textsubscript{3}Pb) which gave the tetravalent R\textsubscript{3}PbX derivatives.

In 1923, Calingaert and coworkers\textsuperscript{1140} showed that Et\textsubscript{3}PbPbEt\textsubscript{3} was cleaved by HCl with the formation of Et\textsubscript{3}PbCl, PbCl\textsubscript{2} and C\textsubscript{2}H\textsubscript{6}. In 1931, Austin\textsuperscript{1262} obtained (2-MeC\textsubscript{6}H\textsubscript{4})\textsubscript{3}PbBr by the cleavage of hexa-ortho-tolyldiplumbane by HBr.

In 1939, the R\textsubscript{3}PbPbR\textsubscript{3} cleavage by hydrohalic acids was frequently used to form R\textsubscript{3}PbX\textsuperscript{791,1170,1254}. Belluco and coworkers\textsuperscript{1390} (1962) as well as Krebs and Henry\textsuperscript{1337} (1963) concluded that the reaction of R\textsubscript{3}PbPbR\textsubscript{3} with hydrohalic acid was not a single-stage process because R\textsubscript{3}PbH was not formed. In their opinion, the process was more complicated and could be described by Scheme 2 (for X = Cl). The general equation of the process was equation 35.

\[
\begin{align*}
R_3PbPbR_3 & \xrightarrow{[R_3Pb]} R_4Pb + [R_2Pb] \\
R_4Pb + HX & \xrightarrow{} R_3PbX + RH \\
[R_2Pb] + 2HX & \xrightarrow{} R_2PbX_2 + 2RH
\end{align*}
\]

SCHEME 2

\[
R_6Pb_2 + 3HX \xrightarrow{} R_3PbX + PbX_2 + 3RH \tag{35}
\]

In 1964, Emeleus and Evans\textsuperscript{1391} found that the C–Pb bond was the first to be cleaved and the Pb–Pb bond was cleaved next in the reactions of HCl with R\textsubscript{3}PbPbR\textsubscript{3}. The process of formation of PbCl\textsubscript{2} was unclear and hence the reaction mechanism was represented by the two equations 36 and 37.

\[
\begin{align*}
R_3PbPbR_3 + 2HCl & \xrightarrow{} ClR_2PbPbR_2Cl \xrightarrow{} R_4Pb + PbCl_2 \tag{36} \\
R_3PbPbR_3 + 3HCl & \xrightarrow{} R_3PbPbCl_3 \xrightarrow{} R_3PbCl + PbCl_2 \tag{37}
\end{align*}
\]

The data of Gilman and Apperson\textsuperscript{1239} (1939) served as proof of the intermediate formation of ClR\textsubscript{2}PbPbR\textsubscript{2}Cl, so they proposed that the reaction of R\textsubscript{3}PbPbR\textsubscript{3} with AlCl\textsubscript{3} could be described by equation 38.

\[
R_3PbPbR_3 + AlCl_3 \xrightarrow{} ClR_2PbPbR_2Cl \xrightarrow{} R_4Pb + PbCl_2 \tag{38}
\]
According to a later point of view of Gilman and coworkers\textsuperscript{1129}, the mechanism of the reaction of hexaorganyldiplumbanes with aluminum chloride can be represented by Scheme 3, which is summarized by equation 39.

\[
\begin{align*}
R_3\text{PbPbR}_3 & \longrightarrow R_4\text{Pb} + R_2\text{Pb} \\
R_2\text{Pb} + 2\text{AlCl}_3 & \longrightarrow \text{PbCl}_2 + 2\text{RAICl}_2 \\
R_4\text{Pb} + \text{AlCl}_3 & \longrightarrow \text{R}_3\text{PbCl} + \text{RAICl}_2
\end{align*}
\]

\textbf{SCHEME 3}

\[R_3\text{PbPbR}_3 + 3\text{AlCl}_3 \longrightarrow R_3\text{PbCl} + \text{PbCl}_2 + 3\text{RAICl}_2 \quad (39)\]

Scheme 3 did not require the initial cleavage of the C–Pb bond by AlCl\textsubscript{3} as well as the intermediate formation of ClIR\textsubscript{2}PbPbR\textsubscript{2}Cl, which has not yet been identified.

In 1952, Kocheshkov and Panov\textsuperscript{1281} found that Ar\textsubscript{3}PbPbAr\textsubscript{3} (Ar = 4-MeC\textsubscript{6}H\textsubscript{4}) was cleaved by HNO\textsubscript{3} to form Ar\textsubscript{3}PbNO\textsubscript{3}. An excess of HNO\textsubscript{3} led to Ar\textsubscript{2}Pb(NO\textsubscript{3})\textsubscript{2}.

Razuvaev and coworkers\textsuperscript{903} showed that Pb(OOCMe)\textsubscript{4} cleaved Et\textsubscript{3}PbPbEt\textsubscript{3} in benzene media with a formation of Et\textsubscript{3}PbOOCMe in 1960. In 1963, Krebs and Henry\textsuperscript{1337} found that the Pb–Pb bond in R\textsubscript{3}PbPbR\textsubscript{3} was cleaved by the reaction of MeCOOH, MeCOSH, \textit{S} and BrCH\textsubscript{2}CH\textsubscript{2}Br. In 1943, Hein and coworkers\textsuperscript{1314} studied the reaction of hexacyclohexyldiplumbane with polyhalomethanes. The organolead products of this reaction were R\textsubscript{3}PbX, R\textsubscript{2}PbX\textsubscript{2} (R = c-C\textsubscript{6}H\textsubscript{11})\textsuperscript{1392} and PbX\textsubscript{2}.

Krohn and Shapiro\textsuperscript{1392} (1951) patented the cleavage reaction of R\textsubscript{3}PbPbR\textsubscript{3} by alkyl halides as a method for the preparation of R\textsubscript{4}Pb (R = Alk) in a high yield from R\textsubscript{3}PbPbR\textsubscript{3} and RX (X = Br, I) at 20–100°C. In 1960, Razuvaev, Vyazankin and their coworkers\textsuperscript{1293,1389} investigated thoroughly the reaction of hexaethyldiplumbane with organobromides. They found that the reaction of Et\textsubscript{3}PbPbEt\textsubscript{3} with EtBr, BrCH\textsubscript{2}CH\textsubscript{2}Br and BrCH\textsubscript{2}CHBrCH\textsubscript{3} led to Et\textsubscript{4}Pb as well as to Et\textsubscript{3}PbBr, Et\textsubscript{2}PbBr\textsubscript{2}, PbBr\textsubscript{2} and Pb in heptane media at 40–70°C. When used in catalytic amounts, the bromides initiated the disproportionation of Et\textsubscript{3}PbPbEt\textsubscript{3} into Et\textsubscript{4}Pb and Pb.

In 1860, Klippel\textsuperscript{1217,1218} found that the reaction of Et\textsubscript{3}PbPbEt\textsubscript{3} with AgNO\textsubscript{3} in alcoholic media led to Et\textsubscript{3}PbNO\textsubscript{3} and metallic silver. According to Krause and Grosse\textsuperscript{155}, during the reaction of hexaorganyldiplumbanes with AgNO\textsubscript{3} in alcohols at low temperature the reaction mixture became green colored, which was attributed to the formation of R\textsubscript{3}PbAg. In 1960–1961, Belluco and coworkers\textsuperscript{1374} and Duffy and Holliday\textsuperscript{1359} studied the reaction of Et\textsubscript{3}PbPbEt\textsubscript{3} with an alcoholic solution of AgNO\textsubscript{3} at room temperature, from which triethylplumbyl nitrate and metallic silver were isolated. Thus, they reproduced the results of Klippel\textsuperscript{1217,1218} one hundred years later.

In 1931–1962 the reactions of the R\textsubscript{3}PbPbR\textsubscript{3} cleavage by chlorides of Cu\textsuperscript{1393,1394}, Au\textsuperscript{1394}, Hg\textsuperscript{1394}, \textit{At}\textsuperscript{1239,1395}, \textit{Tl}\textsuperscript{1176} and \textit{Fe}\textsuperscript{1256,1394} were studied. In 1939, Gilman and Bailie\textsuperscript{1170} found that sterically hindered R\textsubscript{3}PbPbR\textsubscript{3} with R = 2-MeC\textsubscript{6}H\textsubscript{4}, 2,4,6-Me\textsubscript{3}C\textsubscript{6}H\textsubscript{2} and c-C\textsubscript{6}H\textsubscript{11} were cleaved with MgI\textsubscript{2} (Mg itself did not apparently exhibit any effect) giving R\textsubscript{3}PbI. Unlike this, the reaction of R\textsubscript{3}PbPbR\textsubscript{3} having no bulky substituents with a MgI\textsubscript{2}–Mg system led to R\textsubscript{4}Pb, Pb and RMgI. Probably, it proceeded through an intermediate formation of R\textsubscript{3}PbI and R\textsubscript{2}Pb. In 1963, Belluco and coworkers\textsuperscript{1396} studied the cleavage of Et\textsubscript{3}PbPbEt\textsubscript{3} by chlorides and oxychlorides of sulfur. It was found that the yield of Et\textsubscript{3}PbCl was lower as the nucleophilicity of the sulfur atom increased, i.e. in the order: SO\textsubscript{2}Cl\textsubscript{2} > SOCl\textsubscript{2} > SCl\textsubscript{2} > S\textsubscript{2}Cl\textsubscript{2}. 
An unexpected addition of $\text{R}_3\text{PbPbR}_3$ to multiple bonds was reported by Gilman and Leeper\textsuperscript{316} in 1951. They suggested that the reaction of $\text{Ph}_3\text{PbPbPh}_3$ with maleic anhydride led to $2,3\text{-bis}(\text{triphenylplumbyl})\text{succinic anhydride}$. However, in 1964, Willemsens\textsuperscript{109} noted that the product of the reaction was apparently diphenylplumbylen maleate formed from an admixture of maleic acid, which was present in its anhydride. This conclusion was corroborated by the absence of any reaction of $\text{Ph}_3\text{PbPbPh}_3$ with pure maleic anhydride. The formation of diphenylplumbylen maleate (along with $\text{Ph}_4\text{Pb}$) was assumed to result from decomposition of an intermediate product bis(tribenzyllplumbyl) maleate.

In 1941, Bindschadler and Gilman\textsuperscript{1182} showed that $\text{PhLi}$ cleaved $\text{Ph}_3\text{PbPbPh}_3$ with formation of $\text{Ph}_3\text{PbLi}$ and $\text{Ph}_4\text{Pb}$. Gilman and Bailie\textsuperscript{791,1170} (1939) and Foster and coworkers\textsuperscript{1189} (1939) found that the reaction of $\text{Ar}_3\text{PbPbAr}_3$ with $\text{Na}$ in liquid ammonia to $\text{Ar}_3\text{PbNa}$, whose solution was dark-red colored. It was found in 1941–1953 that hexaphenyldiplumbane was similarly cleaved by alkali and alkali earth metals (Li, K, Rb, Ca, Sr, Ba) in liquid ammonia at the Gilman\textsuperscript{316,1182,1378} laboratory. Hein and coworkers\textsuperscript{118,1397} (1942, 1947) found that sodium in ether media cleaved hexacyclohexyldiplumbane. In 1962, Tamborski and coworkers\textsuperscript{1398} showed that $\text{Ph}_3\text{PbPbPh}_3$ was cleaved by $\text{Li}$ in THF to form $\text{Ph}_3\text{PbLi}$ in a high yield.

In 1922, Krause and Reissaus\textsuperscript{1122} succeeded in isolating two monomers of diarylplumbylenes $\text{Ar}_2\text{Pb}$ ($\text{Ar} = \text{Ph}, 2\text{-MeC}_6\text{H}_4$) in about 4% yield by the reaction of $\text{PbCl}_2$ with $\text{ArMgBr}$ at 2°C. For a long period they were the only representatives of organic compounds of two-valent Pb. Unlike analogous compounds of the other elements of the silicon subgroup $\text{R}_2\text{M}$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$), diarylplumbylenes could not be transformed into oligomers or polymers of the ($\text{R}_2\text{M}$)$_n$ type, but they easily disproportionated into $\text{Ar}_4\text{Pb}$ and $\text{Pb}$ at about 2°C. These data became additional proof of the inability of lead to form chains longer than $\text{Pb}-\text{Pb}$.

### K. Biological Activity and Application of Organolead Compounds

Even the first investigators of organolead compounds encountered its harmful physiological action. Thus, for example, in 1860 Klippel\textsuperscript{1217,1218} reported that the vapors of hexaethylidiplumbane affected the mucous membranes and respiratory tract and caused a lachrymatory action and prolonged cold. Similarly, the hexaisoamyldiplumbane vapors irritated the mucous membranes. Klippel even tasted this substance and found that it caused a long-time scratching irritation of his tongue and even of his throat. It must be assumed that trialkylplumbanols, which were formed in the reaction of $\text{R}_3\text{PbPbR}_3$ with moisture from the air and $\text{CO}_2$, caused all these symptoms. Krause and Pohland\textsuperscript{1123} (1922) felt the irritation action of the $\text{R}_3\text{PbX}$ ($\text{R} = \text{Alk}$) dust. Browne and Reid\textsuperscript{1250} (1927) and Gilman and coworkers\textsuperscript{1248,1399} (1930, 1931) found that the organolead compounds of the $\text{Et}_3\text{PbX}$ type showed sternutatory and irritating actions and caused rhinitis symptoms.

In the end of the 1940s McCombie and Saunders synthesized large amounts of $\text{Et}_3\text{PbCl}$ and felt the symptoms of a severe attack of influenza, which, however, disappeared at night and returned by day\textsuperscript{971}. High toxicity was the main effect of organolead compounds on living organisms. Obviously, the first researchers in the field felt this. It is noteworthy that the organolead derivatives turned out to be more toxic than inorganic lead compounds and even pure lead. From 1925 the toxicity of tetraethyllead started to be studied thoroughly because of its wide application as an antiknock of motor fuels\textsuperscript{1400,1401}. The toxic and physiological action of $\text{Et}_4\text{Pb}$ and other organolead compounds was summarized in several monographs and reviews\textsuperscript{109,130,154,1402–1405}. The majority of these investigations were carried out in the second half of the 20th century.

Already in the first half of the 20th century, it was established that the first symptoms of $\text{Et}_4\text{Pb}$ poisoning were a drop in body temperature, a marked decrease in blood pressure,
sleeplessness, headaches, nightmares and hallucinations. Higher doses of tetraethyllead caused insanity. The indicated emotional and nervous deviations indicated that the lipid-soluble Et₄Pb was absorbed rapidly by the soft and nervous tissues and concentrated in the latter. In 1925, Norris and Gettler¹⁴⁰⁶ found that a high concentration of lead occurred in brain, liver and kidney tissues. It was also established that tetraethyllead was able to penetrate human or animals through the integuments or by breathing its vapors. Extra large doses of Et₄Pb (in comparison with other highly toxic substances) caused a lethal outcome. Tetraethyllead was used as a poison in the mystery novel of Ellery Queen ‘The Roman Hat Mystery’. The chronic effect of small doses of tetraethyllead due, for instance, to long respiration of its vapors or a lasting contact with its solutions in motor fuel (ethylated gasoline) resulted in serious poisoning. Removal of tetraethyllead and its metabolites from the body occurred very slowly owing to the resistance of Et₄Pb to hydrolysis and the insolubility of the resulting inorganic lead compounds in tissue liquids. Like tetraalkylstannanes, the toxicity of Et₄Pb depended on the cleavage of one C—Pb bond in vivo which resulted in the formation of the highly toxic cation Et₃Pb⁺.¹⁴⁰⁷

An international arms race started shortly after World War II and was concerned with the creation of new types of chemical weapons, which inspired many prominent scientists in the USA, England, USSR and other countries to conduct investigations in this field. Organolead compounds were also involved in such studies and a search of their suppressing effect on human disturbances was started. In 1939–1941, Saunders in England carried out secret and extensive investigations for the Ministry of Supply with the aim of creating chemical weapons based on organolead compounds, having stertoratory and irritation action. Detailed data about these investigations were published¹¹⁴⁹,¹¹⁵⁰,¹³²⁰,¹⁴⁰⁸–¹⁴¹⁰ in 1946–1950. They synthesized many compounds of the R₃PbX and R₂PbX₂ series. Remarkably, the authors and their coworker-volunteers tested the effects on themselves. They entered a special room, where an alcoholic solution of a tested compound in several concentrations was dispersed. The activity of the compound was determined by the time that the investigators could stay in the room. It was established that the derivatives of the R₃PbX (R = Alk; X = Hal, OH, OR⁰, OOCR⁰, SR’, NHSO₂R’, OCN, CN, SCN, N(CO)₂C₆H₄-o etc.) type were stertorators and irritating agents. The influence rate of the alkyl substituents R and X on the irritating effect of R₃PbX⁹⁷¹ was also studied. On the whole, the activity of these compounds was increased for the following R-substituents in the order: Me < Et < Bu < Pr. Hence, the Pr₃PbX compounds turned out to be the most active. Their representatives with X = OOCH=CH₂, OOCCH=CHMe, OOCCH₂CH₂Cl, N(CO)₂C₆H₄-o, NHSO₂C₆H₄Me-p and NHSO₂Me were the most effective among the compounds mentioned above, and their unbearable concentration in air was lower than 1 ppm. The most powerful stertorators were Pr₃Pb(NHSO₂R with R = CH=CH₂ and Ph, with an unbearable concentration of 0.1 ppm. All the investigators ran out of the room after 40 seconds when the compound with R = Ph in the mentioned concentration was spread. Compounds of Ar₃PbX and R₂PbX₂ type had no effect at all or a little stertoratory action. It is noteworthy that the investigations of McCombie and Saunders, which had doubtless nonhumane but pragmatic aims, made a valuable contribution to the chemistry of organolead compounds. Their work resulted in the synthesis of many new substances of this class and led to new developments or improvements of their preparative methods. Analogous investigations were carried out in Gilman’s laboratory on the other side of the Atlantic Ocean. The results were published in an article by Gilman, Spatz and Kolbezen¹³⁰⁸ only in 1953.

In 1928–1929, Evans and coworkers¹⁴¹¹ and Krause¹¹²⁶ started to investigate the possible use of organolead compounds as medicines, mainly against cancer.

In 1938, Schmidt¹³⁰⁴ examined their application against cancer from a historical aspect. He obtained many complex lead compounds of different types which did
not have the C—Pb bond. Along with them a series of organolead compounds \( \text{Me}_2\text{PbCl}_2 \), \( \text{Me}_2\text{Pb} (\text{OH})_2 \), \( \text{Me}_3\text{PbCl} \), \( \text{Ph}_4\text{Pb} \), \( (2.5\text{-Me}_2\text{C}_6\text{H}_3)_3\text{PbPb} (\text{C}_6\text{H}_3\text{Me}_2-2,5)_3 \), \( \text{Ph}_2\text{Pb(OOCMe)}_2 \), \( \text{Ph}_2\text{Pb(OH)}_2 \), \( (p-O_2\text{N}\text{C}_6\text{H}_4)_2\text{Pb} (\text{OH})_2 \) and \( (p-H_2\text{N}\text{C}_6\text{H}_4)_2\text{Pb(OH)}_2 \) was synthesized. These compounds were transformed into the corresponding water-soluble Na-arylpyridine compounds by the reaction with Na-pyridinodisulfonate.

Carcinogenic activities of the seventeen synthesized compounds mentioned above were studied on mice carcinoma and partially on Brown–Pearce tumors. From all the compounds studied only the above-mentioned diarylsulfonatoplumbanes had a definite carcinogenic action. Testing radioactive lead compounds did not confirm the expected high activity. However, comparatively insufficient investigations in this field as well as studies of the effect of organolead compounds on plants and the possibility of using them in plant cultivation, as well as their use as components of antifouling paints, appeared only after 1970\textsuperscript{1412}. Nevertheless, even in 1952–1953 \( N \)-triethylplumbyl derivatives of phthalimide and phthalohydrazide were patented as fungicides\textsuperscript{1344,1345}. In 1959, a patent for the application of triethyl(diisobutylamino)plumbane as a herbicide\textsuperscript{1346} was granted.

Practical use of organolead compounds will be hardly extended due to their high toxicity and the possibility of sustainable pollution of the environment by the lead compounds. In this connection it must be indicated that the production of tetraethyllead, which achieved 270,000 tons by 1964 only in the USA, started to be reduced at the end of the 20th century.

In the second half of the past century, there were numerous patents dealing with the application of organolead compounds as polymerization catalysts or as pesticides\textsuperscript{109}. However, they did not find any practical application. Regarding the same is true of \( \text{Me}_4\text{Pb} \), which began to be used as an antiknock additive along with \( \text{Et}_4\text{Pb} \) in the 1960s.

**V. CONCLUSION**

The concepts and development of the chemistry of organic compounds of Group 14 of the Periodic Table heavy elements, i.e. germanium, tin and lead, are presented in a historical sequence in the earlier sections of this chapter. We have tried to tell the reader not only about the achievements of researchers in this field of organometallic chemistry, but also to give the names of pioneer researchers and their close successors. The development of organolead and organotin chemistry proceeded almost simultaneously and their study was actually synchronous in the middle of the 19th century. The investigations of organogermanium compounds were started in 1925.

The research interests in organic compounds of the elements above were not the same throughout the historical development of organometallic chemistry. The tin derivatives turned out to be the focus of interest in comparison with organogermaniums, which were less attractive, while organolead compounds attracted the least attention of scientists. Table 3 demonstrates these facts. The number of publications devoted to organic compounds of the elements of the silicon subgroup (mezoids) published in 1966 and in 1969\textsuperscript{47} are presented. In these years the main fields of practical application of organic compounds of the silicon subgroup were determined.

It is not difficult to see that the number of published works generally corresponds to the importance of the elements in various fields of human activity. It is remarkable that the chemistry of organotin compounds was the most intensively developed in these years. In the 1960s, the rate of development of organosilicon chemistry was lower than that of the chemistry of organogermanium compounds. The dynamics of the research and progress in the field of organolead compounds both in the previous and subsequent years was relatively minimal. At the same time organolead compounds, the first of them being tetraethyllead, found practical application. There was a time when the industrial production of this antiknock additive of motor fuels exceeded the total output production...
TABLE 3. The number of investigations devoted to organic compounds of the elements of the silicon subgroup, carried out in 1966 and in 1969

<table>
<thead>
<tr>
<th></th>
<th>1966</th>
<th>1969</th>
<th>Relative increase in the number of publications (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>615</td>
<td>823</td>
<td>34</td>
</tr>
<tr>
<td>Ge</td>
<td>148</td>
<td>208</td>
<td>40</td>
</tr>
<tr>
<td>Sn</td>
<td>207</td>
<td>537</td>
<td>159</td>
</tr>
<tr>
<td>Pb</td>
<td>71</td>
<td>82</td>
<td>15</td>
</tr>
</tbody>
</table>

of all the organotin and organogermanium compounds. At the end of the 20th century, organogermanium compounds found practical application as biologically active products.

Laboratory research on organic compounds of the silicon subgroup elements showed that they ought to be divided into two subgroups (dyads) in accordance with their similarity in chemical properties and biological activity. Silicon and germanium derivatives were placed in the first one while the tin and lead derivatives belong to the second.

Unlike this chapter, the history of organogermanium, organotin and organolead compounds has no end and will probably never have one. The initiation of various new research tendencies in this field of metalloorganic chemistry, which took shape at the end of the 20th and beginning of the 21st centuries, is a witness to this. Some of them are mentioned in Chapter 2. Nevertheless, it must be acknowledged with sorrow that the number of publications devoted to organic compounds of the elements reviewed in this chapter among the organometallic papers is decreasing more and more due to the rapidly growing interest in the transition metal organic derivatives and their complexes.

While working on this chapter, the first author recollected with pleasure, pride and a slight sadness his close acquaintance and friendly connections with many of the heroes of this narration whom he had met not only at international forums or in laboratories throughout the world, but also at home and in other everyday situations. They include H. Gilman, E. Rochow, R. West, D. Seyferth and A. MacDiarmid (USA); M. Schmidt, W. Neumann and H. Schmidbaur (Germany); K. A. Kocheshkov, A. N. Nesmeyanov, G. A. Razuvayev, O. M. Nefedov, V. F. Mironov, M. M. Koton, S. P. Kolesnikov and N. S. Vyazankin (Russia). At the same time, these reminiscences caused some sorrow in that the age of the author has become historical.

The authors cordially thank Dr. Andrey Fedorin for his extensive and valuable assistance in correcting and preparing the manuscript for publication.

This chapter is dedicated to friends and colleagues whose contribution to the organometallic chemistry of the last century was outstanding.

VI. REFERENCES

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CHAPTER 5

Gas-phase chemistry and mass spectrometry of Ge-, Sn- and Pb-containing compounds

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I. INTRODUCTION

Unlike the lighter elements of group 14, namely C and Si, considerably less is known about the gas-phase chemistry and mass spectrometry of Ge-, Sn- and Pb-containing compounds. The poor volatility of the majority of Ge, Sn and Pb compounds has been a major drawback for studies at or near room temperature. In the case of mass spectrometry, the additional problems associated with thermal stability and the complex isotopic patterns displayed by these elements have traditionally restricted the routine use of mass spectra as analytical tools for identifying typical organometallic derivatives of Ge, Sn and Pb. However, the variety of ionization techniques presently available, such as electron ionization (EI), chemical ionization (CI), fast atom bombardment (FAB), matrix assisted laser desorption ionization (MALDI) and electrospray (ESI), among others, coupled with the high resolution and high mass capabilities of modern instruments can nowadays circumvent many of the early problems. Thus, mass spectrometry can increasingly provide a complementary approach for the characterization of organometallic compounds containing elements of group 14 of the periodic table. This can be exemplified by germenes and stannanes, an area that has enjoyed phenomenal growth and interest in recent years, because of their potential applications as synthons in organometallic and organic chemistry. While many germenes have been characterized by a combination of spectroscopic techniques such as NMR and IR, new advances in this area are increasingly taking full advantage of the versatility of modern mass spectrometry for more complete structural identification.

The small number of fundamental mass spectrometric studies on Ge, Sn and Pb derivatives also accounts for our poor knowledge of their thermochemistry. Heats of formation, ionization energies, bond energies and electron affinities of even simple Ge, Sn and Pb species are still scarce and subject to considerable uncertainty, as illustrated in the most recent NIST database.

In spite of the limitations imposed by volatility, studies related to the gas-phase chemistry of simple organogermanes have grown in number in the last two decades because of their implications regarding deposition of Ge through chemical vapor deposition processes (CVD) aimed at surface modifications and film formation. Thus, the characterization of the elementary reactions responsible for the mechanism of these processes has become an important area of research. Likewise, the characterization of Ge clusters by gas-phase techniques has also become a growing field because of the relevance of clusters to semiconductors. Moreover, the detailed outcome of gas-phase reactions involving organostannanes and Pb compounds are extremely useful in mapping out the environmental effects of these elements.

Three main topics relevant to the gas-phase chemistry of Ge, Sn and Pb derivatives are discussed in the present chapter: (a) the mass spectrometry related to organometallic compounds of group 14 with particular emphasis on the more general aspects; (b) the gas-phase ion chemistry comprising the thermochemistry, structure and reactivity of ions; and (c) gas-phase reactions involving neutral species.

II. MASS SPECTROMETRY OF Ge, Sn AND Pb DERIVATIVES

The principles of mass spectrometry as applied to organic compounds have been extensively investigated and are well described according to different functional groups in some of the classical literature of the field. By comparison, there are few systematic approaches towards the interpretation of mass spectral fragmentations for the organometallic derivatives of Ge, Sn and Pb. As a rule, the mass spectra of these organometallic compounds display in high abundance fragment ions that retain the metal element. This is a consequence of the much weaker E−H, E−C or E-halogen bond energies (E = Ge, Sn, Pb) when compared with the carbon analogs, and the lower ionization energy of the
corresponding fragment containing Ge, Sn or Pb. Some of the early reviews\textsuperscript{10,11} on the subject were based mostly on the mass spectra of the trialkyl or tetraalkyl derivatives of these elements. Unfortunately, most of the early studies lacked the information that can be obtained from more recent experimental techniques such as tandem mass spectrometry that are essential for the full understanding of fragmentation processes and ion structures. Nevertheless, the mass spectrometry of organostannanes is probably the best studied among these compounds because of the increasing use of Sn reagents in organic synthesis.

As indicated above, the mass spectra of Ge, Sn and Pb organometallic compounds are uniquely characterized by fragment ions bearing the metal element. These ions are recognized by the distinct isotopic composition of the higher elements of group 14. Several isotopes of Ge, Sn and Pb are known to occur with significant natural abundances, as shown in Tables 1–3. Thus, peaks corresponding to ions containing any of these elements are responsible for characteristic isotope patterns such as those displayed in Figures 1–3.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>70</th>
<th>72</th>
<th>73</th>
<th>74</th>
<th>76</th>
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<tr>
<td>Natural abundance (%)</td>
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<td>27.4</td>
<td>7.8</td>
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<tr>
<td>Natural abundance (%)</td>
<td>14.7</td>
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<td>24.3</td>
<td>8.6</td>
<td>32.4</td>
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<tr>
<th>Isotope</th>
<th>204</th>
<th>206</th>
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<th>208</th>
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<tr>
<td>Natural abundance (%)</td>
<td>1.4</td>
<td>24.1</td>
<td>22.1</td>
<td>52.4</td>
</tr>
</tbody>
</table>

**FIGURE 1.** Typical isotopic pattern (including that of the $^{13}$C) encountered for the Ph$_3$Ge$^+$ fragment ion in the mass spectra of a typical Ph$_3$GeX compound
FIGURE 2. Typical isotopic pattern (including that of the $^{13}$C) encountered for the Ph$_3$Sn$^+$ fragment ion in the mass spectra of a typical Ph$_3$SnX compound.

FIGURE 3. Typical isotopic pattern (including that of the $^{13}$C) encountered for the Ph$_3$Pb$^+$ fragment ion in the mass spectra of a typical Ph$_3$PbX compound.
These patterns become considerably more complex for species containing more than one atom of Ge, Sn or Pb, or a mixture of these metals, leading to potentially very dense isotopic distribution as illustrated in Figure 4 for the \( \text{Ge}_2(\text{OMe})_5^{+} \) ion containing two atoms of Ge. An even more complex pattern often results from ions differing in their chemical composition by one or two hydrogens, as is often the case for compounds containing alkyl groups bonded directly to the metal element. In these cases, the use of high resolution mass spectrometry and careful analysis of relative intensities becomes essential for the full elucidation of the fragmentation patterns.

A second important characteristic of the mass spectra of Ge-, Sn- and Pb-containing compounds is the tendency to display abundant peaks corresponding to the M(IV) and M(II) oxidation states of these elements.

### A. Mass Spectra of Simple Hydrides of Ge, Sn and Pb

The first mass spectrometric studies of the simple hydrides\(^{12}\) date back to the 1950s, and were directed towards the elucidation of important parameters such as ionization and bond energies of GeH\(_4\), SnH\(_4\) and PbH\(_4\). However, a complete analysis and characterization of the mass spectra of germane, stannane and plumbane emerged from the work of Saalfeld and Svec\(^{13,14}\). For all three hydrides, spectra obtained in a sector type mass spectrometer by electron ionization at 60 eV, or higher, revealed negligible peaks corresponding to the molecular ions, \( \text{EH}_4^{+*} \). The observed fragmentation patterns were similar to those encountered in silane with the \( \text{EH}_3^{+} \) and \( \text{EH}_2^{+*} \) fragments as the most abundant species in the mass spectra. The relative abundance of the fragment ions in the mass spectra
obtained at 60 eV follows the order:

\[
\begin{align*}
\text{GeH}_4 & > \text{GeH}_2^{+•} > \text{GeH}_3^+ > \text{Ge}^{+•} > \text{GeH}^+ \\
\text{SnH}_4 & > \text{SnH}_3^+ > \text{Sn}^{+•} > \text{SnH}_2^{+•} > \text{SnH}^+ \\
\text{PbH}_4 & > \text{PbH}_2^{+•} > \text{PbH}_3^+ > \text{Pb}^{+•} > \text{PbH}^+
\end{align*}
\]

While the actual relative abundances are often dependent on the type of mass spectrometer on which the spectrum is recorded because of the time window that is used to sample the ions, it is important to emphasize the significant contribution of the \(\text{EH}^+\) fragment and of the neat metal cation in the recorded spectra. In fact, the presence of the bare metal cation and of \(\text{EH}^+\) among the fragment ions is a common feature in the mass spectra of organogermaines and organostannanes.

The mass spectra of \(\text{GeH}_4\) and \(\text{SnH}_4\) obtained by field ionization\(^{15}\) are simpler with the \(\text{EH}_3^+\) fragments as the base peaks. Since this is a soft ionization method, fragmentation is considerably reduced. For example, no metal cation fragment is observed and the abundance of the \(\text{EH}^+\) is also considerably less than that observed by electron ionization. This technique also allows for the observation of \(\text{GeH}_5^+\) and \(\text{SnH}_5^+\), a fact that is rare and has prevented the characterization of the proton affinity of these substrates (see below).

The determination of accurate and reliable values for the ionization energy (IE) of these simple hydrides has proved a difficult experimental task. Yields of the corresponding molecular ions \(\text{XH}_4^{+•}\) are very low and their ground state geometries are expected to differ considerably from the neutral species because of Jahn–Teller distortions\(^{16,17}\), raising doubts about the true adiabatic ionization energies obtained from experiments. For \(\text{GeH}_4\), the most comprehensive photoionization study\(^{18}\) yields an IE \(\leq 10.53\) eV but the actual value may be as low as 10.44 eV. This value is well below the 11.3 eV threshold value determined from photoelectron spectroscopy\(^{19–21}\). For \(\text{SnH}_4\), photoelectron spectroscopy\(^{19}\) yields a threshold value of 10.75 eV that is probably more representative of the vertical ionization energy, and thus higher than the adiabatic IE. No values are available for \(\text{PbH}_4\).

The mass spectra of some higher hydrides such as \(\text{Ge}_2\text{H}_6\), \(\text{Ge}_3\text{H}_8\) and \(\text{Sn}_2\text{H}_6\) have also been the subject of early investigations\(^{22–24}\). Unlike \(\text{GeH}_4\), the mass spectrum of digermane (\(\text{Ge}_2\text{H}_6\)) exhibits a reasonably intense molecular ion. For \(\text{Ge}_2\text{H}_6\) and \(\text{Sn}_2\text{H}_6\), the base peak corresponds to \(\text{X}_2\text{H}_2^{+•}\) resulting from elimination of two hydrogen molecules from the molecular ion. However, very extensive fragmentation is observed in both cases, particularly for \(\text{Ge}_2\text{H}_6\). The relative abundance of the important fragment ions follows the order:

\[
\begin{align*}
\text{Ge}_2\text{H}_6 & > \text{Ge}_2\text{H}_2^{+•} > \text{Ge}_2\text{H}_4^{+•} > \text{Ge}_2^{+•} > \text{Ge}_2\text{H}^+ > \text{Ge}_2\text{H}_6^{+•} \\
\text{Sn}_2\text{H}_6 & > \text{Sn}_2\text{H}_2^{+•} > \text{Sn}_2^{+•} > \text{Sn}_2\text{H}^+ > \text{Sn}_2\text{H}_2^{+•} > \text{Sn}_2\text{H}_4^{+•} > \text{Sn}_2\text{H}_6^{+•}
\end{align*}
\]

A somewhat similar extensive fragmentation is observed for \(\text{Ge}_3\text{H}_8\) with negligible formation of the molecular ion. The base peak in this case corresponds to \(\text{Ge}_3^{+•}\) (relative abundance 100) while other important fragment ions have been identified as \(\text{Ge}_3\text{H}^+\) (90.1), \(\text{Ge}_2\text{H}_2^{+•}\) (69.5), \(\text{Ge}_2\text{H}_4^{+•}\) (58) and \(\text{Ge}_2^{+•}\) (30.1). These results clearly reveal the tendency for the mass spectra of the higher hydrides to be dominated by ions with high metal content resulting from successive elimination of hydrogen molecules.

**B. Mass Spectra of Simple Alkyl Derivatives of Ge, Sn and Pb**

The most studied compounds by mass spectrometry of Ge, Sn and Pb have been the tri- and tetraalkyl derivatives. Detailed analyses of the results obtained with the simple
tetraalkyl systems provide considerable insight on the general behavior observed in the mass spectra of Ge, Sn and Pb organometallics.

The initial mass spectrometric studies of Me₄Ge, Me₄Sn and Me₄Pb established the Me₃E⁺ (E = Ge, Sn, Pb) ions as the most important fragment peaks. Appearance energies and estimates for the heats of formation of the parent neutral were used to estimate the heats of formation of the different MeₙE⁺ (n = 0–3) ions. However, all of the thermochemistry involved in these processes remains unsettled including the heat of formation of the neutrals. Nevertheless, the fragmentation patterns of the tetramethyl and tetraethyl derivatives were thoroughly studied by assignment of the metastable transitions. These metastable transitions helped to establish some general rules regarding the mass spectra of organometallic compounds of Ge, Sn and Pb.

For the EMe₄ series, the Me₃E⁺ ion is the base peak followed by the MeE⁺ fragment. This latter fragment becomes increasingly important from Ge to Pb, in agreement with the progressive importance of the +2 oxidation state in going from Ge to Pb. A much smaller intensity is observed for the Me₂E⁺ fragment while the peak corresponding to the molecular ion is negligible. Figure 5 displays the mass spectrum of Me₄Ge obtained at 70 eV.

The metastable transitions suggest that the fragmentation pattern of the tetramethyl derivatives follows Scheme 1, where HEMe₂⁺ and H₂EMe⁺ are very minor fragments in the spectra.

Scheme 1 has also been confirmed by studies carried out by unimolecular and collision induced dissociation of Me₃E⁺ ions. In these experiments, Me₃Ge⁺ was found to undergo two low-energy processes: (a) loss of methyl, and (b) loss of ethylene presumably through the mechanism shown in Scheme 2.

![Figure 5. Mass spectrum of Me₄Ge obtained by electron ionization at 70 eV in the authors’ homemade FTMS instrument at the University of São Paulo](image-url)
By comparison, Me₃Sn⁺ and Me₃Pb⁺ only undergo successive losses of methyl groups but no loss of ethylene as shown in Scheme 2. This behavior presumably reflects the decreasing carbon–metal bond strength. On the other hand, a different low energy process is observed for the Me₃E⁺ ions (with E = Sn, Pb) resulting in the elimination of ••CH₂, a rare process in mass spectra. The proposed mechanism for this process is shown in Scheme 3. Loss of ••CH₂ is not enhanced in the collisional activation spectra. Similar conclusions were obtained from experiments designed to identify the neutral fragments generated from ionic fragmentation of the tetramethyl compounds. All of them show loss of •CH₃ to be the most important neutral fragment while no C₂H₄ loss is detected for the case of Pb.

The ionization energies for the EMe₄ series follow the expected trend, decreasing from Ge to Pb, although there is some discrepancy regarding the exact value for PbMe₄. Values obtained from electron impact (EI) and by photoelectron spectroscopy (PES) are compared in Table 4.

The mass spectra of the corresponding tetraethyl derivatives are characterized by a strong base peak corresponding to the Et₃E⁺ fragment ion (see Figure 6) and low abundances of the molecular ion. For Ge and Sn, successive loss of neutral ethylene starting with Et₃E⁺ yields relatively intense peaks corresponding to Et₂EH⁺ and EtEH₂⁺. In the

<table>
<thead>
<tr>
<th>Method</th>
<th>GeH₄</th>
<th>SnH₄</th>
<th>PbH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>El (Reference 34)</td>
<td>9.29 ± 0.14</td>
<td>9.33 ± 0.04</td>
<td>9.38 ± 0.10</td>
</tr>
<tr>
<td>PES (Reference 35)</td>
<td>8.76 ± 0.12</td>
<td>8.93 ± 0.04</td>
<td>8.85 ± 0.10</td>
</tr>
<tr>
<td>PES (Reference 36)</td>
<td>8.26 ± 0.17</td>
<td>8.50 ± 0.04 eV</td>
<td>8.83 ± 0.10 eV</td>
</tr>
</tbody>
</table>
case of Pb, the preferred fragmentation pathway is successive losses of Et that are rationalized in terms of the weak Pb–C bond. The identification of the metastable transitions reveals that Scheme 4 adequately represents these mechanisms. Nevertheless, it should be emphasized that there are no detailed studies on the actual structure of the different ions and alternative connectivities are always possible for gas-phase positive ions.

Higher symmetrical tetraalkyl derivatives of Ge and Sn have also been extensively studied by mass spectrometry. For saturated alkyl groups, some general rules can be established:

(a) The molecular ion peak is generally negligible under electron ionization.
(b) Ions containing only carbon and hydrogen, or ions resulting from a carbon–carbon bond fission, are rare but their abundance tends to increase with larger alkyl groups.
(c) The abundance of the $R_3E^+$ fragments decreases in going from $R = \text{Pr}$ to $R = \text{Hex}$, but subsequent fragmentation by loss of a neutral olefin to yield abundant $HER_2^+$ and $H_2ER^+$ is essentially the only pathway as confirmed by the study of metastable transitions. While no studies have been carried out with deuteriated derivatives, it is assumed that the
mechanism for olefin elimination for alkyl groups with β hydrogens proceeds as shown in Scheme 5.

Unlike the spectra obtained by conventional electron ionization, the mass spectra of a number of tetraalkyl and trialkyl derivatives of Sn under field ionization conditions reveal almost exclusively formation of the molecular ions, i.e. ER₄⁺⁺, and fragmentation by loss of a single alkyl group⁴³.

The mass spectra of Ph₄Ge, Ph₄Sn and Ph₄Pb are of considerable interest as prototype systems for the widely used triphenyl derivatives (particularly those of Sn)¹⁰,₃⁹,₄₄,₄₅. As in the case of simple alkyl groups, the most important fragment ion is Ph₃E⁺. For Ge, the relative abundance of the other fragment ions follows the order Ph₂E⁺⁺ > PhE⁺, but this trend is completely reversed for Sn and Pb (Ph₂E⁺⁺ is negligible for the Pb compound). The detailed mechanism for the fragmentation processes in Ph₄Ge and Ph₄Sn has been characterized recently by tandem mass spectrometry⁴⁶–⁴⁸. In the meantime, the study of metastable transitions has established the importance of processes involving the elimination of biphenyl (presumably) as shown in equations 1 and 2.

\[
\begin{align*}
\text{Ph₄Sn}^{⁺⁺} & \rightarrow \text{Ph₃Sn}^{⁺⁺} + \text{Ph}_₂ \quad (1) \\
\text{Ph₂Sn}^{⁺⁺} & \rightarrow \text{Sn}^{⁺⁺} + \text{Ph}_₂ \quad (2)
\end{align*}
\]

Interestingly enough, both the Sn and Pb derivatives reveal very strong bare metal ion peaks. Other less important metastable transitions have also been well characterized in Reference 45.

The relative abundance of the Ge and Sn ions originating from the primary loss of C₁₂H₁₀ (equation 1), measured in the source and in the first and second field-free regions of a multi-sector mass spectrometer, suggests that equation 1 is a fast process. This observation implies that the elimination of biphenyl is not a concerted process but that it is likely to be mediated by the type of structure shown in Scheme 6. On the other hand, the kinetic energy release during the loss of the second phenyl group suggests a second mechanism by which Ph₂Ge⁺⁺ ions are also formed through a sequential process.
The FAB spectra of the Ph₄E compounds show no molecular ions, or molecular ions coordinated to a molecule of the liquid matrix, and do not differ considerably from EI spectra except for the appearance of the Ph₃E⁺ and PhE⁺ ions coordinated to a molecule of the matrix⁴⁹,⁵⁰.

The effect of substituents on the mass spectral disintegration pattern of a large number of Ar₄Sn derivatives has been investigated both by EI and by FAB⁵¹,⁵². In all cases, the Ar₃Sn⁺, Ar₂Sn⁺⁺ and ArSn⁺ species dominate the EI mass spectra with no molecular ion peaks. By comparison, the FAB mass spectra display the Ar₃Sn⁺ and ArSn⁺ species, and ions coordinated to one molecule of the liquid matrix (Mat) in the form of Ar₃Sn⁺(Mat). Collisional activation shows the processes given by equations 3 and 4 to be very characteristic of the FAB-MS of these compounds.

\[
\text{Ar₃Sn(Mat)⁺} \rightarrow \text{ArSn(Mat)⁺} + \text{Ar}_2 \\
\text{ArSn(Mat)⁺} \rightarrow \text{Sn(Mat)⁺⁺} + \text{Ar}^* 
\]

The EI spectra of the Ar₄Sn compounds reveal some further interesting features⁵¹–⁵⁴. For m- and p-substituted halophenyl (F, Cl) aromatics, there are noticeable peaks corresponding to Sn(halogen)⁺ that have been identified as originating from a halide migration in the fragmentation process as shown in equation 5.

\[
(p- \text{ or } m-\text{FC₆H₄})\text{Sn⁺} \rightarrow \text{SnF⁺} + \text{C₆H₄} 
\]

The appearance of SnF⁺ ions is also observed in the mass spectra of (p- or m-CF₃C₆H₄)₄Sn and it becomes the major ion in the spectra of the perfluorinated (C₆F₅)₄Sn species. This fluorine migration has been rationalized in terms of hard/soft acid base theory (HSAB) by considering Sn²⁺ as a hard acid that favors fluoride transfer⁵⁵.

Another interesting rearrangement observed in the spectra of the Ar₄Sn species occurs in the case of Ar = o-Tol for which a prominent peak corresponding to the ArSnC₇H₆⁺ ion has been identified. This fragment ion is not apparent in the spectra of the m- or p-tolyl system. This position effect has been claimed to be a typical example of the ‘ortho effect’ that is commonly encountered in organic mass spectrometry⁵⁶.

C. Mass Spectra of Mixed Alkyl and Aryl Derivatives of Ge and Sn

A wide variety of mass spectrometric studies has been carried out for mixed hydrides, and mixed alkyl and aryl derivatives⁵⁰,⁵³,⁵⁴,⁵⁷–⁶⁴. While many of the main features regarding E–C or E–H bond cleavages, and olefin elimination, are similar to those discussed in the previous section, there are some specific aspects that need to be considered explicitly.

The mass spectrum⁵⁰ of Me₃GeH yields as a base peak the Me₂GeH⁺ ion (relative abundance 100) reflecting the fact that the Ge–H bond dissociation energy is larger than that of the corresponding Ge–C bond energy. However, important fragments are also observed (in decreasing order of abundance): MeGe⁺ (35), Me₂G⁺⁺ (28) and Me₃Ge⁺ (22). For the corresponding Et₃GeH, the base peak is the EtGeH⁺ ion resulting from elimination of ethylene from the second most important fragment Et₂GeH⁺. A detailed analysis of the mass spectra of a number of R₃EH compounds (R = Me, Et, Pr, Bu and E = Ge, Sn) shows that the observed fragmentation patterns are consistent with the predictions of the quasi-equilibrium theory (QET) of mass spectra⁶⁵. Similar conclusions were obtained in a study involving Me₂GeH₂ and Me₂SnH₂ including the combined use of photoelectron spectroscopy and mass spectrometry⁶⁶.
The presence of phenyl groups changes the situation considerably. For Ph$_3$GeH, elimination of benzene from the molecular ion results in the base peak Ph$_2$Ge$^+$. The fragment PhGe$^+$ is also important and its formation is attributed to elimination of benzene from Ph$_2$GeH$^+$. For Ph$_3$GeR (R = Me, Et, CH$_2$Ph), the Ph$_3$Ge$^+$ fragment is the predominant peak in the spectra with negligible amounts of the mixed fragment Ph$_2$GeR$^+$. For these cases, mass spectrometry is not an effective means to distinguish among different triphenyl compounds as all the compounds yield low abundances of fragment ions containing the distinct R group.

For mixed alkyl stannanes like RSnMe$_3$ and RSnEt$_3$ (with R = Me, Et, i-Pr, Bu, t-Bu, c-Hex, p-MeC$_6$H$_4$CH$_2$, m-MeC$_6$H$_4$CH$_2$ and o-MeC$_6$H$_4$CH$_2$) the most notorious fragment ions are Me$_3$Sn$^+$ and Et$_3$Sn$^+$, respectively, although several other fragment ions can also be observed as a result of different bond scissions and elimination of olefins. In all cases, the important fragment ions are those corresponding to Sn(IV) or Sn(II) species that are reached by loss of an alkyl radical from the next higher unfavorable valence state, or by loss of an alkane or alkene molecule from a favorable valence state. A somewhat more complex pattern is observed in the mass spectra of s-BuRMe$_2$Sn compounds for which several fragment ions of the IV oxidation state of Sn are possible.

A very extensive set of data is available for a variety of (p-$Y$C$_6$H$_4$)EMe$_3$ compounds (Y = NO$_2$, CF$_3$, Br, F, Me, OMe, OH, OSI$_3$) for E = Ge, Sn. For this series, the (M-15)$^+$ ion is consistently the base peak except for the case of Y = F, where the EMe$^+$ becomes the most abundant species. As in many previous examples, the molecular ion appears with negligible abundance or is simply not detected. An interesting observation has been the positional dependence of the fragmentation processes for (MeOC$_6$H$_4$)SnMe$_3$. For the three possible isomers, the (M-Me)$^+$ is the base peak but the ortho isomer reveals two important differences with respect to the meta- and para-isomers: (1) the spectrum of the ortho isomer exhibits an (M-C$_2$H$_6$)$^+$ fragment with significant abundance that has been assumed to proceed through the mechanism shown Scheme 7. This mechanism is consistent with the results obtained by deuterium substitution. (2) PhSn$^+$ originating by

\[
\text{Scheme 7}
\]
loss of CH₂O (presumably as shown in Scheme 8) is two times more abundant for the ortho isomer than for the other two isomers.

$$\text{Sn}^+ + \text{CH}_2\text{O}$$

**SCHEME 8**

For the case of aryl-substituted stannanes⁴⁵,⁶⁹, the most important fragment ions are those with the highest number of phenyl groups attached to Sn. In fact, cleavage of the alkyl-tin bond in the molecular ion is always the preferred fragmentation route for RSnPh₃ compounds rather than cleavage of the phenyl-tin bond⁷⁰. As in the case of the equivalent germanes, mass spectrometry is not well suited for analytical applications for these compounds.

Closely associated sets of compounds that have also been investigated by mass spectrometry are species like RₙEX₄₋ₙ (E = Ge, Sn and X = halogen). The early investigations on organogermanes³⁰ reveal that for Me₃GeCl, Et₃GeCl and Et₃GeBr, the most abundant ions result from loss of an alkyl radical (R*) by the molecular ion to yield R₂EX⁺. Multiple chlorine substitution on simple organogermanes along the series Me₃GeCl, Me₂GeCl₂ and MeGeCl₃ has been shown to favor loss of a Me* for the first two compounds to yield (M-Me)⁺ as the most abundant ion. In the meantime, loss of Cl* is responsible for the base peak⁷¹ in the mass spectrum of MeGeCl₃. This trend becomes somewhat different for Ph₃GeX derivatives³⁰,⁴⁹ reflecting the differences between Ge—X bond strengths and the stability of the Ph₃Ge⁺ ion. The resulting spectra show that the relative abundance of the first cleavage of the molecular ions follows the order:

\[
\text{Ph}_2\text{GeCl}^+ > \text{Ph}_3\text{Ge}^+ \text{ (for Ph}_3\text{GeCl)}
\]

\[
\text{Ph}_3\text{Ge}^+ > \text{Ph}_2\text{GeBr}^+ \text{ (for Ph}_3\text{GeBr)}
\]

\[
\text{Ph}_3\text{Ge}^+ \gg \text{Ph}_2\text{GeI}^+ \text{ (for Ph}_3\text{GeI)}
\]

However, the base peak for all three compounds results from the fragmentation shown in equation 6.

\[
\text{Ph}_3\text{GeX}^{*+} \rightarrow \text{Ph}_2{}^{**+} + \text{PhGeX} \quad (6)
\]

This is one of the rare cases where a non-containing Ge ion is the base peak. The effect of multiple chlorine substitution on the mass spectra of the phenyl derivatives⁴⁶ is shown in Table 5.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Relative abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph₃GeCl</td>
<td>Ph₂⁺⁺ &gt; Ph⁺ &gt; Ph₃Ge⁺ ∼ Ph₂GeCl⁺</td>
</tr>
<tr>
<td>Ph₂GeCl₂</td>
<td>Ph₂⁺⁺ &gt; Ph₂GeCl⁺⁺ &gt; Ph⁺</td>
</tr>
<tr>
<td>PhGeCl₃</td>
<td>PhCl⁺⁺ &gt; Ph⁺ ∼ PhGeCl₂⁺⁺ &gt; PhGeCl₃⁺⁺</td>
</tr>
</tbody>
</table>

*The full spectra with the appropriate relative intensities have been reported in Reference 46.*
A somewhat similar situation is observed for the tin derivatives. For a large number of \( R_3SnX \) \((R = Me, Et, Pr, Bu, i-Bu and X = F, Cl, Br, I)\) the base peak of the spectra corresponds to the \( R_2SnX^+ \) ion except for the case of \( Pr_3SnI \), where the base peak is \( R_2SnH^+ \). Loss of the alkyl group has also been demonstrated in the mass spectra of \((1-, 2- and 3- butenyl)3GeBr\), where \( R_2SnBr^+ \) and \( SnBr^+ \) are the major fragment ions. For the \( Ph_3SnX \) series, the base peak corresponds to the \( Ph_2SnX^+ \) ion for \( C = F, Cl and Br \), and to \( Ph_3Sn^+ \) for \( X = I \) without any appreciable formation of \( Ph_2^{++} \). The corresponding \( Pb \) compounds display a similar trend.

Finally, the mass spectra of a series of \( PhMeSnRR' \) compounds have been compared for \( R = Me, Et, PhCH_2 and R' = PhCH_2 \). Loss of \( PhCH_2^+ \) is found to give rise to the base peak ion, \( MePhSnR^+ \), for all cases.

### D. Further Examples of Mass Spectra of Ge, Sn and Pb Compounds

The previous sections covered a systematic approach of simple families of Ge, Sn and Pb compounds that have been among the best characterized over the years. However, there are several isolated examples in the literature that describe in detail important characteristics of the mass spectrometry of relevant Ge, Sn and Pb compounds.

Germacyclopentanes, 1, and germacyclopentenes, 2, are good examples of Ge-containing cyclic compounds. Their mass spectra exhibit a noticeable molecular ion but the individual fragmentations depend on the substituents. For 1, the base peak is \( Ge^{++} \) for \( R = \) simple alkyl, and there is a general propensity towards the loss of the groups attached to the Ge. The relative abundance of \( Ge^{++} \) is greatly reduced for \( R = Ph \), and PhGe\(^+\) becomes the base peak. Another characteristic feature of these spectra is the elimination of ethylene (as shown in Scheme 9), that has been identified as occurring through expulsion of a moiety containing C2 and C3. Germacyclopentenes, 2, do not display an ion corresponding to ethylene loss and the base peak corresponds to \( RR'Ge^+ \). The mechanism for this process is shown in Scheme 10.

![Scheme 9](image_url)

Other germacyclopentenes and germacyclopentanols have also been characterized by mass spectrometry with particular emphasis on the elimination processes and migrations.
leading to the major fragment ions. Another example of a cyclic compound is found in the reported mass spectrum of 5-plumbaspiro[4,4]-nonane (3) for which the base peak corresponds to Pb⁺.

A somewhat different behavior is observed in the mass spectrum of the alkoxygermanes. For example, the mass spectrum of Ge(OMe)₄ reveals two important cleavage pathways (Scheme 11): (a) loss of formaldehyde to yield the molecular ion of simpler alkoxygermanes and (b) Ge–O cleavage.

Skeletal rearrangements are less common in the mass spectra of Ge, Sn and Pb compounds but some good examples have been illustrated for the case of ketoorganotins and hydroxyorganotins. For example, the mass spectra of a number of RCO(CH₂)ₙSnMe₃ species reveal that for n = 3, very strong peaks are observed that correspond to loss of ethylene. Scheme 12 illustrates the proposed rearrangement that accounts for the formation of the RCO(CH₂)₃SnMe₃⁺ ion. A very similar mechanism has been invoked for the observation of very abundant fragment ions, Me₂SnOH⁺, in the mass spectra of the stannyl alcohols Me₂Sn(CH₂)ₙOH.
The effect of a norbornene group on the fragmentation pattern of organotin compounds has been reported for a number of trimethylstannynorbornene isomers. Comparison of the spectra of the exo- and endo-5-trimethylstannynorborn-2-enes, 4 and 5, reveal similar fragmentation but some differences in the relative abundances of ions. On the other hand, the mass spectra of the syn- (6) and anti-7-trimethylstannynorborn-2-ene (7) exhibit major differences. At 70 eV, the base peak of 7 is a non-metal-containing ion, namely C\textsubscript{7}H\textsubscript{9}\textsuperscript{+}, a rare situation for these organometallic compounds.

Mass spectrometry has also been used to characterize organostannoxanes of the type Me\textsubscript{2}Sn(Cl)OC(O)CF\textsubscript{3} and their products of hydrolysis. The base peak in all cases has been tentatively assigned to the CF\textsubscript{3}OSn\textsuperscript{+} ion but the mechanism leading to this rearrangement has not been explored in detail.

Additional examples of the application of mass spectrometry have been described for less common compounds such as furyl and thieryl germanes, germatranes, acetylene derivatives of Ge, and alkyl and aryltin oxinates.

E. Mass Spectra of Compounds Containing Metal–Metal Bonds or More Than One Element of Group 14

Glocklin and coworkers, starting with Me\textsubscript{6}Ge\textsubscript{2}, initially reported the mass spectra of several alkylpolygermanes. The base peak for this compound corresponds to Me\textsubscript{5}Ge\textsuperscript{+} with a strong fragment ion corresponding to Me\textsubscript{5}Ge\textsubscript{2}\textsuperscript{+} resulting from a Ge–Me bond cleavage. Similar results were obtained for the other hexa-substituted dimetals. Me\textsubscript{5}Ge\textsuperscript{+} is also the base peak for Me\textsubscript{8}Ge\textsubscript{3}, but in the case of Et\textsubscript{8}Ge\textsubscript{3} the mass spectrum yields trigermanium ions in high abundance due to successive eliminations of ethylene. The primary process for higher oligomers of Ge has been illustrated to be cleavage of a germanium–alkyl bond. By analogy, early studies on simple polytin compounds showed a similar behavior. For example, trimethylstannyln methylanes, (Me\textsubscript{3}Sn)\textsubscript{n}CH\textsubscript{4−n} (n = 1–4), exhibit a base peak corresponding to loss of a methyl group by cleavage of a Sn–C bond. The fragments Me\textsubscript{3}Sn\textsuperscript{+} and MeSn\textsuperscript{+} are also present in large abundances for n = 2 and 3. However, without additional mass spectrometric information such as collisional activation spectra (CAD), it is difficult to establish clearly the fragmentation pathways due to the intricate isotopic pattern of these spectra.
A rather surprising finding is the fact that Ge–C and Sn–C bond cleavage are the major fragmentation pathways over metal–metal bond cleavage in compounds such as Bu$_3$GeGeBu$_3$ and Bu$_3$SnSnBu$_3$, resulting in Bu$_3$EEBu$_2^+$ as the base peak. This behavior, unlike what is observed in Si, parallels the trend observed in photoinduced electron transfer reactions$^{95}$. This argument also follows the proposed similarity between electron transfer reactions and fragmentation pathways in the mass spectrum of organometallic compounds$^{96}$.

An interesting case is the cyclic phenyl derivatives (Ph$_2$E)$_n$ ($n = 4 - 6$) of Ge and Sn for which a small abundance of the molecular ions was reported followed by a series of fragmentations and rearrangements leading to Ph$_3$Ge$^+$ and PhGe$^+$, or Ph$_3$Sn$^+$ and PhSn$^+$, as the most abundant fragment ions$^{97}$. However, there is considerable doubt about the actual mechanisms for the proposed processes as poor thermal stability of these compounds may actually be responsible for some of the experimental observations$^{98}$. Furthermore, analysis of the metastable transitions in this case is complicated by the isotopic complexity of the spectra.

The tendency for the R$_3$E$^+$ ions to be the base peak in the mass spectra of compounds containing more than one Sn atom is well illustrated for the case of sulfides$^{99}$ such as (Me$_3$Sn)$_2$S and (Ph$_3$Sn)$_2$S. For cyclic polysulfides, cyc-(Me$_2$SnS)$_3$, cyc-(Bu$_2$SnS)$_3$ and cyc-(Ph$_2$SnS)$_3$, the mass spectra show significant abundance of R$_3$SnS$_2^+$ (the base peak for R = Bu), R$_3$Sn$^+$ (the base peak for R = Me) and R$_2$SnS$^+$ (the base peak for R = Ph) besides the R$_3$Sn$^+$ fragment.

Compounds containing a metal–metal bond between different elements of group 14 represent an interesting case for mass spectrometry. For example, the mass spectrum$^{24}$ of H$_3$GeSiH$_3$ shows GeSiH$_4^+$ and GeSiH$_2^+$ as the most abundant peaks while the abundance of GeH$_3^+$ is higher than that of SiH$_3^+$, as might be predicted by the expected trend in ionization energies of the corresponding radicals. However, the most extensive study was carried out for a series of R$_3$EE'R$_3'$ compounds involving Ge and Si, and Sn and Ge$^{100}$. In general, bond cleavage of the molecular ion proceeds primarily in the direction of the weakest bond of the molecule but product ions originating from cleavage of all four main bonds are encountered in the mass spectrum. While the resulting spectra are quite complex, identification of the metastable transitions has made it possible to identify different processes. These can be exemplified for the case of Ph$_3$GeSnMe$_3$ with their respective relative abundances:

(a) bond cleavage from the molecular ion giving rise to Ph$_3$GeSnMe$_2^+$ (58), Ph$_3$Ge$^+$ (100);
(b) molecule elimination (i.e. biphenyl) by cleavage of two bonds as in Ph$_3$Ge$^+ \rightarrow$ PhGe$^+$ (42);
(c) rearrangement of ions by group transfer to yield ions such as Ph$_2$GeMe$^+$ (48) and PhSn$^+$ (45).

While these results show great preference for the formation of Ge-containing ions, the stabilizing effect of the phenyl groups plays an enormous role. By comparison, the most abundant ions in the mass spectrum of the corresponding Ph$_3$SnGeMe$_3$ follow the rules above with the difference that the resulting fragments are Sn-containing ions.

An even wider set of R$_3$EE'R$_3'$ compounds [E = Si, E' = Ge; and R or R' = Ph, Me, ($\eta^5$-C$_5$H$_4$)Fe(C$_5$H$_5$), ($\eta^5$-C$_5$H$_4$)Fe(CO)$_2$ and ($\eta^5$-C$_9$H$_7$)Fe(CO)$_2$] has been recently investigated by mass spectrometry$^{101}$. Several general conclusions stem from this study: (a) significant ligand exchange occurs in the ions for non-metal-substituted Si–Ge isomers as shown above; (b) Fe–Si–Ge complexes undergo preferential Si–Ge cleavage while the Fe–Ge–Si undergo preferential Fe–Ge bond cleavage; (c) in the case of the symmetrical complex ($\eta^5$-C$_5$H$_4$)Fe(C$_5$H$_5$)Si(Ph)$_2$Ge(Ph)$_2$($\eta^5$-C$_5$H$_4$)Fe(C$_5$H$_5$), Si–Ge
bond cleavage is the major fragmentation, and \((\eta^5\text{-C}_5\text{H}_4)\text{Fe(C}_5\text{H}_5)\text{Si(Me)_2}^{+}\) is observed as the most abundant ion.

The mass spectrum of PhSn(Me)\(_2\)Ge(Ph)\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)COCH\(_3\) is one example where cleavage of the metal–metal bond is the major fragmentation pathway resulting in \((\text{Ph)}_2\text{Ge(CH}_2\text{CH}_2\text{CH}_2\text{COCH}_3)^{+}\) (assumed structure) as the base peak\(^{102}\). This is also the case when the keto group is replaced by dioxolane. However, in both cases Ge- and Sn-containing ions such as PhSn\(^{+}\) and PhGe\(^{+}\) are important fragments.

It is therefore possible to conclude that in the case of compounds containing metal–metal bonds of elements of group 14, cleavage of this bond is an important process in mass spectrometry but not necessarily the preferred fragmentation pathway. Furthermore, the most abundant fragment ions from the metal–metal bond cleavage are ions containing the lighter element of the group.

### III. GAS-PHASE ION CHEMISTRY

The fundamental aspects related to the thermochemistry, structure and reactivity of gas-phase ions are usually considered the domain of gas-phase ion chemistry. By extension, some of these same properties are often obtained for simple neutrals and radicals from methods used in gas-phase ion chemistry. A wide range of experimental techniques can be used for this purpose, and instrumental developments have contributed a great deal to our knowledge of gas-phase ions. Theoretical calculations have also played an important role and gas-phase ion chemistry has witnessed a very lively interplay between experiment and theory in recent years.

This section discusses these different aspects of positive and negative Ge, Sn and Pb ions. Negative ions have not been discussed in the previous section as they have rarely been used to identify Ge, Sn and Pb compounds\(^{103}\), even though negative ion chemical ionization based on Cl\(^{-}\) attachment can often be a useful technique for compounds that display low abundance of the molecular ion in conventional mass spectrometry\(^{104}\).

#### A. Thermochemistry, Structure and Reactivity Related to the Gas-phase Positive Ion Chemistry of Ge, Sn and Pb Compounds

Photoelectron spectroscopy has been extensively used for Ge, Sn and Pb compounds to understand the bonding of these systems and to determine ionization energies\(^{19-21,105-119}\). Mass spectrometry has also been used in this respect although in general with a lower energy resolution. The results are reviewed in Reference 5 and in many cases the main uncertainty in the reported ionization energies is related to the ability in determining the true adiabatic IE.

Trends in ionization energies have been illustrated previously but other examples are of particular interest. The halides of Ge, Sn and Pb can be singled out because they have been extensively characterized for both the (IV) and (II) oxidation states. As in the case of C and Si, the tetrafluoro derivatives display very high ionization energies, and the observed trends in Ge demonstrate the decrease in IE in going from F to I, and the decrease in going from the (IV) to the (II) oxidation state, i.e.

\[
\text{GeF}_4 (15.69 \text{ eV})^{105,120} > \text{GeCl}_4 (11.88 \text{ eV})^{105} > \text{GeBr}_4 (10.62 \text{ eV})^{121} > \text{GeI}_4 (9.84 \text{ eV})^{122} \\
\text{GeF}_2 (11.65 \text{ eV})^{123} > \text{GeCl}_2 (10.55 \text{ eV})^{123} > \text{GeBr}_2 (10.02 \text{ eV})^{123} > \text{GeI}_2 (9.08 \text{ eV})^{123}
\]

By comparison, determination of the ionization energies and thermodynamic data for the Sn and Pb dihalides represent classical benchmarks in high temperature photoelectron
spectroscopy and mass spectrometry\textsuperscript{124--127}. The combined results for the Pb series shows a similar trend to that shown for the IE of the GeX\textsubscript{2} compounds.

\begin{align*}
PbF_{2} (11.5 \text{ eV}) &> PbCl_{2} (10.2 \text{ eV}) > PbBr_{2} (9.6 \text{ eV}) > PbI_{2} (8.86 \text{ eV})
\end{align*}

Thermochemistry for some Ge-, Sn- and Pb-fragment ions has been obtained from appearance energies in mass spectrometry. This is a traditional method that can be used for determining bond energies, the ionization energy of simple radicals and heats of formation of ions. A typical example of this approach for characterizing neutral and ionic Me\textsubscript{3}Sn and Sn–X bond energies was used in an extensive study by Yergey and Lampe\textsuperscript{58}. However, values obtained by this method rely on knowledge of the thermochemistry of the stable neutrals\textsuperscript{34,128}. The experimental difficulties in determining threshold appearance energies in mass spectrometry are well known and most of the values derived from the early literature must be viewed with great caution. This is particularly true because of the revised values for the neutral thermochemistry of organometallics\textsuperscript{5}.

The question of bond dissociation energies for the elements considered here has also been an area of lively discussion. The accurate determination of bond dissociation energies from mass spectrometric, photoionization or gas kinetics experiments is often subject to considerable uncertainty. The most recent critical review dealing with experimental methods recommends a value of 343 ± 8 KJ mol\textsuperscript{-1} for the H\textsubscript{3}Ge–H bond energy\textsuperscript{129} derived from the photoionization of monogermane\textsuperscript{18}. Other bond energies for these elements are less certain and values obtained by high-level theoretical calculations\textsuperscript{130} are probably very good estimates for bond energies of Ge, Sn and Pb.

Considerable insight about fundamental aspects of the behavior of simple Ge, Sn and Pb species can be obtained from studies aimed at characterizing the reactivity of gas-phase ions. Reactions of the primary ions obtained by electron ionization of GeH\textsubscript{4} with the neutral monogermane precursor have been characterized both by low- and high-pressure mass spectrometric techniques\textsuperscript{131,132}, and more recently by ion trap techniques (ITMS)\textsuperscript{133}. The ability to select a particular isotopic species (usually the \textsuperscript{70}Ge-containing ion) in low pressure studies carried out by Fourier Transform Mass Spectrometry (FTMS) has been essential in understanding the mechanism of these processes. The main results can be summarized as follows:

(i) The primary ions GeH\textsuperscript{+} and GeH\textsubscript{2}\textsuperscript{+} react readily with GeH\textsubscript{4} to yield GeH\textsubscript{3}\textsuperscript{+} with the resulting ion retaining the original isotope (equations 7 and 8),

\begin{align*}
70\text{GeH}^{+} + \text{GeH}_{4} &\rightarrow 70\text{GeH}_{3}^{+} + \text{GeH}_{2} \quad (7) \\
70\text{GeH}_{2}^{+} + \text{GeH}_{4} &\rightarrow 70\text{GeH}_{3}^{+} + \text{GeH}_{3} \quad (8)
\end{align*}

(ii) \textsuperscript{70}Ge\textsuperscript{+} ions in turn react with GeH\textsubscript{4} by hydrogen atom abstraction to yield \textsuperscript{70}GeH\textsuperscript{+}, a reaction similar to that shown in equation 8.

(iii) GeH\textsubscript{3}\textsuperscript{+}, both a primary and secondary ion in these processes, reacts with GeH\textsubscript{4} by hydride abstraction as verified by the isotope scrambling shown in equation 9,

\begin{align*}
70\text{GeH}_{3}^{+} + \text{GeH}_{4} &\rightarrow \text{GeH}_{3}^{+} + 70\text{GeH}_{4} \quad (9)
\end{align*}

(iv) GeH\textsubscript{2}\textsuperscript{+} and Ge\textsuperscript{+} also undergo slow condensation reactions followed by elimination of molecular hydrogen as illustrated in equations 10 and 11,

\begin{align*}
\text{GeH}_{2}^{+} + \text{GeH}_{4} &\rightarrow \text{Ge}_{2}\text{H}_{4}^{+} + \text{H}_{2} \quad (10a)
\end{align*}
By comparison, GeH$_3^+$ undergoes very slow condensation-type reactions to yield Ge$_2$H$_5^+$ and Ge$_2$H$_3^+$. These reactions are not observed in the time regime of the ITMS experiments$^{133}$.

(vi) Protonated germane, GeH$_5^+$, is not observed as a product ion in these reactions, and this fact is further discussed below.

(v) Digermanium species, Ge$_2$H$_n^+$ ($n = 2−7$), become more important ionic products in experiments carried out by high-pressure mass spectrometry (ca 0.1 Torr) where termolecular processes become favorable.

One of the most important thermochemical parameters in ion chemistry is the proton affinity (PA) (equation 12), and considerable experimental and theoretical work has been carried out in the last 30 years to determine this property accurately.

\[
\text{M}(g) + \text{H}^+(g) \rightarrow \text{MH}^+(g) \quad \text{PA(M)} = -\Delta H^\circ
\]  

Yet, the experimental determination of the proton affinity of GeH$_4$ has been a considerable problem due to the difficulty in observing the GeH$_5^+$ ion. An early ion beam experiment$^{134}$ concluded that the proton affinity of germane was higher than that of acetylene, C$_2$H$_2$, and that proton transfer from H$_3$S$^+$ to GeH$_4$ was endothermic. In the most recent update of gas-phase proton affinities$^{135}$, the recommended value for the PA of germane at 298 K amounts to 713.4 kJ mol$^{-1}$. However, this value is probably too high since recent high level calculations$^{136}$ placed the proton affinity of GeH$_4$ at 0 K at 654.4 kJ mol$^{-1}$ while at 298 K a value 673 kJ mol$^{-1}$ is predicted by G2 calculations$^{137}$.

The difficulty encountered in observing GeH$_5^+$ in the gas phase accounts for the uncertainty in the experimental value for the proton affinity of GeH$_4$. Ab initio calculations$^{136−138}$ reveal that the structure of the GeH$_5^+$ ion corresponds to that of a germyl cation weakly attached to molecular hydrogen, GeH$_3^+(\text{H}_2)$. The binding energy of such a moiety has been estimated$^{138,139}$ to be in the range of 30 to 35 kJ mol$^{-1}$, a value that is indicative of the poor stability and ease of dissociation of the GeH$_5^+$ ion at room temperature.

A considerably more complex reactivity pattern has been observed for the ions generated from CH$_3$GeH$_3$ reacting with the parent neutral$^{140,141}$. The minor fragments GeH$_m^+$ ($m = 0, 2, 3$) react rapidly with CH$_3$GeH$_3$ to yield ions CH$_2$Ge$^+$ (of unknown atom connectivity) and CH$_3$GeH$_2^+$ (assumed structure). The CH$_3$Ge$^+$ and CH$_3$GeH$_2^+$ ions, obtained both as main fragments by electron ionization and by ion/molecule reactions, undergo a variety of condensation reactions that yield ions with the generic composition Ge$_2$CH$_n^+$ ($n = 4, 5, 6, 7$ and $9$) as well as GeC$_2$H$_7^+$. The structure of these ions has not been elucidated and it is presently unclear as to what are the most stable isomers for these different ions.

The structure of [GeCH$_2$]$^+$ and [GeCH$_3$]$^+$ ions has been examined by collisional activation (CA) and neutralization–reionization (NR) mass spectrometry$^{142}$. Regardless of how these ions are formed, the prevalent connectivity for these ions is GeCH$_n^+$ ($n = 2$, $3$). The modeling of the cationic and neutral surfaces for the [GeCH$_2$] species suggests the unlikelihood that significant amounts of neutral or cationic germaacetylene or germavinylidene can be generated in these experiments. Similar experiments with the [GeCH]$_n^+$ ion also suggest that GeCH$^+$ is the preferred connectivity and theoretical calculations support the conclusion that this structure is substantially more stable than the HGeC$^+$ isomer$^{143}$.
The proton affinity of CH$_3$GeH$_3$ is also unknown. An \textit{ab initio} calculation\textsuperscript{144} at the Hartree–Fock level predicts that the structure of protonated methylgermane corresponds to a CH$_3$GeH$_2$\textsuperscript{+} (H$_2$) complex and that the proton affinity of CH$_3$GeH$_3$ is 22 kJ mol\textsuperscript{−1} higher than that of germane.

Interest in the fundamental processes involved in formation of amorphous Ge-containing compounds by chemical vapor deposition processes assisted by radiolysis has been responsible for a number of studies dedicated to the reactions of Ge ions with O$_2$, NH$_3$, PH$_3$, SiH$_4$ and simple alkanes and alkenes\textsuperscript{131,145–150}.

These studies have revealed a number of interesting observations:

(i) O$_2$ reacts with Ge$_2$H$_2$\textsuperscript{+}, a secondary product ion formed through ion/molecule reactions of germane (see reactions 10b and 11), to yield GeOH\textsuperscript{+} through the reaction given in equation 13.

\[
\text{Ge}_2\text{H}_2\textsuperscript{+} + \text{O}_2 \rightarrow \text{GeOH}^+ + (\text{HGeO})^* \tag{13}
\]

This unusual reaction has been proposed to occur via a four-center mechanism\textsuperscript{131}. While no structural information was derived from the original experiments, calculations at the HF level predict that a linear structure corresponding to protonated germanium oxide, GeOH\textsuperscript{+}, is considerably more stable than the alternative linear HGeO\textsuperscript{+} structure\textsuperscript{151}.

(ii) The primary hydrogen-containing ions obtained from GeH$_4$ react with NH$_3$ primarily by proton transfer to form NH$_4$\textsuperscript{+} while condensation-type reactions are much slower. The notable exception is GeH$_2$\textsuperscript{+}, which undergoes significant reaction to yield both GeNH$_4$\textsuperscript{+} and GeNH$_3$\textsuperscript{+} (structures unknown) by hydrogen elimination\textsuperscript{131,149}. The secondary product Ge$_2$H$_2$\textsuperscript{+}, as in the above reaction, also reacts with NH$_3$ by elimination of hydrogen through the reaction in equation 14.

\[
\text{Ge}_2\text{H}_2\textsuperscript{+} + \text{NH}_3 \rightarrow \text{Ge}_2\text{NH}_3\textsuperscript{+} + \text{H}_2 \tag{14}
\]

(iii) Interest in the mechanism for the formation of ions containing Ge–C bonds has motivated a number of studies involving GeH$_4$ with simple hydrocarbons\textsuperscript{146}, ethylene\textsuperscript{145}, allene\textsuperscript{146,150} and alkynes. Primary ions of germane undergo very slow reaction with methane and ethane and experiments carried out under methane or ethane chemical ionization conditions reveal the formation of small amounts of GeCH$_5$\textsuperscript{+}, GeCH$_7$\textsuperscript{+} and Ge$_2$H$_5$\textsuperscript{+} as the result of tertiary reactions\textsuperscript{146}. Other ions like GeC$_2$H$_5$\textsuperscript{+} and Ge$_2$H$_7$\textsuperscript{+} are observed as minor product ions. By comparison, reaction with alkynes like C$_2$H$_3$ and propyne, C$_3$H$_4$, gives rise to abundant amounts of GeC$_2$H$_3$\textsuperscript{+} (in the case of acetylene) and GeC$_3$H$_n$\textsuperscript{+} ($n = 3$, 4, 5) in the case of propyne under chemical ionization conditions through a sequential set of ion/molecule reactions. Likewise, chemical ionization of GeH$_4$ and C$_2$H$_4$ mixtures produce significant amounts of GeC$_2$H$_5$\textsuperscript{+} and GeC$_2$H$_7$\textsuperscript{+} ions. Since reactions observed under chemical ionization conditions are promoted both by ions originating from GeH$_4$ and those from the corresponding carbon compound, the overall mechanism for these reactions is quite complex. On the other hand, the reaction of GeH$_3$\textsuperscript{+} with C$_2$H$_4$ has been shown to yield GeC$_2$H$_5$\textsuperscript{+} in a tandem mass spectrometer\textsuperscript{152} via initial formation of a GeC$_2$H$_7$\textsuperscript{+} adduct.

The structure of the newly formed ions containing Ge–C bonds is a matter of considerable interest. While there is no experimental evidence at present, theoretical calculations\textsuperscript{153} predict that for the GeC$_2$H$_5$\textsuperscript{+} ion the lowest energy structures correspond to CH$_3$CH(H)Ge\textsuperscript{+}, with one hydrogen bridging the middle carbon and germanium, and to H$_3$GeCH$_2$\textsuperscript{+}, reminiscent of an allyl cation. On the other hand, theoretical calculations\textsuperscript{154} predict that for the GeC$_2$H$_7$\textsuperscript{+} ion, the most stable structure corresponds to that of a dimethyl germyl ion, (CH$_3$GeHCH$_3$)$^+$.
A mixture of GeH₄ and CO yields GeCO⁺ as the most important cross reaction product under chemical ionization conditions. The structure of this ion is an interesting problem with respect to the question of model systems for main group carbonyls. A recent study by collisional activation spectroscopy strongly supports the idea that this ion retains a Ge—CO connectivity. At lower pressures, experiments carried out by FTMS reveal that the main reaction (equation 15a) leading to a cross ionic product is promoted by a secondary Ge-containing ion. In this case, the reaction in equation 15b is a minor channel.

\[
\begin{align*}
\text{Ge}_2\text{H}_5^+ + \text{CO} & \longrightarrow \text{GeH}_5\text{O}^+ + \text{GeC} \quad (15a) \\
& \longrightarrow \text{GeH}_3\text{O}^+ + (\text{GeCH}_2) \quad (15b)
\end{align*}
\]

In both cases, the resulting ions involve the formation of a Ge—O covalent bond. A very similar set of reactions is observed with CO₂ with formation of GeH₅O⁺ and GeH₂O⁺.

Ionic reactions between fragment and secondary ions of PH₃ and GeH₄ give rise to a number of interesting ions from a bonding point of view. The following reactions, among others, have been identified by ion trap mass spectrometry to proceed rapidly and to lead to the formation of ions with Ge—P bonds (equations 16–18):

\[
\begin{align*}
P_2^+ + \text{GeH}_4 & \longrightarrow \text{GePH}_2^+ + \text{PH}_2 \quad (16a) \\
& \longrightarrow \text{GeP}_2^+ + 2\text{H}_2 \quad (16b) \\
P_2\text{H}^+ + \text{GeH}_4 & \longrightarrow \text{GePH}_2^+ + \text{PH}_3 \quad (17a) \\
& \longrightarrow \text{GeP}_2\text{H}_3^+ + \text{H}_2 \quad (17b) \\
\text{GeH}_2^+ + \text{PH}_3 & \longrightarrow \text{GePH}_3^+ + \text{H}_2 \quad (18)
\end{align*}
\]

Reactions between ionic fragments in GeH₄/SiH₄ and GeH₄/CH₃SiH₃ mixtures yield GeSiH₅⁺ as the most important Ge—Si reaction product. Very similar studies to those described above have also been carried out for methyl-germane and the same substrates discussed above. While the number of reaction channels is even greater in these cases, these reactions reveal the pathways for Ge—C, Ge—Si, Ge—O, Ge—N and Ge—P bond formation.

Very different and distinct ion chemistry has been observed in the reaction between the fragment ions obtained by electron ionization of tetramethoxygermane, Ge(OMe)₄, and the parent neutral. Reactions in this system proceed by nucleophilic addition followed by elimination of formaldehyde and/or elimination of methanol. An overview of the reactions of the different ions with Ge(OMe)₄ is shown in Scheme 13 for the even electron ions, and in Scheme 14 for the radical ions originating from tetramethoxygermane. In these schemes, the neutral reagent of the ion/molecule reactions, Ge(OMe)₄, is not shown for the sake of simplicity but the schemes include the neutral products that are eliminated upon addition of the reagent ion to the parent neutral molecule.

While the actual structure of the product ions has not been clearly established, it is likely that the product ions Ge₂(OMe)₆⁺⁺, Ge₂(OMe)₄⁺⁺⁺, Ge₂(OMe)₂⁺ and Ge₂(OMe)₃⁺ are species where Ge—Ge bonds have been formed in the process of elimination of MeOH and H₂CO. This implies that while the reaction of germyl-type cations like Ge(OMe)₃⁺ and HGe(OMe)₂⁺ are probably initiated by attachment of a Ge to an oxygen lone pair in Ge(OMe)₄, the reaction must proceed through a rearrangement that allows for an incipient Ge—Ge bond formation.

Additional examples of the ionic reactivity of germanium and tin systems in the gas phase deserve particular attention. For example, tritiated methyl cations have been used
5. Gas-phase chemistry and mass spectrometry

\[
\begin{align*}
\text{Ge(OMe)_3}^+ & \rightarrow \text{Ge_2(OMe)_5}^+ \\
\text{HGe(OMe)_2}^+ & \rightarrow \text{GeOMe}^+ \\
\text{HGe(OMe)_2}^+ & \rightarrow \text{GeOMe}^+ \\
\text{H_2Ge(OMe)_2}^+ & \rightarrow \text{Ge_2(OMe)_3}^+ \\
\end{align*}
\]

SCHEME 13

\[
\begin{align*}
\text{HGe(OMe)_3}^{++} & \rightarrow \text{Ge(OMe)_6}^{++} \\
\text{H_2Ge(OMe)_2}^{++} & \rightarrow \text{Ge_2(OMe)_4}^{++} \\
\end{align*}
\]

SCHEME 14

to promote a methide abstraction from tetramethylgermane and tetramethylstannane\(^{158}\) (equation 19).

\[
\text{CT}_3^{+} + \text{Me}_4E \rightarrow \text{MeCT}_3 + \text{Me}_3E^+ \quad (E = \text{Ge}, \text{Sn}) \quad (19)
\]

This same kind of reaction was shown to occur with Me_3Si^+ as the reagent ion\(^{159}\) and the same substrates. The mechanism for such unusual reactions has not been elucidated, but a proposal has been made for the participation of an intermediate containing a Me^+ group bridging the C, or Si, and Ge, or Sn, center through a two-electron three-center bond. A somewhat similar reaction has been reported in radiolytical and chemical ionization experiments with trimethylgermylbenzene (equation 20), where the actual mechanism here involves an *ipso* substitution presumably through a sigma-type complex\(^{160,161}\).

\[
\text{Me}_3\text{Si}^{+} + \text{PhGeMe}_3 \rightarrow \text{Me}_3\text{Ge}^{+} + \text{PhSiMe}_3 \quad (20)
\]

The R_3E^+ ions (E = Si, Ge, Sn) are strong electrophiles that display great propensity to form adducts with n-donor bases (B)\(^{162,163}\). This has been shown to occur with simple aliphatic neutrals containing N, O or S as shown in equation 21.

\[
\text{Me}_3\text{Ge}^{+} + :B \rightarrow [\text{MeGe}_3B]^+ \quad (21)
\]

The relative binding strength of the adducts follows the qualitative trend of the gas-phase basicities of the donor base, i.e., t-BuOH > i-PrOH > EtOH > MeOH > H_2O. The binding to alcohols can be sufficiently selective to the point where 1,2-cyclopentanediols isomers have been distinguished by their reactivity towards Me_3Ge^+ in tandem mass spectrometry\(^{164}\). The actual binding energy has been measured for H_2O (equation 22)\(^{165}\).
and it reveals the reasonable stability of such adducts.

\[
\text{Me}_3\text{Ge}^+ + \text{H}_2\text{O} \longrightarrow [\text{Me}_3\text{GeOH}_2]^+ \quad \Delta H^\circ = -119.7 \pm 2.0 \text{ kJ mol}^{-1} \quad (22)
\]

\[
\Delta G^\circ(300 \text{ K}) = -76.5 \pm 3.0 \text{ kJ mol}^{-1}
\]

The Me\textsubscript{3}Ge\textsuperscript{+} cation can also form adducts with arenes\textsuperscript{166} and quantitative gas-phase equilibrium measurements show that the stability of the adducts (\(-\Delta G^\circ\)) obeys the order 1,3-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{4} > H\textsubscript{2}O > MePh. The thermochemistry and reactivity of the \([\text{Me}_3\text{Ge}^+.\text{arene}]\) adducts suggest that the most likely structure is that of a sigma complex.

Similar kind of data is available for the gas-phase adducts of Me\textsubscript{3}Sn\textsuperscript{+} with alcohols, amines, H\textsubscript{2}O, ketones, esters and simple arenes\textsuperscript{167}. Using methanol as a standard, the values for H\textsubscript{2}O are shown in equation 23.

\[
\text{Me}_3\text{Sn}^+ + \text{H}_2\text{O} \longrightarrow [\text{Me}_3\text{SnOH}_2]^+ \quad \Delta H^\circ = -107 \pm 4 \text{ kJ mol}^{-1} \quad (23)
\]

\[
\Delta G^\circ(300 \text{ K}) = -76 \pm 6 \text{ kJ mol}^{-1}
\]

The relative trends for the stability of the adducts of Me\textsubscript{3}Sn\textsuperscript{+} also parallel very closely the relative order of proton affinity of the different neutral bases.

While similar data are not available for the corresponding Me\textsubscript{3}Pb\textsuperscript{+} ion, the thermochemistry of the gas-phase association of Pb\textsuperscript{+} with several molecules of NH\textsubscript{3} and H\textsubscript{2}O, and with one molecule of MeOH, MeNH\textsubscript{2} and benzene has been thoroughly characterized\textsuperscript{168–171}. By comparison with the above examples, the association of Pb\textsuperscript{+} with H\textsubscript{2}O is weaker than that of the trimethylgermanium and trimethyltin ions (see equation 24)\textsuperscript{169}.

\[
Pb^+ + \text{H}_2\text{O} \longrightarrow Pb^+(\text{H}_2\text{O}) \quad \Delta H^\circ = -93.7 \text{ kJ mol}^{-1} \quad (24)
\]

In summary, the gas-phase ion chemistry of Ge, Sn and Pb positive ions reveals some very unusual reactivity and will probably witness important advances in the near future regarding structural aspects of these ions.

B. Thermochemistry, Structure and Reactivity of Negative Ions of Ge, Sn and Pb

Negative ions are less common species in mass spectrometry for a variety of reasons:
(a) Stable negative ions are only detected for molecules or radicals with positive electron affinities (equation 25).

\[
\text{M}(g) + e^- \longrightarrow \text{M}^-(g) \quad \text{EA}(\text{M}) = -\Delta E \quad (25)
\]

(b) Direct formation of negative ions by electron impact generally occurs through a resonance process over a narrow range of electron energy that coincides with capture of the electron to yield either a long-lived anion, or undergoes dissociation to yield a fragment negative ion. These mechanisms have been reviewed in the literature\textsuperscript{172}. On the other hand, stable negative ions for which no convenient precursor is available for direct formation can often be generated indirectly by ion/molecule reactions. Electrospray ionization is an alternative method for obtaining negative ions since ions are introduced in the mass spectrometer directly from solution.

Negative ions containing Ge, Sn or Pb have been obtained in mass spectrometry from the halides of these elements. For example, GeF\textsubscript{4} has been shown to yield F\textsuperscript{-}, GeF\textsubscript{3}\textsuperscript{-} and GeF\textsubscript{4}\textsuperscript{-} and traces of GeF\textsubscript{2}\textsuperscript{-} by electron impact\textsuperscript{173}. Formation of these ions is typically a
resonance process that is observed at electron energies between 8 and 11 eV. In principle, the appearance energy (AE) of a species like GeF$_3^-$ can be used to determine important thermochemical parameters (equation 26).

\[
\text{GeF}_4 + e^- \longrightarrow \text{GeF}_3^- + F
\]  
(26a)

\[
\text{AE(GeF}_3^-) = D(F_3\text{Ge} - F) + \text{EA(F}_3\text{Ge}^*) + E^*
\]  
(26b)

In equation 26b, $E^*$ represents the excess energy (vibrational, translational and eventually electronic) with which the fragments of equation 26a are formed. By assuming a F$_3$Ge$^*$ bond energy of 518 kJ mol$^{-1}$ obtained from the positive ion data and measuring the translational energy of GeF$_3^-$ formed at the onset, a value for the electron affinity of F$_3$Ge$^*$ was thus obtained. The uncertainty in this approach is well illustrated by the fact that three different experiments$^{174-176}$ yield very different values for the electron affinity of F$_3$Ge$^*$, namely 3.1 eV, 1.6 eV and 1.1 eV. Thus, this method suffers serious limitations for determining electron affinities. As a general guideline, recent high-level calculations$^{137,177}$ estimate the EA of F$_3$Ge$^*$ to be in the range of 3.5 to 3.7 eV.

Similar mass spectrometric experiments$^{178-180}$ were carried out for GeCl$_4$ and GeBr$_4$, and for SnF$_4$, SnCl$_4$, SnBr$_4$ and SnI$_4$. For these compounds, the observed negative ions are EX$_3^-$, EX$_2^-$, X$_2^-$ and X$^-$ (E = Ge, Sn; X = Cl, Br, I). Appearance energy measurements coupled with measurements of the translational energies of the ions were again used to obtain estimates of the electron affinities for the different EX$_2$ and *EX$_3$ species. However, the electron affinities estimated for GeCl$_3$ and SnCl$_3$ from these experiments are substantially lower than those obtained from the energy threshold for reactions studied by atom beam techniques$^{181,182}$ (equation 27).

\[
\text{M} + \text{ECl}_4 \longrightarrow \text{M}^+ + \text{Cl}_3\text{E}^- + \text{Cl} \quad (\text{M} = \text{Cs, K}; \text{E} = \text{Ge, Sn})
\]  
(27)

The only other family of compounds that have been characterized by negative ion mass spectrometry has been the organo-tin compounds RSnCl$_3$ (R = Me, $n$-Bu, Octyl, Dodecyl and Ph), R$_2$SnCl$_2$ (R = Me, Et, $n$-Bu, Octyl, Dodecyl and Ph) and R$_3$SnCl (R = Me, $n$-Pr, $n$-Bu, c-Hex, Ph). For all of these compounds, primary negative ions are observed that correspond to loss of an alkyl group generating the [R$_{n-1}$SnCl$_{4-n}$]$^-$ ($n = 1-3$) ions and chloride ions$^{103}$. These observations clearly indicate the well-known ease for halides to yield negative ions by electron impact in the gas phase.

Accurate measurements of the electron affinity of simple Ge and Sn radicals have been obtained by threshold photodetachment experiments carried out in ion cyclotron resonance experiments$^{183}$. In these experiments, measurement of the threshold frequency for removing the electron from the anion yields an upper limit for the electron affinity of the species, as shown for GeH$_3^-$ in equation 28.

\[
\text{GeH}_3^- + h\nu_{th} \longrightarrow \text{*GeH}_3 + e^- \quad \text{EA(}^\text{*GeH}_3) \leq h\nu_{th}
\]  
(28)

These experiments can provide the true electron affinity in cases where the geometry of the anion and the neutral are reasonably similar or where favorable Franck–Condon factors allow observation of the adiabatic transition. Using this approach$^{184,185}$, the electron affinities of *GeH$_3$, *GeMe$_3$ and *SnMe$_3$ have been obtained and are listed in Table 6.

For the case of *GeH$_3$, recent high-level theoretical calculations$^{137,186}$ suggest that the actual value for the electron affinity is somewhat lower than the upper limit suggested by experiment. The calculations estimate values in the range of 1.55 to 1.60 eV.

Electron affinities can be determined with even higher accuracy by photoelectron spectroscopy of negative ions. This technique has been used to determine the electron affinity
TABLE 6. Electron affinity and gas-phase acidity of some simple Ge and Sn systems

<table>
<thead>
<tr>
<th>Radical</th>
<th>EA (eV)</th>
<th>Compound</th>
<th>$\Delta H_{\text{acid}}^\circ$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>*GeH$_3$</td>
<td>$\leq 1.74$ (Reference 184)</td>
<td>GeH$_4$</td>
<td>$1502.0 \pm 5.1$ (Reference 190)</td>
</tr>
<tr>
<td>*GeMeH$_2$</td>
<td>—</td>
<td>MeGeH$_3$</td>
<td>$1536.6 \pm 5.0$ (Reference 190)</td>
</tr>
<tr>
<td>*GeMe$_3$</td>
<td>$1.38 \pm 0.03$ (Reference 185)</td>
<td>Me$_2$GeH</td>
<td>$1512 \pm 12$ (Reference 185)</td>
</tr>
<tr>
<td>*SnMe$_3$</td>
<td>$1.70 \pm 0.06$ (Reference 185)</td>
<td>Me$_3$SnH</td>
<td>$1460 \pm 8$ (Reference 185)</td>
</tr>
</tbody>
</table>

The gas-phase acidity of some of the simplest organogermanes and of trimethylstannane have been determined by a combination of gas-phase equilibrium measurements and proton-transfer bracketing experiments using FTMS$^{185,190}$. The experimental values of $\Delta H_{\text{acid}}^\circ$ are shown in Table 6 and refer to the enthalpy change associated with reaction 29.

$$\text{AH}(g) \rightarrow \text{A}^- (g) + \text{H}^+ (g) \quad \Delta H_{\text{acid}}^\circ (\text{AH}) = \Delta H^\circ$$  \hspace{1cm} (29)$$

Methyl substitution decreases the gas-phase acidity of the Ge system similarly to what has been found in methyilsilane$^{191}$. On the other hand, the increase observed in trimethylgermane is more difficult to analyze as relative variations of $\Delta H_{\text{acid}}^\circ$ along a given family reflect changes in electron affinity and in Ge$^-\text{H}$ bond dissociation energies.

Very few studies are available on the reactivity of negative ions in Ge, Sn and Pb compounds. However, some interesting results have emerged from the study of gas-phase reactions between Ge(OMe)$_4$ and simple nucleophiles (F$^-$, MeO$^-$) using FTMS techniques$^{192}$. The low-pressure reaction ($10^{-8}$ Torr range) of F$^-$ reveals that the reaction proceeds by addition to yield a pentacoordinated Ge anion that can undergo selective elimination as shown in Scheme 15.

$$\text{F}^- + \text{Ge}(\text{OMe})_4 \rightarrow [\text{FGe(OMe)}_4]^-$$.  \hspace{1cm} (30)$$

While the FGe(OMe)$_4$ anion is the main reaction product, it is interesting to note that the most favorable elimination process involves loss of MeOH and CH$_2$O to yield Ge(OMe)$_3$$. This behavior is very reminiscent of what is observed in the positive ion chemistry of tetramethoxygermane$^{81}$. An additional interesting observation in this system is the fact that the pentacoordinated anion can undergo successive exchange reactions with fluorine-containing neutrals (BF$_3$, SO$_2$F$_2$) (equation 30).

$$\text{FGe(OMe)}_4^- + \text{BF}_3 \rightarrow \text{F}_2\text{Ge(OMe)}_3^- + (\text{MeO})\text{BF}_2$$  \hspace{1cm} (30)$$

SCHEME 15
This type of exchange reaction is similar to what has been observed in the corresponding Si ions. Theoretical calculations indicate that the most stable structure for the $\text{FGe(OMe)}_4^{-}$ ion corresponds to a trigonal bipyramid with the F occupying an apical position.

IV. GAS-PHASE CHEMISTRY OF NEUTRAL Ge, Sn AND Pb SPECIES

Gas-phase reactions of some of the simplest Ge, Sn and Pb compounds have been the subject of a number of investigations. For example, the detailed mechanism responsible for the thermal and photochemical decomposition of germanes, as well as some of the simple radical- and atom-molecule reactions of germanes, have attracted considerable attention in recent years because of the interest in Ge deposition processes. In the case of Sn and Pb compounds, the main interest has been related to environmental problems.

Monogermane was first shown to undergo mercury photosensitized decomposition at low pressures and at 298 K through the overall equation (31).

$$\text{Hg}(6^3\text{P}_1) + \text{GeH}_4 \rightarrow \text{Hg}(6^1\text{S}_0) + \text{Ge} + 2\text{H}_2 \quad (31)$$

Later studies revealed that Ge$_2$H$_6$, and small amounts of Ge$_3$H$_8$ and Ge$_4$H$_{10}$, are also produced in this process. The significant yield of HD obtained in the Hg sensitized photolysis of GeH$_4$ and GeD$_4$ mixtures led to the suggestion that reaction 32 is the primary photochemical quenching process.

$$\text{Hg}(6^3\text{P}_1) + \text{GeH}_4 \rightarrow \text{Hg}(6^1\text{S}_0) + \text{•GeH}_3 + \text{H}^* \quad (32)$$

The same type of decomposition in the presence of NO yields substantial amounts of GeH$_3$OGeH$_3$, lending further support to the idea that reaction 32 is the main process. While the mercury photosensitized reaction is generally accepted to proceed primarily via Ge–H bond cleavage, a different process (equation 33) involving the initial formation of germylene, GeH$_2$, becomes the most important primary reaction under direct photochemical and thermal decomposition.

$$\text{GeH}_4 \rightarrow \text{•GeH}_2 + \text{H}_2 \quad (33)$$

The direct photodecomposition of GeH$_4$ in argon-GeH$_4$ matrices by vacuum-UV radiation in the temperature range of 4–25 K was shown by spectroscopic measurements to generate •GeH$_2$ and *GeH$_3$. A more detailed and recent study has shown that the 147-nm gas-phase photolysis of GeH$_4$ proceeds by both primary channels with relative quantum yields of $\Phi_{33}(\text{•GeH}_2) = 0.66$ and $\Phi_{32}(\text{*GeH}_3) = 0.34$. Based on these primary processes a number of possible radical reactions have been proposed to account for the final products, including formation of the higher germanes.

The gas-phase thermal decomposition of GeH$_4$ proved to be a more complex process. In fact, pyrolysis of GeH$_4$ at $T \sim 600$ K revealed a heterogeneous reaction sensitive to surface effects. The use of shock tube techniques over an effective temperature range of 962–1063 K allowed for the study of the reaction free of heterogeneous effects. Under these conditions, the activation energy for the thermal decomposition of GeH$_4$ amounts to 212.3 ± 14.9 kJ mol$^{-1}$. This activation energy is considerably less than that of the Ge–H bond energy (ca 343 kJ mol$^{-1}$), indicating that the primary process in the mechanism involves a collision-assisted three-center elimination of hydrogen and formation of germylene (equation 34).

$$\text{M} + \text{GeH}_4 \rightarrow \text{•GeH}_2 + \text{H}_2 + \text{M} \quad (34)$$
Initial formation of germylene in the thermal process has also been inferred for the decomposition process sensitized by multiphoton vibrational excitation of SiF$_4$ using a pulsed CO$_2$ laser$^{202}$. Thus, it is clear that decomposition of GeH$_4$ through its ground electronic state proceeds by initial formation of $^1$GeH$_2$ while decomposition from excited electronic states can proceed both by formation of $^1$GeH$_2$ and $^3$GeH$_3$.

The homogeneous gas-phase thermal decomposition of methylgermane is considerably more complicated since several primary processes are possible in principle$^{203}$. Three primary processes have been proposed based on the following considerations: (i) the activation energy of the reaction measured from the temperature dependence of the rate; (ii) the question of the source of methyl radicals in the overall mechanism; and (iii) measurements of the yields of HD and D$_2$ in the decomposition of CH$_3$GeD$_3$. These processes can then be identified as: (a) a three-center elimination of H$_2$ accounting for 40% of the overall reaction (equation 35a); (b) a three-center elimination of CH$_4$ accounting for about 30% of the overall reaction (equation 35b); and (c) a four-center elimination of hydrogen (HD in the case of MeGeD$_3$) accounting for about 30% of the reaction (equation 35c).

\[
\begin{align*}
\text{CH}_3\text{GeH}_3 & \longrightarrow \text{CH}_3\text{GeH} + \text{H}_2 \quad (35a) \\
& \longrightarrow \text{CH}_4 + ^1\text{GeH}_2 \quad (35b) \\
& \longrightarrow \text{H}_2\text{C} = \text{GeH}_2 + \text{H}_2 \quad (35c)
\end{align*}
\]

Formation of methyl radicals in this case was considered to be the result of secondary reactions arising from further decomposition of methylgermylene, CH$_3$GeH.

Higher germanes have also been studied for the purpose of investigating routes for chemical vapor deposition (CVD) of germanium. For example, the results obtained from the sensitized thermal decomposition of Me$_4$Ge promoted by multiphoton vibrational excitation of SF$_6$ using a pulsed CO$_2$ laser$^{204,205}$, are consistent with the pyrolytic decomposition$^{206–208}$ that points out to a Ge–C bond cleavage as the primary process (equation 36).

\[
\text{Me}_4\text{Ge} \longrightarrow \text{Me}^* + ^1\text{GeMe}_3 \quad (36)
\]

By comparison, the photolysis of Me$_4$Ge with an argon fluoride laser at 193 nm yields trimethylgermane, ethane, methane, ethylene and layers of Ge as the end products$^{209}$. These results have been interpreted as indicative of electronically excited Me$_4$Ge undergoing preferential molecular elimination (equations 37a and 37b) over the dissociation shown in equation 36.

\[
\begin{align*}
\text{(Me}_4\text{Ge)}^* & \longrightarrow \text{Me}_2\text{Ge}^* + \text{C}_2\text{H}_6 \quad (37a) \\
& \longrightarrow \text{CH}_4 + \text{Me}_2\text{Ge} = \text{CH}_2 \quad (37b)
\end{align*}
\]

Ethylgermanes, Et$_n$GeH$_{4-n}$ ($n = 1–4$), yield primarily ethane and ethylene as the main end product of 193 nm laser photolysis in ratios that vary from 2 to 5 depending on the number of Et groups present in the original molecule$^{210}$. Very small quantities of ethylgermanes with a lower number of Et groups in the molecule are also observed as minor products. Experiments carried out in the presence of GeD$_4$ suggest that ethane and ethylene are probably formed in a primary process which results in their elimination (equations 38a and 38b).

\[
\begin{align*}
\text{Et}_n\text{GeH}_{4-n}^* & \longrightarrow \text{Et}_{n-1}\text{GeH}_{3-n} + \text{C}_2\text{H}_6 \quad (38a) \\
& \longrightarrow \text{C}_2\text{H}_4 + \text{Et}_{n-1}\text{GeH}_{5-n} \quad (38b)
\end{align*}
\]
By comparison, the thermal dissociation of the ethylgermanes has been proposed to proceed by cleavage of the Ge−C bond (equation 48) followed by hydrogen abstraction by the nascent ethyl radical$^{211,212}$.

$$\text{Et}_n\text{GeH}_4^-n^* \rightarrow \text{Et}_{n-1}\text{GeH}_4^-n + \cdot\text{Et} \quad (39)$$

Unfortunately, the unequivocal elucidation of these mechanisms requires real time measurements of the nascent products and an analysis of the kinetics of the propagation steps. Some studies on individual elementary reactions are discussed below.

The chemical vapor deposition processes obtained from the laser induced multiphoton decomposition of neat organogermaines or sensitized by SF$_6$ have also been characterized for several systems. For example, the decomposition of Ge(OMe)$_4$ leads to the formation of organoxogermanium polymers$^{213}$, while EtOGeMe$_3$ leads to materials rich in Ge and containing small amounts of oxygen and carbon$^{214}$. In the latter case, two primary processes have been proposed to be responsible for the chain reactions leading to the final products (equations 40a and 40b)$^{215}$.

$$\text{EtOGeMe}_3 \rightarrow \text{Me}^* + \text{Me}_2\text{Ge(OEt)}^* \quad (40a)$$

$$\rightarrow \text{EtO}^* + \text{Me}_3\text{Ge}^* \quad (40b)$$

However, the ethylene and acetaldehyde appearing among the final products may also originate through non-radical mechanisms, namely $\beta$ elimination processes that are prevalent for these alkoxystermaines (equations 41 and 42).

$$\text{EtOGeMe}_3 \rightarrow \text{Me}_3\text{GeH} + \text{CH}_3\text{CHO} \quad (41)$$

$$\text{EtOGeMe}_3 \rightarrow \text{Me}_3\text{GeOH} + \text{C}_2\text{H}_4 \quad (42)$$

A few gas-phase atom-GeH$_4$ elementary reactions have been studied in detail because of their role in the general mechanism of thermal deposition processes. The most widely studied reaction is that involving H atoms and GeH$_4$ for which hydrogen abstraction (equation 43) is considered the only pathway.

$$\text{H} + \text{GeH}_4 \rightarrow \text{H}_2 + \cdot\text{GeH}_3 \quad (43)$$

Recent measurements$^{216,217}$ for this reaction in the range of $T = 293–473$ K have settled the question of the rate constant that was in serious doubt from the early experiments$^{218,219}$. Reaction 43 is characterized by a very low activation energy of $7.3 \pm 0.2$ kJ mol$^{-1}$, and an isotope effect $k_H/k_D = 2.0 \pm 0.4$ at 300 K obtained by comparison with the reaction of H atom with fully deuteriated monogermane$^{220}$. The rate constant for the prototype reaction 43 increases with progressive methyl substitution on the germane. This fact has been used to suggest a lowering of the Ge−H bond dissociation energy upon methyl substitution$^{221}$.

The dynamics of hydrogen abstraction reactions promoted by F, O, OH and OD with monogermane have been studied as a function of the vibrational and rotational state by infrared chemiluminescence$^{222–224}$. While this technique provides enormous insight on the energy disposal in a reaction, it also led to a value of $326 \pm 4$ kJ mol$^{-1}$ for the H$_3$Ge−H bond dissociation energy at 0 K. This value is somewhat lower than the value of $346 \pm 10$ kJ mol$^{-1}$ obtained from a kinetic study of reaction 44 and its thermochemistry$^{225,226}$.

$$\text{I}_2 + \text{GeH}_4 \rightarrow \text{GeH}_3\text{I} + \text{HI} \quad (44)$$
This same approach was used by Doncaster and Walsh to study the iodine reaction with Me₃GeH and to derive a bond dissociation energy of 340 ± 10 kJ mol⁻¹ for Me₃Ge−H²²⁷. These results suggest that methyl substitution has no appreciable effect on the Ge−H bond energy within experimental error. On the other hand, iodine substitution as in GeH₃I was shown²²⁸ to decrease the Ge−H bond energy by 14 kJ mol⁻¹.

Hydrogen atom abstraction reactions are usually characterized by very low activation energies (Eₐ). This is the case for the reaction of the t-BuO⁺ radical with germane²²⁹ for which Eₐ was determined to be 7.9 kJ mol⁻¹. A somewhat higher activation energy has been measured for the hydrogen abstraction by O (³P) from methyl groups attached to germanium²³⁰. For example, an activation energy of 22.3 kJ mol⁻¹ was obtained for Me₄Ge, 13.5 kJ mol⁻¹ for Et₄Ge and 16.6 kJ mol⁻¹ for (MeO)₄Ge. These higher activation energies reflect the fact that the C−H bond energies are higher than the Ge−H bond energy in monogermane.

A new and exciting development in the gas-phase chemistry of Ge has been the ability to characterize the behavior of germylenes, RR'Ge⁺²³¹. While the chemistry of germylenes has been extensively explored in solution to promote a series of reactions²³², it is only recently that GeH₂ has been detected in the gas phase by laser-induced fluorescence as a result of the 193 nm photolysis of phenylgermane²³³. This has opened the possibility to investigate some of the elementary reactions involved in CVD processes using germanes.

The rate constants for the reaction of GeH₂, generated by laser flash photolysis from either PhGeH₃ or 3,4-dimethylgermacyclopentane, with O₂, C₂H₂, i-C₄H₈, 1,3-C₄H₆, C₃H₈ and Me₃SiH has been recently determined by time-resolved laser induced fluorescence²³⁴. Analysis of the end products for the reaction with 2,3-dimethyl-1,3-butadiene reveals addition of GeH₂ onto the double bond to yield 3,4-dimethylgermacyclopentane, as shown in Scheme 16.

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
+ \quad \text{GeH}_2 & \quad \rightarrow \\
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
\text{GeH}_2 & \quad \text{GeH}_2 \\
\end{align*}
\]

SCHEME 16

From these measurements it has been possible to conclude that GeH₂ can insert readily into Si−H bonds but not into C−H bonds, and can undergo addition to π bonds.

More detailed studies on the insertion of GeH₂ have been obtained from the reaction with Me₃SiH and GeH₄ (equations 45–47)²³⁵,²³⁶.

\[
\begin{align*}
\text{GeH}_2 + \text{Me}_3\text{SiH} & \rightarrow \text{Me}_3\text{SiGeH}_3 & (45) \\
\text{GeH}_2 + \text{GeH}_4 & \rightarrow \text{Ge}_2\text{H}_6 & (46)
\end{align*}
\]

Both of these reactions proceed with very high rate constants at room temperature (within a factor of 5 of the collision rate for GeH₄) and insertion in the Ge−H bond is more facile than for the Si−H bond. Reaction 46 has been found to be pressure-dependent, so that formation of Ge₂H₆ is best described as a third body assisted association. The analogous reaction to 46, but using SiH₂, reveals that silylene insertion in the Ge−H bond is faster than that of the corresponding germylene²³⁷.

These fast insertion reactions display a negative activation energy²³⁸, and high level ab initio calculations²³⁶ confirm the suggestion that these reactions proceed through a
transient state where a hydrogen bridge between the two germanium atoms mediates formation of the final product in reaction 46.

By comparison with the reactivity of GeH₂, dimethylgermylene (GeMe₂) has been found to be unreactive towards C−H, Si−H and Ge−H insertion but reacts rapidly with π-bonded systems²³⁹.

A very recent study²⁴⁰ reveals that an activation energy of at least 19 ± 6 kJ mol⁻¹ can be estimated from the upper limit for the rate constant of the insertion of germylene into molecular hydrogen (equation 47).

\[
\text{GeH}_2 + \text{D}_2 \rightarrow \text{GeH}_2\text{D}_2 \quad (47)
\]

Theoretical calculations predict a significant barrier of 58 kJ mol⁻¹ for this reaction.

Much less information is available on the gas-phase chemistry of Sn derivatives. The thermal decomposition of SnH₄ (equation 48) was characterized as a heterogeneous process where Sn was found to promote the reaction autocatalytically²⁴¹,²⁴².

\[
\text{SnH}_4 \rightarrow \text{Sn} + 2\text{H}_2 \quad (48)
\]

The 193 nm laser induced photodecomposition of SnH₄ suggested that stannylene, SnH₂, is the main intermediate of this process in analogy with what is observed for silane and germane²⁴₃. A similar photolysis study at 147 nm results in the final products as shown in reaction 48 plus a small amount of Sn₂H₆. However, the quantum yield of hydrogen, Φ(H₂), at 0.20 Torr of SnH₄ was measured to be 11.4 ± 0.6, indicating a somewhat more complex mechanism than that predicted by a simple initial formation of SnH₂ and hydrogen²⁴⁴. The quantum yield decreases with increasing pressure, but extrapolation to zero pressure yields a value similar to that obtained at 0.20 Torr. At the 147 nm wavelength, it is possible to consider two primary pathways that are energetically feasible (equations 49 and 50).

\[
\begin{align*}
\text{SnH}_4 & \rightarrow \text{SnH}_2 + 2\text{H} \quad (49) \\
& \rightarrow \text{SnH} + 3\text{H} 
\end{align*}
\]

The ensuing propagation steps promoted by the hydrogen atoms can lead to quantum yields as high as 12 for hydrogen if reaction 50 is the exclusive channel.

Distannane, Sn₂H₆, is known to have extremely poor thermal stability leading to Sn and hydrogen²⁴⁵. Recent measurements²⁴⁶ show that the activation energy for thermal decomposition of Sn₂H₆ is only 5.3 ± 0.6 kJ mol⁻¹ but the low pre-exponential factor obtained for the rate constant suggests that the decomposition is a heterogeneous process.

The trend for heterogeneous reactions in these systems is well illustrated in studies carried out for gas-phase auto-oxidation of simple tin compounds at higher temperatures (200–450 °C)²⁴⁷. These reactions are of environmental concern and serve as complementary information to what is known about lead-containing systems. For Et₄Sn, auto-oxidation is believed to be initiated by the initial decomposition shown in equation 51 followed by reaction with O₂ (equation 52), by analogy to the mechanism for auto-oxidation of organic compounds.

\[
\begin{align*}
\text{Et}_4\text{Sn} & \rightarrow \text{Et}_3\text{Sn}^* + \text{Et}^* \quad (51) \\
\text{Et}_3\text{Sn}^* + \text{O}_2 & \rightarrow \text{EtSn(OH)}_2^* + \text{C}_4\text{H}_8 
\end{align*}
\]

Generation of OH radicals can then lead to formation of triethyltin hydroxide, Et₃SnOH, which undergoes heterogeneous dehydration and oxidation.
However, for environmental purposes the most important gas-phase chemistry is that related to the tetraalkyl lead derivatives. Me$_4$Pb and Et$_4$Pb have been used extensively as a gasoline additive to prevent pre-ignition, but considerable concern has been raised over the last 30 years regarding its long-lasting effects on the environment and as a health hazard. While these compounds tend to yield a complex mixture of lead salts upon combustion$^{248}$, incomplete combustion accounts for a non-negligible amount of lead-containing fuel to enter the atmosphere.

A classical study on the fate of tetraalkyl compounds in the atmosphere$^{249}$ shows the effect of photochemical oxidation on the breakdown of R$_4$Pb. Direct ozonolysis of Me$_4$Pb (equation 53) presumably proceeds by analogy to the process in tetraethyltin$^{250}$.

\[
\text{Me}_4\text{Pb} + \text{O}_3 \rightarrow \text{Me}_3\text{PbOOH} + \text{CH}_2\text{O}
\]  

(53)

However, reactions promoted by O (from photolysis of O$_3$) are much faster and more important in the atmosphere. Reaction 54 leads to formation of OH, and the ensuing reactions are responsible for the degradation of Me$_4$Pb in the atmosphere.

\[
\text{Me}_4\text{Pb} + \text{O} \rightarrow \text{Me}_3\text{PbCH}_2 + \text{OH}
\]  

(54)

The rate constants for the reaction of OH with Me$_4$Pb and Et$_4$Pb reveal that consumption of the tetraalkyl lead is very rapid$^{251}$. The fact that these reactions are much faster than for the corresponding carbon analogs has led to the suggestion that hydrogen abstraction cannot be the dominant reaction channel. The fact that Et$_4$Pb reacts much faster than Me$_4$Pb is consistent with the proposal that the initial step in the reaction is addition of OH to yield an R$_4$PbOH intermediate from which either H$_2$O or an alkyl radical can be eliminated. From these rate constant measurements and considering typical tropospheric concentrations of OH, a lifetime of $ca$ 50 hours was estimated for Me$_4$Pb and of 4 hours for Et$_4$Pb in ambient air.

A different type of gas-phase chemistry has also been explored for simple germanium, tin and lead compounds, namely that induced by radiolysis. While germanium compounds have been the main targets and modeling of CVD processes the ultimate goal, radiolysis involves reactions of transient neutral and ionic species for which the overall mechanism is not always clear. On the other hand, analysis of the ultimate solid products$^{252}$ obtained from radiolysis of different mixtures provides an exciting approach towards the synthesis of polymers and thin films.

V. ACKNOWLEDGMENTS

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VI. REFERENCES

3. See, for example:
5. Gas-phase chemistry and mass spectrometry


See, for example:


5. Gas-phase chemistry and mass spectrometry

5. Gas-phase chemistry and mass spectrometry

5. Gas-phase chemistry and mass spectrometry

For some typical radiolysis studies, see:
Recent advances in structural chemistry of organic germanium, tin and lead compounds

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I. INTRODUCTION

A. List of Abbreviations

Most of the chemistry reported here depends on the presence of bulky ligands which will be denoted by the following abbreviations:

<table>
<thead>
<tr>
<th>R</th>
<th>Abbreviation</th>
<th>R</th>
<th>Abbreviation</th>
<th>R</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHMe₂</td>
<td>i-Pr</td>
<td>CH(SiMe₃)₂</td>
<td>Bsi</td>
<td>2-t-Bu-4,5,6-Me₅C₆H</td>
<td>Bmp</td>
</tr>
<tr>
<td>CMe₃</td>
<td>t-Bu</td>
<td>C(SiMe₃)₃</td>
<td>Tsi</td>
<td>2,6-[P(O)(OEt)₂]₂-4-t-BuC₆H₂</td>
<td>R⁹</td>
</tr>
<tr>
<td>SiMe₃</td>
<td>Tms</td>
<td>Si(Bu-t)₃</td>
<td>Sup</td>
<td>C₁₀H₁₅ (adamantyl)</td>
<td>Ad</td>
</tr>
<tr>
<td>Si(SiMe₃)₃ Hyp</td>
<td>Si(Bu-t)₃</td>
<td>Sup</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2,6-Di-substituted and 2,4,6-tri-substituted aryl groups:

<table>
<thead>
<tr>
<th>R =</th>
<th>Abbreviation</th>
<th>R =</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et</td>
<td>Det</td>
<td>Me</td>
<td>Mes</td>
</tr>
<tr>
<td>i-Pr</td>
<td>Dip</td>
<td>Et</td>
<td>Tret</td>
</tr>
<tr>
<td>Mes</td>
<td>Btm</td>
<td>i-Pr</td>
<td>Tip</td>
</tr>
<tr>
<td>Trip</td>
<td>Btp</td>
<td>t-Bu</td>
<td>Mes⁺</td>
</tr>
<tr>
<td>2'-naphthyl</td>
<td>Btn</td>
<td>CF₃</td>
<td>Ar²F</td>
</tr>
<tr>
<td>2'-i-PrC₆H₄</td>
<td>Bip</td>
<td>CH(SiMe₃)₂</td>
<td>Tbt</td>
</tr>
<tr>
<td>CH₂NMe₂</td>
<td>Dmdm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMe₂</td>
<td>Ar²N</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

GED denotes electron diffraction (gas phase).

B. General Comments

In the first edition of this book Mackay gave an excellent overview about most types of compounds containing E−C bonds, E being a heavier member of Group 14 (tetrels): germanium, tin and lead¹. In his introduction he stated that most of the differences between C and the heavier tetrels derive from the ability of carbon (and the disability of its higher congeners) to form

(i) strong element–element bonds giving homonuclear chains and rings, and
(ii) \( \pi \)-overlap of p-orbitals and hence alkenes, alkynes, aromatic compounds and the like.

Secondly, he stressed

(iii) the existence of a distinct two-valent state already for Ge and its increasing stability through Sn to Pb, and
(iv) the ability of the heavier elements to show higher coordination numbers than 4, resulting in different structures for compounds of the same stoichiometry and providing lower-energy intermediates.

During the last five years only statement (ii) has had to be revised. It is now well established that it is not the insufficiency of the heavier group 14 elements of $\pi$-bonding that prevents them from giving multiply-bonded species — $\pi$-bonds may in fact be very strong, even or especially for Pb$^{2a,b}$. Instead, an imbalance between increasing promotion energies of the constituting tetrylene (tetrelandiyl) ER₂ or tetrylyne (tetrelantriyl) ER fragments from their singlet or doublet ground-state to the triplet or quartet valence-state, respectively, on the one hand, and generally decreasing bond energies going from lighter to heavier elements on the other hand are responsible for this fact$^{2,3}$. Additionally, the kinetic lability of such compounds, partially related to (iv), surely prevented many unusual multiple-bonded systems from being isolated under ambient conditions.

The electronic structure of carbene homologues R₂E, the major building blocks of such systems, has been investigated by many groups using quantum-mechanical methods$^{2-4}$. Their chemistry and the nature of bonding within their dimers, i.e. alkene homologues R₂E=ER₂, and their cyclic oligomers c-EₙR₂ₙ is now understood more deeply. On the other hand, only little really novel information is available about the title elements in their ‘normal’ oxidation state. Thus, this chapter will deal mostly with low valent germanium, tin and lead derivatives such as carbene homologues, mono- and oligocyclic systems and species containing homonuclear and heteronuclear multiple bonds between Ge, Sn and Pb. Numerous reviews have been published, especially on multiply bonded compounds of group 14$^5$ and, in line with the title of this chapter, I will concentrate on the structural aspects of these species.

Some of the novel systems are known only with silyl, germyl or other inorganometallic substituents, but not with simple organyl substituents. Since no principal differences from the related organyl derivatives are expected, these compounds are also included in the present discussions. Excluded are compounds in which the tetrel exclusively bears halido, amido and alkoxo substituents or other hetero-element atoms with lone-pairs.

II. TETRYLENES (TETRELANEDIYLS) R₂E AND THEIR DERIVATIVES

A. Tetrylenes with Two-coordinate Tetrel Atom

Numerous compounds with divalent two-coordinate tetrel atoms have been synthesized during the last twenty years and many of them have been characterized by absolute structure methods$^{5c}$. In this chapter I will discuss the structural features of such derivatives which bear at least one $\sigma$-bonded organyl group or related homologous inorganometallic substituents with a heavier tetrel bonded directly to the divalent atom. Most of the cyclopentadienyl compounds will be excluded from this discussion, since in most cases these are coordinated in a multi-hapto $\pi$-fashion and so the bonding becomes more ionic. Moreover, the structural chemistry of such derivatives has grown to such an extent during recent years$^{6}$ and many of them form complicated 3-dimensional network structures or polynuclear oligomers, and so they should be treated in a different chapter.

Before going into a detailed discussion of the structural peculiarities of homoletic and heteroleptic tetrylenes (Tables 1–7), two features common to all such species should be briefly mentioned:

(a) small C—E—C bond angles which, in most cases, are significantly smaller than the ideal tetrahedral angle of about 109.5°;

(b) C—E bond lengths which are markedly longer than the appropriate parameters in the corresponding tetravalent species.
Both features are based on the fact that all known (isolable) heavier tetrylenes ER₂ exist in a singlet ground-state, the lone-pair on E residing in an almost pure s-type orbital. As a consequence almost pure p-orbitals are utilized for bonding to the substituents, leading to small C–E–C angles and, since pure p-orbitals are less directed than spⁿ-hybrides, to longer E–C bonds. Only in cases where extreme sterical congestion or significant additional interactions such as Lewis-acid/Lewis-base interactions are present, widening of the C–E–C angles or shortening of the C–E bonds may be observed.

1. Homoleptic species — diorganyltetrylenes R₂E

In this chapter the focus is laid on species comprising two E–C bonds, including however those rare examples where two different organyl groups are bonded to the two-coordinate tetrel atom (Table 1) and which are not homoleptic within a stricter definition.

a. Germynes (germandiyls). Many germynes are stable in the gas phase or in dilute solutions only, and they tend to dimerise to digermenes in concentrated solutions and in the solid-state. Hence Bsi₂Ge (1) is monomeric in the gas phase⁷, in solution an equilibrium with its dimer Bsi₂Ge=GeBsi₂ is observed and in the solid-state digermene molecules with a typical trans-bent conformation (see Section III) has been found⁸. This delicate equilibrium between germylene and digermene—which is discussed in more detail in Section III—may be, however, influenced by small structural (and electronic) changes as can be seen by the example of the cyclic analogue (2), which is strictly monomeric in solution and even in the solid-state (C–Ge 202 pm; C–Ge–C 90.98°)⁹; the same holds, besides, for the analogous tin derivative 3 (C–Sn, 213 pm; C–Sn–C, 86.7°)¹⁰.

The stability of the monomer can be rationalized by the pronounced rigidity of the ligand system and by the fact that in the case of the cyclic system all Me₃Si groups must be orientated towards the Ge atom (syn, syn-conformer) whereas in Bsi₂Ge (1) two of them may turn away (syn, anti-conformer) and are indeed turned away in the solid-state structure of the respective digermene; in the gas-phase Bsi₂Ge adopts the syn, syn-conformation, however. This rigid orientation in the cyclic compounds leads to an increased sterical congestion (destabilization of the dimer) and to additional hyperconjugative stabilization of monomer 2 (Figure 1), since all four Me₃Si groups are in the right orientation for interaction of the Si–C σ-bond orbitals with the empty p-orbital on Ge; the latter is in turn crucial for interaction with external electron-pair donors such as a second germylene entity. Indeed, the C–Si bonds to the SiMe₃ groups are slightly elongated in the germylene 2 (190 pm) compared with other derivatives of the substituent where no similar hyperconjugation is possible. Notably, the same cyclic substituent was very recently utilized to synthesize the first isolable dialkylsilylene (4) (C–Si, 190.4 pm; C–Si–C, 93.87°); here the C–SiMe₃ bond (190.6 pm) is even more elongated¹¹. The acyclic derivative Bsi₂Si and its dimer Bsi₂Si=SiBsi₂ are still unknown.
4. Recent advances in structural chemistry

![Molecular structure of cyclic germylene 2 (top) and scheme for the proposed hyperconjugative σ(SiC) → p(Ge) interaction (bottom)](image)

**TABLE 1.** Parameters (bond length in pm, angle in deg) of germylenes $R_1R_2Ge$ with two-coordinate tetrel atom

<table>
<thead>
<tr>
<th>Homoleptic</th>
<th>$R^1$</th>
<th>$R^2$</th>
<th>Ge−$R^1$</th>
<th>Ge−$R^2$</th>
<th>$R^1$−Ge−$R^2$</th>
<th>Reference</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(C, C)$^a$</td>
<td>Bis</td>
<td>Bis</td>
<td>201</td>
<td>202</td>
<td>91.0</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bis</td>
<td>Tris</td>
<td>204</td>
<td>204</td>
<td>107</td>
<td>7</td>
<td>GED</td>
</tr>
<tr>
<td></td>
<td>Btm</td>
<td>Btm</td>
<td>203</td>
<td>203</td>
<td>114.4</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Btm</td>
<td>BtmGe</td>
<td>203</td>
<td>204</td>
<td>102.7</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ArF</td>
<td>ArF</td>
<td>207</td>
<td>208</td>
<td>100.0</td>
<td>15</td>
<td>Ge−F contacts</td>
</tr>
<tr>
<td></td>
<td>ArN</td>
<td>ArN</td>
<td>202</td>
<td>202</td>
<td>105.1</td>
<td>16</td>
<td>Ge−N contacts</td>
</tr>
<tr>
<td></td>
<td>Mes*</td>
<td>Mes*</td>
<td>204</td>
<td>205</td>
<td>108.0</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Heteroleptic</td>
<td>Btp</td>
<td>Cl</td>
<td>199</td>
<td>220.3</td>
<td>101.3</td>
<td>18</td>
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</tr>
<tr>
<td></td>
<td>Btm</td>
<td>BtmGe</td>
<td>202</td>
<td>242.2</td>
<td>111.3</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$H(Si, N)^a$</td>
<td>246.1 (Si)</td>
<td>183 (N)</td>
<td>97.5</td>
<td>19</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Btp</td>
<td>Cp(CO)$_3$Cr</td>
<td>199</td>
<td>259.0</td>
<td>117.8</td>
<td>20a</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Btp</td>
<td>Cp(CO)$_3$W</td>
<td>199</td>
<td>268.1</td>
<td>114.7</td>
<td>20a</td>
<td></td>
</tr>
<tr>
<td>For comparison</td>
<td>F</td>
<td>F</td>
<td>173.2</td>
<td>173.2</td>
<td>97</td>
<td>21</td>
<td>GED</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>Cl</td>
<td>218.3</td>
<td>218.3</td>
<td>100</td>
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<td>Br</td>
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<td>233.7</td>
<td>233.7</td>
<td>101</td>
<td>23</td>
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<tr>
<td></td>
<td>N(SiMe$_3$)$_2$</td>
<td>N(SiMe$_3$)$_2$</td>
<td>187</td>
<td>189</td>
<td>107.1</td>
<td>24</td>
<td></td>
</tr>
</tbody>
</table>

$^a$For the definition of substituents $I$ and $II$, see Chart 1 atomic symbols in parentheses denote the type of atom binding to Sn.
Factors that are definitely known to contribute to the stabilization of germylene monomers are (a) substituents even bulkier than Bsi or (b) electron-withdrawing ligands. Apart from cyclopentadienyl ligands, especially bulky aryl substituents such as 2,4,6-tri-tert-butylphenyl (supermesityl; Mes∗) and o,o′-disubstituted terphenyls 2,6-(2′,4′,6′-R3C6H2)2C6H3 (e.g., R = Me, i-Pr) have been used to stabilize not only germyles, but also many other sensitive compounds which tend to dimerize otherwise.

The extreme steric congestion present in Mes∗2Ge (5)17 and to a somewhat lesser extent in the homologous stannylene Mes∗2Sn (6)25 (since the Sn-C bond is markedly longer than the Ge−C bond) can be easily recognized by a strong distortion of the phenyl rings and the out-of-plane positioning of the tetrel atom. In the germylene 5 the two aryl rings are distorted to a quite different extent (Table 2a); the Ge atom is lying within the best plane through the only slightly distorted ring, but 158 pm (!) above the best plane through the other ring (Figure 2). In the stannylene 6, the aryl rings are both substantially distorted and the Sn atom lies out-of-plane by 105 and 112 pm with respect to both (Table 2b). The corresponding plumbylene Mes∗2Pb (7), because of its low kinetic stability, rearranges at about −30°C to the isomeric alkyl(aryl)plumbylene Mes∗PbCH2CMe2(3,5-t-Bu2C6H3) (8)26.

Utilizing extremely bulky terphenyl substituents Power and coworkers recently reported the synthesis of another strictly monomeric germylene: Btm2Ge (9)13. Despite the huge 2,6-dimesitylphenyl (Btm) substituents the distortion around Ge observed for 9 is much smaller than for the supermesityl derivative 5. Thus Power and coworkers claimed that these terphenyl ligands are different from other bulky groups by protecting the space surrounding the central atom, whereas most of the other bulky ligands such as Mes∗ occupy the space in the immediate proximity of the central atom. This is even more true for the 2,6-bis(1′-naphthyl)phenyl (Btm) substituent 10 which was used very recently by Schmidbaur and coworkers in preparing the ‘ligand-protected strain-free’ diarylgermylene Btm2Ge14; herein short Ge−C bonds (203 pm) and a very small C−Ge−C angle (102.7°) have been determined. Therefore he claimed these values to be the ‘natural’ bond parameters of diarylgermylenes.

In the case of the derivative ArF2Ge (11)15 the introduction of the electron-withdrawing ArF-substituent (2,4,6-(F3C)3C6H2) destabilizes the hypothetical dimer for electronic
4. Recent advances in structural chemistry

TABLE 2. Deviation from planarity measured by the distance (pm) to the best plane through the respective aromatic ring in Mes$_2^*$Ge (5) and in Mes$_2^*$Sn (6)$^a$

<table>
<thead>
<tr>
<th>Ring I</th>
<th>Ring II</th>
<th>(a) Mes$_2^*$Ge (5)</th>
<th></th>
<th></th>
<th>(b) Mes$_2^*$Sn (6)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>Ge</td>
<td></td>
<td></td>
<td></td>
<td>Sn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+158.0</td>
<td>+11.5</td>
<td>C11</td>
<td>+0.9</td>
<td></td>
<td>+105.1</td>
<td>+9.8</td>
<td></td>
</tr>
<tr>
<td>C11</td>
<td>C21</td>
<td>C12</td>
<td>-6.5</td>
<td></td>
<td>C11</td>
<td>+0.9</td>
<td></td>
</tr>
<tr>
<td>-6.5</td>
<td>-3.4</td>
<td>C121</td>
<td>-39.8</td>
<td></td>
<td>-5.8</td>
<td>-2.6</td>
<td></td>
</tr>
<tr>
<td>C13</td>
<td>C22</td>
<td>C14</td>
<td>+8.3</td>
<td></td>
<td>+7.2</td>
<td>+3.3</td>
<td></td>
</tr>
<tr>
<td>-3.4</td>
<td>C23</td>
<td>C141</td>
<td>+30.0</td>
<td></td>
<td>+7.2</td>
<td>+3.3</td>
<td></td>
</tr>
<tr>
<td>C14</td>
<td>C24</td>
<td>C15</td>
<td>-3.2</td>
<td></td>
<td>-3.1</td>
<td>-5.4</td>
<td></td>
</tr>
<tr>
<td>-8.3</td>
<td>C25</td>
<td>C16</td>
<td>-6.7</td>
<td></td>
<td>-5.4</td>
<td>-3.1</td>
<td></td>
</tr>
<tr>
<td>C15</td>
<td>C26</td>
<td>C261</td>
<td>-45.7</td>
<td></td>
<td>-3.1</td>
<td>-5.4</td>
<td></td>
</tr>
<tr>
<td>C16</td>
<td>C261</td>
<td>Ge</td>
<td>-158.0</td>
<td></td>
<td>C261</td>
<td>-105.1</td>
<td></td>
</tr>
</tbody>
</table>

$^a$For atom numbering see Figure 2.

FIGURE 2. Molecular structure of sterically encumbered germyle 6 (Me groups are omitted for clarity) illustrating the distortion present: (left) view within the best plane through ring I; (right) view within the best plane through ring II (see Table 2a)
reasons (see Section III) and simultaneously stabilizes the monomer by intramolecular F → Ge interactions. A particular orientation of the ortho-CF₃ groups is observed (Figure 3); one group for each aryl substituent is orientated in a way that short Ge···F distances are formed (255.2 and 256.3 pm), indicating an interaction of a lone-pair on F with the empty p-orbital on Ge. The two remaining ortho-CF₃ groups show orientations less effective for interaction and hence lead to significantly longer Ge···F distances (278.3 and 278.9 pm). The monomers of the homologues Sn and Pb derivatives of 11, Ar₂SnF (12) and Ar₅PbF (13)²⁷,²⁸ are stabilized by analogous interactions, the discrimination between the short and long F → E distances being somewhat smaller (see below).

Finally, I would like to make some remarks on related germylenes bearing silyl or germyl substituents instead of organyl groups. In sharp contrast to bis(silyl)stannylenes (R₃Si)₂Sn and plumbylenes (R₃Si)₂Pb, there is no report of an isolable bis(silyl)germylene (R₃Si)₂Ge in the literature. If bulky tris(alkyl)silyl substituents are employed, dimers, i.e. digermenes (R₃Si)₂Ge=Ge(SiR₃)₂, are obtained (see Section III). If the hypersilyl group: Si(SiMe₃)₃ (Hyp) — a tris(silyl)silyl group — is introduced, neither germylenes nor digermenes are isolated. Instead, rearrangements to cyclic products are observed. Heine and Stalke, for instance, reported the almost quantitative formation of hexakis(trimethylsilyl)disilagermirane (14)²⁹ when reacting (thf)₃LiSi(SiMe₃)₃ with GeCl₂·dioxane. In an analogous reaction using (thf)₃LiGe(SiMe₃)₃ instead, Geanangel and coworkers observed the formation of the cyclotetragermane (HypGeCl)₄ — a tetramer of the mono-substitution product — and hexakis(trimethylsilyl)cyclotrigermane (15)³⁰. In our laboratory, we investigated the reactions of GeCl₂·dioxane and HSiCl₃ with unsolvated lithium hypersilanide LiSi(SiMe₃)₃. Again, products which could be isolated in high yields were 14 and the homologous trisilirane 16, respectively³¹. Most probably, germylenes and silylene of type 17 are intermediates in the formation of these cyclic products, which then undergo a

FIGURE 3. Molecular structure of germylene 11. The stronger F → Ge interactions are represented as wide (=), the weaker ones as thin (−) lines
rapid diatropic rearrangement by the shift of two Me$_3$Si groups from the hypersilyl or the respective tris(trimethylsilyl)germyl substituent to the electron-deficient Ge(II) or Si(II) centre (Scheme 1). Further very probable intermediates, in fact the first ones which could be postulated in the course of these reactions, are silagermenes, germenes or silenes of type 18. A related compound, the silene (19), has been unambiguously identified as the only product from heating the cyclic silylene (4) (equation 1)\textsuperscript{11}. It is noteworthy that the respective stannylene and plumbylene with two hypersilyl substituents Hyp$_2$Sn 20 and Hyp$_2$Pb 21\textsuperscript{32} show no tendency for rearrangement and may be isolated as dimer and monomer, respectively. The reason for this different behaviour probably lies in the different energy balance of broken and new-formed bonds: while along the rearrangement of 17 to 14, 15 and 16 two relatively strong bonds (Si–Si or Ge–Si) are broken, but three nearly equally strong bonds (Ge–Si, Si–Si or Ge–Ge) are formed, in the case of 20 and 21 two strong bonds are to break, but only one new strong Si–Si and two weak Sn–Si or Pb–Si bonds would form.

\[
\text{ECI}_2\cdot\text{dioxane} + 2\text{LiE'(Tms)}_3 \ [E = \text{Ge}; E' = \text{Si, Ge}]
\]

\[
\xrightarrow{\sim 2\text{LiCl}}
\]

<table>
<thead>
<tr>
<th>17</th>
<th>18</th>
<th>14</th>
<th>15</th>
<th>16</th>
</tr>
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<tbody>
<tr>
<td>\text{Tms}</td>
<td>\text{Tms}</td>
<td>\text{E'}</td>
<td>\text{E'}</td>
<td>\text{E}</td>
</tr>
<tr>
<td>\text{Tms}</td>
<td>\text{E'}</td>
<td>\text{E'}</td>
<td>\text{E'}</td>
<td>\text{E'}</td>
</tr>
<tr>
<td>\text{Tms}</td>
<td>\text{Tms}</td>
<td>\text{Tms}</td>
<td>\text{Tms}</td>
<td>\text{Tms}</td>
</tr>
</tbody>
</table>

\[
\text{HECl}_3 + 3\text{LiE'(Tms)}_3 \ [E = E' = \text{Si}]
\]

SCHEME 1. Putative rearrangement paths of germynes and silylenes bearing silyl or germyl substituents. Proposed intermediates are given in brackets

\[
\Delta
\]

<table>
<thead>
<tr>
<th>4</th>
<th>19</th>
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<tbody>
<tr>
<td>\text{Tms}</td>
<td>\text{C}</td>
</tr>
<tr>
<td>\text{Tms}</td>
<td>\text{C}</td>
</tr>
</tbody>
</table>

\( b. \text{ Stannylenes (stannandiyls).}\) Due to the larger singlet–triplet gap (see Section III), the tendency of stannylenes for dimerisation or oligomerisation is significantly lower than for the lighter congeners, hence all known dimers readily dissociate in solution or in the gas phase (see, for example, SnBsi$_2$\textsuperscript{7,42}).
TABLE 3. Parameters (bond length in pm, angle in deg) of stannylenes R₁R₂Sn with two-coordinate tetrel atom

<table>
<thead>
<tr>
<th>R¹</th>
<th>R²</th>
<th>Sn−R¹</th>
<th>Sn−R²</th>
<th>R¹−Sn−R²</th>
<th>Reference</th>
<th>Remarks</th>
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<tbody>
<tr>
<td>Homoleptic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bis</td>
<td>Bis</td>
<td>222</td>
<td>222</td>
<td>97</td>
<td>7</td>
<td>GED</td>
</tr>
<tr>
<td>Ar⁺</td>
<td>Ar⁺</td>
<td>228</td>
<td>228</td>
<td>98.2</td>
<td>27a</td>
<td>four Sn···F contacts: 266; 268; 281; 283</td>
</tr>
<tr>
<td>Ar⁺</td>
<td>Ar⁺</td>
<td>228</td>
<td>229</td>
<td>95.1</td>
<td>27b</td>
<td>loose dimer: Sn-Sn: 363.9; four Sn···F contacts: 269; 271; 280; 282</td>
</tr>
<tr>
<td>I (C, C)ᵃ</td>
<td></td>
<td>222</td>
<td>222</td>
<td>86.7</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Btm</td>
<td>Btm</td>
<td>223</td>
<td>223</td>
<td>114.7</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>Ar⁺</td>
<td>Ar⁺</td>
<td>222</td>
<td>221</td>
<td>105.6</td>
<td>16, 33</td>
<td>Sn-N contacts: 261; 267</td>
</tr>
<tr>
<td>Mes⁺</td>
<td>Mes⁺</td>
<td>226</td>
<td>227</td>
<td>103.6</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>compound 22</td>
<td>(C, C)</td>
<td>231</td>
<td>231</td>
<td>98.7</td>
<td>34</td>
<td>two N-Sn-N units present: Sn-N: 216–226; N-Sn-N: 103.0–104.0</td>
</tr>
<tr>
<td>IIIa (Si)ᵃ</td>
<td>IIIa (Si)ᵃ</td>
<td>271.2</td>
<td>271.2</td>
<td>106.8</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>Heteroleptic</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar⁺</td>
<td>compound 23</td>
<td>225</td>
<td>212</td>
<td>108.4</td>
<td>36</td>
<td>two independent molecules two Sn···F contacts: 273, 273</td>
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<tr>
<td>Btp</td>
<td>I</td>
<td>221</td>
<td>276.6</td>
<td>102.7</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>Btp</td>
<td>N(Tms)₂</td>
<td>223</td>
<td>209</td>
<td>108.4</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>Ar⁺</td>
<td>IIIb (Si)ᵇ</td>
<td>221</td>
<td>263.7</td>
<td>107.0</td>
<td>37</td>
<td>two Sn-N contacts: 257; 258</td>
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<tr>
<td>Btp</td>
<td>Btp(Me)₂Sn</td>
<td>223</td>
<td>289.1</td>
<td>101.2</td>
<td>38</td>
<td></td>
</tr>
</tbody>
</table>

For comparison

| Cl          | Cl          | 233.5  | 233.5  | 99       | 39        | GED                                  |
| Br          | Br          | 250.1  | 250.1  | 100      | 40        | GED                                  |
| I           | I           | 268.8  | 268.8  | 105      | 39        | GED                                  |
| N(Tms)₂     | N(Tms)₂     | 209    | 210    | 105      | 41        | GED                                  |

ᵃFor the definition of substituents I and III, see Chart 1 atomic symbols in parentheses denote the type of atom binding to Sn.

Less than ten homoleptic stannylenes are known which are strictly monomeric in the solid state and which are not stabilized by substantial further coordination at the divalent Sn (Table 3). Additionally, one monomeric homoleptic bis(silyl)stannylene 24³⁵ had been reported, formed unexpectedly by the reaction of a bis(amino)silylene 25 and a bis(amine)stannylene 26 alongside a formal insertion of the electron-deficient Si atom of 25 into a Sn−N bond of 26. A most probable reaction path, starting with subsequent addition and rearrangement steps, is depicted in Scheme 2. The second known bis(silyl)stannylene, Hyp₂Sn (20)³², is monomeric only in dilute solution and forms dimers with very unusual structural features in the solid state (Section III). Very recently, Power and coworkers reported the first example of triorganylstannyl-substituted stannylene 27 with two-coordinate Sn⁴³. Such compounds are discussed as being intermediates in rearrangement reactions of distannenes, since they are thought to be easily accessible isomers on the hypersurface of the latter.
SCHEME 2. Probable mechanism for the formation of stannylene 22 from stannylene 26 and silylene 25
The crystal structures of three bis(organyl)stannylenes reveal weak coordinative intra-
molecular interactions between Sn and electron-donating groups and one of them shows
additional weak intermolecular interaction to adjacent stannylene species in the crystal.

The tris(trifluoromethyl)phenyl derivative (2,4,6-(F_3C)_3C_6H_2)_2Sn (ArF_2Sn) 12 crystal-
lizes in two polymorphs. The yellow polymorph\(^{27a}\), exhibiting no notable intermolecular
interactions, displays two sets of relatively tight intramolecular contacts from \(\text{ortho-CF}_3\)
groups to the divalent tin, a shorter set: Sn−F = 266.3, 268.1 pm, and a longer set: 280.7,
283.3 pm (cf 11). In the second red polymorph\(^{27b}\) these contacts are still present, the
shorter set, however, is significantly lengthened by 5 pm (av.), whereas the longer set is
nearly unchanged. The reason probably lies in competing weak intermolecular Sn⋯Sn
interactions between two stannylene moieties with a distorted \(\text{trans-bent} \) arrangement
of the substituents. Similar conformations are found for ‘real’ distannenes, though the
Sn−Sn distances in the latter are much shorter than the value of 363.9 pm found for
(12)\(_2\) which is significantly shorter than twice the van der Waals radius of Sn. Similar
Sn⋯F interactions are also observed in two heteroleptic stannylenes: Ar^F(Hyp)Sn (28)\(^{44}\)
and Ar^F–C(O)=C(PPh_3)–SnAr^F (23)\(^{36}\); here, one Ar^F group is replaced by a hypersilyl
((Me_3Si)_3Si) substituent or an oxoethenyl group, respectively. In the dimer of compound
28 the Sn−Sn bond is strengthened by the strongly electron-releasing silyl group, leading
to a Sn−Sn bond length of 283.3 pm. This strengthening of the Sn−Sn bond — by com-
petitive usage of the empty p-orbital on Sn by the second stannylene moiety — leads to
dramatically reduced F⋯Sn interactions with Sn−F distances of 294.9 and 295.6 pm.

The remaining stannylene with weak intramolecular stabilization by a Lewis base is the
bis[2,6-(N,N-dimethylamino)phenyl]stannylene [2,6-(Me_2N)_2C_6H_3]_2Sn (Ar^NSn) (29)\(^{33}\).
Two Me_2N groups show close Sn⋯N contacts of 259.9 and 266.3 pm, the proposed
lone-pair being directed to the space above and below the C−Sn−C plane where the
empty p-orbital of Sn is assumed (Figure 4). Similar interactions are found in the related
heteroleptic aryl(silyl)stannylene 42 mentioned in Section II. A.2.b\(^{37}\).

One further unique diarylstannylene which is worth discussing in more detail is the
polycyclic derivative (22)\(^{34}\). This particular molecule possesses three divalent Sn atoms,
two of them being coordinated by two amido ligands and the remaining one by two aryl
substituents. The Sn atom (Sn\(_A\)) of the bis(aryl)stannylene fragment shows no unusual
tight contacts to any other atom — there are close intramolecular contacts to the other Sn
atoms, but they are most probably superimposed by the geometric needs of a bicyclic
system. The two bis(amino)stannylene (SnB) fragments, however, do display unusual short contacts (Figure 5) which are not forced, since they are intermolecular. Within the tetrahedral array SnB···SnB distances between 367 and 388 pm are observed, thus lying between typical covalent and van der Waals interactions. There are many examples of similar unsupported contacts in heavy element chemistry, the nature of which is not understood in most cases and is still under controversial discussion. In main-group element chemistry some related electron-deficient species such as some In(I) and many Tl(I) derivatives exhibit a similar type of short intermolecular contacts in the solid state. Various closed-shell species\textsuperscript{45} such as stibanes, bismutanes, selenans and tellanes, and related compounds tend also to associate in the condensed phase.
In contrast to the lighter congeners, until very recently, plumbylenes were thought to be strictly monomeric even in the solid state, though weakly bonded dimers and even cyclo-oligomers had been postulated by quantum-chemical calculations — at least for the parent compound PbH₂. Unlike carbenes, their higher homologues should have different possibilities of dimerisation, thereby not only and not

<table>
<thead>
<tr>
<th>R¹</th>
<th>R²</th>
<th>Pb–R¹</th>
<th>Pb–R²</th>
<th>R¹–Pb–R²</th>
<th>Reference</th>
<th>Remarks</th>
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<td>Bis</td>
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<td>230</td>
<td>230</td>
<td>103.6</td>
<td>46</td>
<td>GED</td>
</tr>
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<td>Bis</td>
<td>Bis</td>
<td>231</td>
<td>232</td>
<td>93.6</td>
<td>47</td>
<td>loose dimer</td>
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<td></td>
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<td>Pb–Pb: 412.9</td>
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<tr>
<td>ArF</td>
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<td>237</td>
<td>94.5</td>
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<td>233</td>
<td>114.5</td>
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<tr>
<td>Tbt</td>
<td>Tbt</td>
<td>233</td>
<td>233</td>
<td>116.3</td>
<td>48</td>
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<tr>
<td></td>
<td>IV (C, C)</td>
<td>240</td>
<td>241</td>
<td>117.1</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>Tret</td>
<td>Tret</td>
<td>235</td>
<td>234</td>
<td>99.4</td>
<td>50</td>
<td>MgBr₂(thf)₄ adduct</td>
</tr>
<tr>
<td>Mes</td>
<td>Mes</td>
<td>231</td>
<td>232</td>
<td>97.4</td>
<td>51</td>
<td>MgBr₂(thf)₄ adduct</td>
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</tbody>
</table>

| Heteroleptic|           |       |       |          |           |                       |
| compound 8 | (C, C)    | 234   | 249   | 94.7     | 26        |                       |
| Btm       | Hyp (Si)  | 229   | 271.2 | 109.2    | 54        |                       |
| ArF       | Hyp (Si)  | 237   | 270.6 | 96.6     | 44        |                       |
| Bmp       | Hyp (Si)  | 236   | 271.1 | 106.0    | 26        |                       |
| Btp       | Br        | 233   | 278.9 | 95.4     | 52        |                       |
| Btp       | Cp(CO)₃Cr | 229   | 290.9 | 113.6    | 55        |                       |
| Btp       | Cp(CO)₃Mo | 229   | 298.5 | 110.0    | 55        |                       |
| Btp       | Cp(CO)₃W  | 228   | 298.1 | 108.6    | 55        |                       |
| Btp       | Cp(CO)₃W  | 228   | 300.6 | 109.4    | 55        |                       |
| For comparison|           |       |       |          |           |                       |
| F         | F         | 203.6 | 203.6 | 96       | 40        | GED                   |
| Cl        | Cl        | 244.4 | 244.4 | 98.0     | 40        | GED                   |
| Br        | Br        | 259.7 | 259.7 | 100      | 40        | GED                   |
| I         | I         | 280.4 | 280.4 | 100      | 40        | GED                   |
| N(Tms)₂   | N(Tms)₂   | 222.2 | 226.0 | 103.6    | 41        |                       |

For the definition of IV and V, see Chart 2; atomic symbols in parentheses denote the type of atom binding to Pb.
even preferably yielding alkene homologues $E_2R_4$, but also by forming three-centre bonds with substituents $R$ in a bridging position. This topic will be discussed in detail later (Section III). Here we will mainly discuss the structural features of the well-characterized monomers (Table 4).

The first bis(organyl)plumbylene isolated and structurally characterized (at first in the gas phase only) was the dark blue bis[bis(trimethylsilyl)methyl]plumbylene $Bsi_2Pb$ \textsuperscript{30}. Recently we were able to determine the crystal structure of the low-melting solid and, to our surprise, found (very) weakly associated dimers (Figure 6)\textsuperscript{49}. Despite a Pb–Pb distance not much shorter than twice the van der Waals radius of Pb, the dimer adopts a trans-bent conformation typical for the heavier congeners of the alkenes. In spite of the same conformation (syn, syn) in the gas phase and in the solid state, the structure displays markedly differing $C−Pb−C$ angles of $103.6^\circ$ (30) and $93.6^\circ$ (30)$^2$, respectively.

\begin{center}
\begin{tikzpicture}
\begin{scope}[scale=0.5]
\node (a) at (0,0) {Me};
\node (b) at (1,0) {Si};
\node (c) at (2,0) {Me};
\node (d) at (3,0) {Tms};
\node (e) at (4,0) {Tms};
\node (f) at (5,0) {Me};
\node (g) at (6,0) {Si};
\node (h) at (7,0) {Me};
\node (i) at (8,0) {Tms};
\node (j) at (9,0) {Tms};
\node (k) at (10,0) {Me};
\node (l) at (11,0) {Si};
\node (m) at (12,0) {Me};
\node (n) at (13,0) {Tms};
\node (o) at (14,0) {Tms};
\node (p) at (15,0) {Me};
\node (q) at (0,-1) {Me};
\node (r) at (1,-1) {Tms};
\node (s) at (2,-1) {Tms};
\node (t) at (3,-1) {Me};
\node (u) at (4,-1) {Si};
\node (v) at (5,-1) {Me};
\node (w) at (6,-1) {Tms};
\node (x) at (7,-1) {Tms};
\node (y) at (8,-1) {Me};
\node (z) at (9,-1) {Si};
\node (aa) at (10,-1) {Me};
\node (ab) at (11,-1) {Tms};
\node (ac) at (12,-1) {Tms};
\node (ad) at (13,-1) {Me};
\node (ae) at (14,-1) {Si};
\node (af) at (15,-1) {Me};
\node (ag) at (0,-2) {Me};
\node (ah) at (1,-2) {Si};
\node (ai) at (2,-2) {N};
\node (aj) at (3,-2) {Bu-t};
\node (ak) at (4,-2) {Tms};
\node (al) at (5,-2) {Tms};
\node (am) at (6,-2) {Me};
\node (an) at (7,-2) {N};
\node (ao) at (8,-2) {Me};
\node (ap) at (9,-2) {Bu-t};
\node (aq) at (0,-3) {Me};
\node (ar) at (1,-3) {Si};
\node (as) at (2,-3) {N};
\node (at) at (3,-3) {Bu-t};
\node (au) at (4,-3) {t-Bu};
\node (av) at (5,-3) {Me};
\node (aw) at (6,-3) {N};
\node (ax) at (7,-3) {Me};
\node (ay) at (8,-3) {t-Bu};
\node (az) at (9,-3) {Bu-t};
\node (aa0) at (0,-4) {Me};
\node (aa1) at (1,-4) {O};
\node (aa2) at (2,-4) {Bu-t};
\node (aa3) at (3,-4) {t-Bu};
\node (aa4) at (4,-4) {H};
\node (aa5) at (5,-4) {N};
\node (aa6) at (6,-4) {Me};
\node (aa7) at (7,-4) {Si};
\node (aa8) at (8,-4) {N};
\node (aa9) at (9,-4) {t-Bu};
\node (aa10) at (0,-5) {Me};
\node (aa11) at (1,-5) {Si};
\node (aa12) at (2,-5) {N};
\node (aa13) at (3,-5) {Bu-t};
\node (aa14) at (4,-5) {t-Bu};
\node (aa15) at (5,-5) {N};
\node (aa16) at (6,-5) {Me};
\node (aa17) at (7,-5) {Si};
\node (aa18) at (8,-5) {N};
\node (aa19) at (9,-5) {t-Bu};
\end{scope}
\end{tikzpicture}
\end{center}

CHART 2. Abbreviations used in tables. Heavy dots and arrow heads indicate the connection point of the substituent
There are only two other homoleptic plumbylenes which form dimers in the solid state and which will be discussed in more detail later, i.e. bis(2,4,6-tri-isopropylphenyl)plumbylene (Tip$_2$Pb) and dimesitylplumbylene (Mes$_2$Pb). All remaining derivatives are monomers for steric and/or electronic reasons. Pure steric congestion had been achieved by substituents such as 2,6-Mes$_2$C$_6$H$_3$ (Btm)$_{13,2}$, 2-t-Bu-4,5,6-Me$_3$CH (Bmp)$_{26}$ or the bidentate ligand [H$_2$CSi(Me)$_2$C(SiMe$_3$)$_2$]$_2$ (31)$_{49}$.

Surprisingly, in compound (31) two relatively short Pb···Si contacts to adjacent Me$_3$Si groups are observed$_{49}$ which are only about 20% longer than the covalent Pb(II)–Si bonds in heteroleptic aryl(silyl)plumbylenes.

[2,4,6-(F$_3$C)$_3$C$_6$H$_2$]$_2$Pb (Ar$_F^5$Pb) 13$_{28}$ as its lighter congeners 11$_{15}$ and 12$_{27}$ comprises electronegative substituents and short intramolecular Pb···F contacts (278.4; 279.3; 284.0; 296.7 pm), thus preventing the compound from dimerisation. Replacing one Ar$_F$ substituent by the electron-releasing hypersilyl group yielding Ar$_F$(Hyp)Pb (32)$_{44}$ again favours the formation of a Pb–Pb bond. Since a Pb–Pb interaction is markedly weaker than an analogous Sn–Sn interaction (this especially holds for trans-bent double bonds), no lengthening of Pb···F contacts is observed (as it is for the pair 12 and 28), but rather an even slight shortening, reflecting perhaps that the number of F → Pb contacts is reduced from four to two.
An unprecedented type of intramolecular coordination is found in the alkyl(aryl)plumbylene $^{8}$.$^{26}$. This particular plumbylene is formed via a rearrangement from homoleptic bis(supermesityl)plumbylene $^{7}$ (equation 2) which, in contrast to the respective derivatives of Ge and Sn ($^{5}$ and $^{6}$), could not be structurally characterized so far due to its low stability. In the course of the rearrangement process a C−H bond of one tert-butyl group may interact with the electron-deficient two-coordinate Pb atom and subsequently undergo an addition reaction to the Pb−C bond. There is one structural feature remaining in the resulting heteroleptic species $^{8}$ which may serve as a possible model for this proposed H$_3$C⋯Pb interaction: two tert-butyl substituents of the remaining aryl substituent indeed show unusual short contacts of one methyl group each with the divalent Pb atom (Figure 7). These particular methyl groups are positioned in the voids above and below the C−Pb−C plane where the empty p-orbital of the Pb atom is thought to be located. This orientation leads to Pb⋯C distances of 280 and 283 pm, which are only about 15% or 20% longer than the covalent Pb−C$_{alkyl}$ and Pb−C$_{aryl}$ bonds in $^{8}$. Unfortunately, but not unexpectedly, the positions of the hydrogen atoms at these particular methyl groups could not be located from the diffraction data. Thus no detailed picture of the interaction may be derived from the present structural data. However, a donor/acceptor interaction with C−H bonds as Lewis base and the electron-deficient Pb atom as Lewis acid seems to be possible.

Very recently, Power and coworkers reported the synthesis and structural characterization of a series of alkyl(aryl) and bis(aryl) substituted plumbylenes $^{33a–c}$ with one extremely bulky terphenyl ligand Btp = 2,6-Tip$_2$C$_6$H$_3$(Tip = 2,4,6-(i-Pr)$_3$C$_6$H$_2$) and one simple alkyl or aryl group such as methyl, tert-butyl and phenyl, by reacting the heteroleptic bromo(aryl)plumbylene 2,6-BtpPbBr with the appropriate Grignard or lithium organyl agent$^{52}$. Despite the extreme bulk of the Btp substituent, the observed Pb−C bond lengths as well as the C−Pb−C angles are in the lower part of the range found for Pb(II) derivatives.

2. Heteroleptic species $^{R−E−X}$

Heteroleptic carbene homologues with two-coordinate tetrel atoms still bearing one organyl group are relatively rare, since in most cases the second substituent is an amido, alkoxy or halido group which possesses one or more free electron pairs and thus tend to
give rise to the formation of bridged oligomers. Only if the second substituent has almost no Lewis basic properties, such as a silyl group, stanny group or an appropriate transition metal fragment, and in cases where oligomerization is prevented by steric congestion, monomers with two-coordinate tetrel atoms may be observed.
4. Recent advances in structural chemistry 301

a. Germynes (germandiyls). There are only few papers about structure elucidation of heteroleptic germynes with two-coordinate Ge bearing at least one organyl ligand. Power and coworkers reported the synthesis of the synthetically very valuable aryl(chloro)germylene BtpGeCl \(^\text{34}\)\(^\text{18}\). Its existence as a monomeric species is due to the extremely bulky Btp substituent. Compound \(\text{35}\) with the related, but smaller, Btm = 2,6-Mes\(_2\)C\(_6\)H\(_3\) ligand dimerises in the solid state to a unique digermene (see below)\(^\text{56}\). The crystal structure of \(\text{34}\) shows Ge–C = 198.9 pm, Ge–Cl = 220.3 pm and C–Ge–Cl = 101.3°; hence the Ge–C bond in \(\text{34}\) is markedly shorter than in all structurally characterized dialkyl and diarylgermylenes ranging from 201 to 208 pm, and the GeCl distance is somewhat longer than in the gas-phase structure of GeCl\(_2\)\(^\text{22}\) [GED: Ge–Cl = 218.3(4), Cl–Ge–Cl = 100.3(4)°].

\[
\text{(36)}
\]

Apart from the silyl(amino)germylene \(\text{36}\), which is obtained from the reaction of a cyclic silylene with a cyclic bis(amino)germylene\(^\text{19}\) (cf \(\text{24}\)), the remaining heteroleptic germynes with two-coordinate Ge which had been structurally characterized are the metallogermynes \(\text{37a,c}\)\(^\text{20a}\). As discussed in the literature\(^\text{20a,b}\), these compounds may be regarded in a good approximation as germynes. In other species comprising two-coordinate Ge atoms, a varying degree of multiple-bond character may be present, depending on the nature of the bonded metal fragment, i.e. its \(\pi\)-accepting and \(\pi\)-donating ability. We will not go into detail here, since it is beyond the scope of this chapter. Nevertheless, the two species, \(\text{37a,c}\) must be addressed as metallogermynes, since the bonded metal fragment as a 17-electron moiety is neither a good \(\pi\)-acceptor nor a good \(\pi\)-donor. As expected, the M–Ge–C unit (M = Cr, W) is strongly bent, with M–Ge–C = 117.8°(M = Cr) and 114.7°(M = W); the Ge–M bond with 259 and 268 pm, respectively, is definitely a single bond. The compounds were synthesized by metathesis of Na[M(\(\eta^5\)-C\(_5\)H\(_5\))(CO)\(_3\)] · 2DME and the heteroleptic aryl(chloro)germylene \(\text{34}\) at low temperatures. Heating the resulting germynes under reflux in toluene or irradiating with UV light leads to CO loss and formation of the related metallogermynanes \(\text{38a,c}\) (equation 3). The Mo analogue \(\text{37b}\) could not be isolated at all; it looses CO at temperatures below −20°C and yields directly the metallogermlyne \(\text{38b}\) under the given reaction conditions.
b. Stannylenes (stannandiyls). Heteroleptic stannylenes are known with a greater variety of substituents, although the total number is also small. In solution, even a hydrido species BtpSnH was characterized very recently\(^\text{(38)}\). However, it dimerises in the solid state and will be discussed below. The same bulky aryl ligand allowed also the isolation of the monomeric aryl(iodo) and aryl(amido)stannylenes BtpSnI \((\text{39})\) and BtpSn[N(Tms)\(_2\)] \((\text{40})\)\(^\text{18}\). Both resemble the related aryl(chloro)germylene \(\text{(34)}\) discussed above. Whereas the Sn—I bond in \(\text{39}\) with 276.6 pm is again markedly lengthened compared with SnI\(_2\) (268.8 pm), no change in Sn—N bond lengths is observed going from Sn[N(Tms)\(_2\)]\(_2\) \((\text{26})\)\(^\text{41}\) to \(\text{40}\).

A remarkable compound, comprising divalent and tetravalent tin atoms within one molecule, is the already mentioned triorganylstannylstannylene \(\text{(38)}\); the observed Sn(II)—Sn(IV) bond distance of 286.9 pm is much longer than the Sn(IV)—Sn(IV) bonds in distannanes; responsible are the larger covalent radius of Sn(II) compared with Sn(IV) and the extremely bulky Btp group present. It should be noted that a closely related donor-stabilized stannylene \(\text{(41)}\)\(^\text{57,58}\) is known which exhibits the same feature, but comprises a three-coordinate Sn(II) centre with intramolecular Sn ← N coordination (Sn—N: 228.8 pm). In spite of the higher coordination number at Sn(II), but expected from the presence of less demanding substituents, a somewhat shorter Sn—Sn bond (286.9 pm) is found. Whereas the heteroleptic stannylenes bearing one extremely bulky Btp group are accessible from Sn(II) halides and successive treatment with appropriate nucleophiles, the remaining heteroleptic species had been synthesized from diarylstannylenes with other electronically or coordinatively unsaturated compounds.
The unique oxoethenyl substituted stannylene 23 is obtained via the reaction of $\text{Ar}_2^\text{F} \text{Sn}$ with a ketene 36. In spite of two close $\text{F} \cdots \text{Sn}$ contacts (274 pm), a very short $\text{Sn} \cdots \text{C}$ bond (212.2 pm) to the oxoethenyl moiety is found. This short $\text{Sn} \cdots \text{C}$ bond as well as $\text{C} \cdots \text{O}$ and $\text{C} \cdots \text{C}$ bond lengths of 129 and 141 pm, respectively, and the virtually coplanar $\text{O} \cdots \text{C} \cdots \text{C} \cdots \text{Sn}$ arrangement, indicates $\pi$-delocalization and $\text{Sn} \cdots \text{C}$ multiple bonding.

All aryl(silyl)stannylenes known are monomers in dilute solution. One of them, the stannylene 42, stays as a monomer even in the solid state, most probably for steric reasons. It is formed alongside an unusual insertion reaction of silylene 25 into one tin carbon bond of the diarylstannylene $\text{Ar}_2^\text{N} \text{Sn}$ (cf 24 and 36). The others bearing at least one hypersilyl group ($\text{Hyp} = \text{Si}((\text{SiMe}_3)_3)$) all form dimers (distannenes) in the solid state. They are synthesized via ligand exchange between the respective homoleptic stannylenes or between $\text{Hyp}_2\text{Sn}$ (20) and CuMes. The proposed reaction scheme for the ligand exchange between stannylenes is similar to the one given for the formation of 24, 36 and 42 (see above), since in all cases the first step is a formation of doubly-bonded mixed dimers, which then rearrange by migration of a substituent from one of the doubly-bonded atoms to the other, the first step having almost no activation barrier and the second step in most cases having a very small barrier.
c. Plumbylenes (plumbandiyls). Heteroleptic plumbylenes with two-coordinate Pb are known with very bulky substituents only. Apart from the already discussed alkyl(aryl)plumbylene \(^8\), either a hypersilyl or a terphenyl substituent (Btm or Btp) or even both are present. Whereas most terphenyl-substituted plumbylenes are monomers both in solution and in the solid state, most of the hypersilyl derivatives — according to the low electronegativity of the Hyp group — give dimers in the solid state. Despite the long Pb−Pb bonds, the latter may be addressed as diplumbenes \(R_2\text{Pb} = \text{PbR}_2\) and will be discussed in detail in Section III. Terphenyl-substituted plumbylenes never form dimers with a Pb−Pb bond for steric reasons, even if the second substituent is as small as methyl (see 33a–c)\(^52\). Only if the second substituent is a halogen, such as Br, may dimers be observed (see below)\(^52\).

We recently synthesized a new class of heteroleptic plumbylenes which, in spite of the presence of Lewis-basic centres, form no oligomers but only monomers with a three-coordinate Pb. The reaction of azides (RN\(_3\); R = SiMe\(_3\); 1-adamantyl) with Hyp\(_2\text{Pb}\) 21 did not lead to iminoplumbanes Hyp\(_2\text{Pb} = \text{NR}\) as intended; instead, the formation of hypersilyl(triazenyl)plumbylenes 43a,\(^\text{a, b}\) (equation 4) had been observed\(^61\), putatively formed via formation of an azide adduct and subsequent migration of one hypersilyl substituent from the lead to the terminal nitrogen atom. The crystal structure of 43a had been determined (Figure 8) and revealed the presence of a pyramidally coordinated Pb and an \(\eta^2\)-coordinated triazenyl moiety. The latter shows two markedly different N−N bonds of 129 and 135 pm, the longer one directed towards a slightly pyramidally coordinated and the shorter one to a planar coordinated nitrogen atom, indicating at least a partial localization of the double bond.

\[
\begin{align*}
\text{Hyp} & \quad \text{Pb} + N\equiv N\equiv N \quad R \\
\text{Hyp} & \quad \text{Pb} \\
\text{Hyp} & \quad \text{Pb}
\end{align*}
\]

(21) \hspace{5cm} \text{(4)}

(a) R = 1-Ad
(b) R = Tms

A further interesting class of heteroleptic plumbylenes are the metalloplumbylenes BtpPb[M(CO)\(_3\)Cp] \(^44\) (M = Cr, Mo, W)\(^55\) — the homologues of the metallogermylenes 37 mentioned above — which were synthesized only very recently by reaction of BtpPbBr with (thf)\(_2\)Na[M(CO)\(_3\)Cp](M = Cr, Mo, W). The nature of the metal fragment (17e\(^−\)) as well as long M−E bonds and small C−Pb−M angles between 108.6 pm (W) and 113.6 pm (Cr) clearly indicate the absence of notable M → Pb backbonding, i.e. of M−Pb multiple bonding.

B. Tetrylenes with Higher-coordinate Tetrel Atoms

There is a lot of structural information available on intramolecular and intermolecular Lewis acid/Lewis base complexes of tetrylenes. In this section I will concentrate on basic structural principles which are valid throughout the series of the tetrylenes.

Whereas amino groups are used most frequently as intramolecular Lewis bases (Tables 5–7), stable unsupported intermolecular complexes are typically accomplished by carbenic-type donors, such as carbenes, isonitriles and ylides (Table 8). To my knowledge, no unsupported intermolecular adduct of ethers, amines or phosphanes have been structurally characterized so far (except for the more ionic cyclopentadienyl derivatives\(^62\)).
Most probably, it is the softness of the E(II) centre that is mainly responsible for this fact. Nevertheless, *intra*molecular E ← N bonds may be relatively short and may lead to significant differences in reactivity compared to tetrylenes missing such interactions, since the acceptor orbital at the tetrel is (partially) blocked towards interactions with external Lewis bases (see discussion in Section III). Substantial structural changes within the R–Sn–R skeleton (apart from those caused by steric interactions) are not observed and are not expected for most species, however, since bonding of the Lewis-basic centres is accomplished by the LUMO of the R–E–R fragment which is an empty p-orbital of the respective tetrel E. Contributions of antibonding R–E orbitals—for symmetry reasons—should only play a significant role if E–R–π-bonds were present. Thus, the Ge–Cl and Sn–Cl bond lengths in the carbene complexes of GeCl₂ and SnCl₂, 45a–c, are by about 12 pm longer than in gaseous GeCl₂ and SnCl₂ (218 pm²² and 234 pm²⁹, respectively, some Sn–Hal π-bonding)²², whereas the Sn–C bond in the isonitrile complex Ar₂F⁺Sn ← CNMes is only by 3 pm longer than in the parent stannylene (228 pm; no Sn-C π-bonding)⁶³. The length of the E ← D bond in turn may also be influenced by different Lewis-acidities of the tetrel in different tetrylenes.

Thus, in the series of the stannylenes 41 and 46a–c⁵⁷,⁵⁸,⁶⁴,⁶⁵ the shortest intramolecular Sn ← N contact of 226 pm is observed for 46a which is still about 20 pm longer than typical covalent and Sn(II)–N bonds. A similar observation was very recently made for two germynes (47a,b)⁶⁶ with intramolecular Ge ← O contacts: again the aryl(chloro)germylene 47a exhibits a by far shorter Ge ← O bond of 207 pm than the respective diaryl derivative 47b (219 pm). If the acidity of the tetrel is enhanced by coordination of an external Lewis acid, as can be seen by the only two examples of main-group Lewis-acid adducts 48a,b¹⁶ to tetrylenes (see Table 9), the shortening in the E ← D bond is dramatic. Whereas the parent germylene Ar₅Ge and stannylene 29 display only weak Ge ← N and Sn ← N interactions (Ge-N: 239; Sn-N: 261, 267 pm, respectively), the complexation with BH₃ results in a shortening of these contacts by 28 pm and 18 pm, respectively.

In the unique adduct 49⁶⁷ (Figure 9), which is built from four stannyylene sub-units, the interplay between different Lewis bases bonded to the same Lewis-acidic stannylene can be demonstrated impressively. The compound comprises three chloro(dimethylamino)-3-methylbut-2-yl stannylene fragments, two of which (A and A’) act as Lewis acid and
as Lewis base towards a bridging chloride anion and a SnCl\(^{+}\)-cation, respectively, and
one such fragment (B) which acts only as base towards the SnCl\(^{+}\)-cation (C). Since no
competing donor is present, the observed N\(_B\) → SnC bond in fragment B is by far shorter
(221 pm) than the respective bond in the fragments A (N\(_A\)−SnC: 243 and N\(_A\)'−SnC:
247 pm), where the bridging chloride anion Cl\(_{D}\) is competing for the same acceptor orbital
on the Sn\(_A\) atom. Similar reasons lead to the markedly different Sn−Sn bonds: the longer
Sn\(_B\)−Sn\(_C\) bond (315.6 pm) is formed by fragment B, since it competes with the terminal
TABLE 5. Parameters (bond length in pm, angle in deg) of germynes R₁R₂Ge with higher coordinated tetrel atom (donor atom D)

<table>
<thead>
<tr>
<th>R₁(\text{VI (C)})</th>
<th>R₂</th>
<th>D</th>
<th>Ge–R₁</th>
<th>Ge–R₂</th>
<th>Ge–D</th>
<th>R₁–Ge–R₂</th>
<th>R₂–Ge–D</th>
<th>Reference</th>
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<tr>
<td>Cl</td>
<td>N</td>
<td>214</td>
<td>229.5</td>
<td>208</td>
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<td>67.2</td>
<td>91.9</td>
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<td>102.5</td>
<td>66.9</td>
<td>93.0</td>
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<tr>
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<tr>
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<td>225</td>
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<td>225</td>
<td>230</td>
<td>115.6</td>
<td>119.0</td>
<td>—</td>
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<td>Mes* MCP₉</td>
<td>C</td>
<td>209</td>
<td>231</td>
<td>232</td>
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<td>100.0</td>
<td>—</td>
<td>70</td>
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For comparison

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<tbody>
<tr>
<td>Cl</td>
<td>MCP₉</td>
<td>C 238.4</td>
<td>221; 222</td>
<td>96.8; 100.6</td>
<td>—</td>
<td></td>
<td>71</td>
<td>(\eta²)-coordination (Mcp)</td>
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<tr>
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<td>MCP₉</td>
<td>F 293.7 (F) 225–226</td>
<td>—</td>
<td>—</td>
<td>71</td>
<td>(\eta²)-coordination (Mcp)</td>
<td></td>
<td></td>
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<tr>
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<td>Me₄C₅(C₂H₄NMe₂)</td>
<td>C 236.8</td>
<td>218; 240</td>
<td>229</td>
<td>—</td>
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\(\text{VI, VII and VIII, see Chart 2; atomic symbols in parentheses denote the type of atom binding to Ge. MCP₉ = pentamethylcyclopentadienyl.}\)
TABLE 6. Parameters (bond length in pm, angle in deg) of stannylenes \( R_1R_2\text{Sn} \) with higher coordinated tetrel atom (donor atom D)

| \( R^1 \) | \( R^2 \) | D | \( \text{Sn}–R^1 \) | \( \text{Sn}–R^2 \) | \( \text{Sn}–D \) | \( \text{R}^1–\text{Sn}–\text{R}^2 \) | \( \text{R}^1–\text{Sn}–\text{D} \) | \( \text{R}^2–\text{Sn}–\text{D} \) | Reference | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|
| VI | Cl | N | 232.9 | 244.0 | 227 | 101.4 | 61.1 | 91.7 | 65 | two independent molecules |
| VI | N(SiMe\(_3\))\(_2\) | N | 235.6 | 214 | 230 | 105.4 | 61.1 | 97.3 | 65 |
| VI | Tip | N | 237.2 | 225 | 235 | 111.9 | 60.5 | 107.6 | 64 |
| VI | CH(PPh\(_2\))\(_2\) | N | 235.9 | 231 | 230 | 100.8 | 61.1 | 93.0 | 57 |
| VI | Sn(SiMe\(_3\))\(_3\) | N | 230.4 | 286.9 (Sn) | 229 | 108.3 | 61.3 | 89.7 | 57, 58 |
| VI | Hyp | N | 234.5 | 272.4 (Si) | 234 | 113.5 | 61.3 | 93.4 | 57 |
| IX | C\(_5\)H\(_5\)(\(\pi\)) | N | 247.4 | 212 | 247 | 102.1 | 88.8 | 67.6 | 73 |
| IX | C\(_9\)H\(_7\)(\(\sigma\)) | N | 234.3 | 212 | 231 | 98.2 | 92.5 | 70.7 | 73 |
| R\(^P\) | SiPh\(_3\) | O | 222.9 | 275.1 (Si) | 245 | 96.4 | 76.7 | 89.2 | 74 |
| Mes\(^*\) | Mes\(^*\)CS\(_2\) | S | 222.3 | 265.3 (S) | 266.2 | 91.7 | 99.2 | 119.3 | 75 | two independent molecules |
| CH(PPh\(_2\))\(_2\) (C) | CH(PPh\(_2\))\(_2\) (P) | P | 228.2 | 265.9 (P) | 267.8 | 90.3 | 99.4 | 63.4 | 76 |

\(^a\)For the definition of substituents VI and IX, see Chart 2 atomic symbols in parentheses denote the type of atom bonding to Sn.

TABLE 7. Parameters (bond length in pm, angle in deg) of plumbylenes \( R_1R_2\text{Pb} \) with higher coordinated tetrel atom (donor atom D)

| \( R^1 \) | \( R^2 \) | D | \( \text{Pb}–R^1 \) | \( \text{Pb}–R^2 \) | \( \text{Pb}–D \) | \( \text{R}^1–\text{Pb}–\text{R}^2 \) | \( \text{R}^1–\text{Pb}–\text{D} \) | \( \text{R}^2–\text{Pb}–\text{D} \) | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| CH(PPh\(_2\))\(_2\) (C) | CH(PPh\(_2\))\(_2\) (P) | P | 237 | 275.8 (P) | 278.2 | 88.7 | 96.6 | 61.5 | 76 |
| Hyp | HypN\(_3\)Ad-1 | N | 273.7 | 234 | 237 | 100.1 | 105.8 | 54.2 | 61 |

\(^a\)Atomic symbols in parentheses denote the type of atom binding to Pb.
TABLE 8. Parameters (bond length in pm, angle in deg) of unsupported Lewis-base adducts to tetrylenes $L \rightarrow ER_2$ ($E = Ge, Sn, Pb$) with donor atoms $D$

**Germynylenes**

<table>
<thead>
<tr>
<th>R</th>
<th>Base</th>
<th>D</th>
<th>Ge–R$^1$</th>
<th>Ge–R$^2$</th>
<th>Ge–D</th>
<th>R$^1$–Ge–R$^2$</th>
<th>R$^1$–Ge–D</th>
<th>R$^2$–Ge–D</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$Xa^a$</td>
<td>C</td>
<td>263.9</td>
<td>268.1</td>
<td>210</td>
<td>99.4</td>
<td>100.2</td>
<td>95.4</td>
<td>79</td>
</tr>
<tr>
<td>Cl</td>
<td>HC[P(NMe$_2$)$_2$]CH</td>
<td>C</td>
<td>229.9</td>
<td>232.9</td>
<td>207</td>
<td>97.7</td>
<td>91.5</td>
<td>91.4</td>
<td>80</td>
</tr>
<tr>
<td>N(Tms)$_2$</td>
<td>c-C[C(NPr$_2$–i)]$_2$</td>
<td>C</td>
<td>197</td>
<td>199</td>
<td>209</td>
<td>105.7</td>
<td>98.6</td>
<td>98.6</td>
<td>81</td>
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**Stannylenes**

<table>
<thead>
<tr>
<th>R</th>
<th>Base</th>
<th>D</th>
<th>Sn–R$^1$</th>
<th>Sn–R$^2$</th>
<th>Sn–D</th>
<th>R$^1$–Sn–R$^2$</th>
<th>R$^1$–Sn–D</th>
<th>R$^2$–Sn–D</th>
<th>Reference</th>
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</thead>
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<tr>
<td>Ar$^7$</td>
<td>CNMes</td>
<td>C</td>
<td>231</td>
<td>232</td>
<td>240</td>
<td>102.6</td>
<td>104.9</td>
<td>83.4</td>
<td>63</td>
</tr>
<tr>
<td>Hyp</td>
<td>CNBu–t</td>
<td>C</td>
<td>265.0</td>
<td>267.9</td>
<td>228</td>
<td>115.4</td>
<td>90.6</td>
<td>91.7</td>
<td>76</td>
</tr>
<tr>
<td>Hyp</td>
<td>CNHex–c</td>
<td>C</td>
<td>265.2</td>
<td>267.8</td>
<td>226</td>
<td>115.0</td>
<td>91.5</td>
<td>86.4</td>
<td>76</td>
</tr>
<tr>
<td>Tip</td>
<td>$Xa^a$</td>
<td>C</td>
<td>230.8</td>
<td>232.0</td>
<td>238</td>
<td>106.7</td>
<td>92.6</td>
<td>109.5</td>
<td>82</td>
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<tr>
<td>Cl</td>
<td>$Xa^a$</td>
<td>C</td>
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<td>245.8</td>
<td>229</td>
<td>95.9</td>
<td>92.5</td>
<td>93.6</td>
<td>83</td>
</tr>
<tr>
<td>Cl</td>
<td>HC[P(NMe$_2$)$_2$]CH</td>
<td>C</td>
<td>248.0</td>
<td>248.0</td>
<td>227</td>
<td>95.4</td>
<td>86.6</td>
<td>91.2</td>
<td>80</td>
</tr>
<tr>
<td>Me$_2$Si[N(Bu–t)]$_2$</td>
<td>CH$_2$PPh$_3$</td>
<td>C</td>
<td>210.4</td>
<td>213</td>
<td>240</td>
<td>72.8</td>
<td>92.2</td>
<td>90.7</td>
<td>84</td>
</tr>
<tr>
<td>Me$_2$Si[N(Bu–t)]$_2$</td>
<td>CH$_2$PPh$_3$</td>
<td>C</td>
<td>211.3</td>
<td>212</td>
<td>244</td>
<td>72.7</td>
<td>99.5</td>
<td>91.8</td>
<td>85</td>
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<tr>
<td>N(Tms)$_2$</td>
<td>c-C[C(NPr$_2$–i)]$_2$</td>
<td>C</td>
<td>215.6</td>
<td>221</td>
<td>230</td>
<td>110.6</td>
<td>94.3</td>
<td>95.2</td>
<td>81</td>
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</table>

**Plumbylenes**

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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Tret</td>
<td>BrMg(thf)$_2$Br</td>
<td>Br</td>
<td>234</td>
<td>235</td>
<td>296.4</td>
<td>99.4</td>
<td>88.6</td>
<td>100.9</td>
<td>50</td>
</tr>
<tr>
<td>Trip</td>
<td>$Xa^a$</td>
<td>C</td>
<td>237</td>
<td>238</td>
<td>254</td>
<td>105.2</td>
<td>90.1</td>
<td>108.8</td>
<td>86</td>
</tr>
<tr>
<td>Hyp (Si)</td>
<td>CNBu–t</td>
<td>C</td>
<td>273</td>
<td>275</td>
<td>250</td>
<td>114.0</td>
<td>89.7</td>
<td>90.8</td>
<td>76</td>
</tr>
<tr>
<td>N(Tms)$_2$</td>
<td>c-C[C(NPr$_2$–i)]$_2$</td>
<td>C</td>
<td>230</td>
<td>231</td>
<td>242</td>
<td>110.2</td>
<td>95.0</td>
<td>91.9</td>
<td>81</td>
</tr>
</tbody>
</table>

$^a$For the definition of substituents $Xa$ and $Xb$, see Chart 3.
CHART 3. Abbreviations used in tables. Heavy dots and arrow heads indicate the connection point of the substituent

chloride Cl\(_C\) for the same acceptor orbital on Sn\(_C\) (Sn\(_B\)–Sn\(_C\)–Cl\(_C\): 157.4°), whereas the two stannylene units A and A′ may use two different acceptor orbitals (Sn\(_A\)–Sn\(_C\)–Sn\(_A′\): 84.3°) and hence form the shorter bonds (287.3 and 288.2 pm, respectively).

Apart from the heteroleptic plumbylenes 43a,b, one homoleptic species is known to form intramolecular N → Pb contacts: bis-1-[2-(N,N′-dimethylaminoethyl)ferrocenyl] plumbylene (50)\(^{53}\), the Pb–N distances in 50 with 266.1 and 270.8 pm being again much longer than covalent Pb\(^{II}\)–N bonds (ca 220 pm) or the Pb–N bonds in the plumbylene 43a (234.4; 232.2 pm).
<table>
<thead>
<tr>
<th>R</th>
<th>Acid</th>
<th>A</th>
<th>Ge–R₁</th>
<th>Ge–R₂</th>
<th>Ge–A</th>
<th>R¹–Ge–R²</th>
<th>R¹–Ge–A</th>
<th>R²–Ge–A</th>
<th>Reference</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar²⁻</td>
<td>BH₃</td>
<td>B</td>
<td>195.9</td>
<td>196.2</td>
<td>204</td>
<td>112.7</td>
<td>117.2</td>
<td>125.7</td>
<td>16</td>
<td>one Ge–N contact: 211.0</td>
</tr>
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</table>

**Stannylenes**

<table>
<thead>
<tr>
<th>R</th>
<th>Acid</th>
<th>A</th>
<th>Sn–R₁</th>
<th>Sn–R₂</th>
<th>Sn–A</th>
<th>R¹–Sn–R²</th>
<th>R¹–Sn–A</th>
<th>R²–Sn–A</th>
<th>Reference</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar²⁻</td>
<td>BH₃</td>
<td>B</td>
<td>217.0</td>
<td>217.0</td>
<td>226.2</td>
<td>119.0</td>
<td>120.5</td>
<td>120.5</td>
<td>16</td>
<td>two Sn–N contacts: 245.6; 245.6</td>
</tr>
</tbody>
</table>
Apart from the unique adduct 51, in which two plumbylene moieties are bridged by a MgBr$_2$(thf)$_4$ molecule via Br $\rightarrow$ Pb interactions [Pb–Br 296.4(2) pm], and few cyclopentadienyl derivatives where chelating amines interact with the two-valent tetrel atom, unsupported adducts of Lewis bases with tetrylenes have been restricted to carbene-type bases so far. However, only donor carbenes, such as Arduengo carbenes, isonitriles or ylids, form simple adducts with dative C $\rightarrow$ E interactions (Table 8). Carbenes or analogous species which also exhibit a substantial acceptor ability form multiple bonds instead (see Section III).

The adducts of Lewis bases known so far often show re-dissociation in solution or under low pressure. If the acceptor ability of the tetrylene is enhanced, stable compounds with shorter (stronger) C $\rightarrow$ E bonds are obtained, however. One possibility of enhancing the acceptor ability of the tetrylene is by the introduction of electropositive substituents such as silyl groups. As shown by theoretical calculations, such substituents will simultaneously raise the energy of the HOMO (lone-pair on E) and lower the energy of the LUMO (empty p-orbital on E) and therefore lead to both an enhanced donor and an enhanced
Recent advances in structural chemistry

acceptor ability of the tetrylene. As will be discussed in Section III, such substitution also enhances the tendency to form dimers (ditetrenes E2R4) or cyclo-oligomers. Thus dihypersilylstannylene Hyp2Sn (20) and Hyp2Pb (21) both form adducts with isonitriles: 52, 53, R′ = t-Bu (53a: Figure 10)61 which show no tendency of re-dissociation in solution or if stored under vacuum, whereas an analogous adduct of Ar5Sn (12), i.e. 54 easily dissociates63 (weak Sn ← F interactions of the CF3 substituents are present and may further decrease the acceptor ability of 12). Consequently, the C → E distances observed for the Hyp2E adducts 52 and 53 are significantly smaller than those of the known diaryltetrylenes by about 10 pm (Sn) or 5 pm (Pb). It is noteworthy that the adducts 52–54 have no cumulated double bonds, thus they are not the analogues of ketenimines R2C=C=NR′: all compounds comprise pyramidal tetrel atoms E with R−E−C angles of about 90°.

\[
\begin{align*}
E & \cdots C \equiv N \cdots R' \\
& \quad R \\
\end{align*}
\]

(52) (E = Sn; R = Hyp; R′ = t-Bu, c-Hex)
(53) (E = Pb; R = Hyp; R′ = t-Bu, c-Hex)
(54) (E = Sn; R = ArF; R′ = Mes)

Apart from BH3 and some certain stannylenes such as SnCl2 (see Section III) which are typical soft acids, no further main-group Lewis acid has been found so far that forms stable adducts with the heavier tetrylenes. Such adducts are known, however, with electron-deficient (Lewis-acidic) transition metal fragments. Adducts have been characterized where the tetrylene acts as a Lewis base towards one, two or even three Lewis-acidic fragments. It is small wonder that, apart from peculiarities derived from steric congestion, such adducts show similar structural features to those of carbon monoxide, since tetrylenes and CO are isolobal, i.e. both have similar frontier orbitals. It is beyond the scope of this chapter to give an overview of that rapidly growing area. The interested reader is referred to additional literature77,78.

![Molecular structure of the pivalonitrile adduct 53, R′ = t-Bu of dihypersilylplumbylene](FIGURE 10)
C. Oligomers

Tetrylenes comprising small organyl substituents (including hydrogen) or Lewis-basic groups X with free electron pairs are usually not stable under ambient conditions and are prone to oligomerize (Ge, Sn) or to disproportionate (Pb). The oligomerization in principle can lead (a) to alkene-homologous dimers (discussed in Section III), (b) to cyclo-oligomers with E–E bonds, (c) to cyclo-oligomers with E–X–E bridges (Table 10) or (d) to infinite polymers, for which detailed structural information is not available to date and which are not treated in this chapter.

There are few open-chain oligomers which are Lewis-acid/Lewis-base adducts of different tetrylenes and which are discussed together with ditetrenes in Section III.

1. Cyclo-oligomers with E–E bonds

Cyclo-oligomers c-(R2E)x (x > 2) with E–E bonds are known for Ge and Sn only\(^87\); cycloplumbanes c-(R2Pb)x had never been detected, although according to quantum-chemical calculations they should form exothermically from appropriate plumbylenes and may adopt very unusual structures\(^88\).

Only little new information on Ge and Sn homocycles was obtained since the earlier volume of this book was published. Thus, only few remarks on recent results will be made. Geanangel and coworkers reported several hypersilyl- or tris(trimethylsilyl)germyl-substituted stannacycles and germacycles, all synthesized from E(II) halides and appropriate alkali metal silyls or germlys using different solvents. The cyclotetratetrelanes \(E_4[E'(\text{SiMe}_3)_3]_4\text{Cl}_4\) \((E = \text{Ge (55)}, \text{Sn (56)}; E' = \text{Si (a), Ge (b)})\)\(^89\) — being tetramers of the respective heteroleptic chloro(silyl) and chloro(germyl)tetrylenes — all consist of puckered four-membered rings [like the related Ge\(_4\)\((\text{Bu-t})_4\text{Cl}_4\)\(^90\)] with the four chlorine atoms in all-trans orientation. Only the hypersilyl-substituted compounds (55a, 56a) (co-crystallizing with pentane or benzene) gave well-ordered crystal structures, whereas the germyl-substituted species show severe disordering. The Ge–Ge and Sn–Sn bond lengths within the \(E_4\text{Hyp}_4\text{Cl}_4\) (55a, 56a) species could be determined reliably to range from 250.6 to 255.8 and 281.1 to 291.5 pm, respectively. Surprisingly, in cyclotetrasilane 56a (Figure 11) alternating long and short bonds are observed. The synthetic procedure leading to Ge\(_4\text{Hyp}_4\text{Cl}_4\) (55a) yields also the unexpected cyclotrisilane Ge\(_5\)\((\text{SiMe}_3)_6\) (15) as already mentioned in an earlier section. Due to the low electronegativity of the silyl groups, which diminishes the singlet–triplet gap for the parent germylene fragments Ge(\text{SiMe}_3)_2 (see the next section), unusually short Ge–Ge bonds of 246.0 pm are observed for 15, which is the shortest yet reported value for cyclotrigermanes.

A cyclic compound which is not related to germynes but to germylanes, i.e. Ge\(_4\)\((\text{Si(Bu-t)})_3\) (57), had been reported by Wiberg and coworkers\(^91\). This is the first tetragermatetrahedrane (Figure 12). It had been obtained in low yields by the reaction of Sup–GeCl\(_2–\text{GeCl}_2–\text{Sup or GeCl}_2\text{ dioxane with NaSup. In this species even shorter Ge–Ge bonds ranging from 243.1 to 244.7 pm are observed. Attempts to synthesize its tin analogue Sn\(_4\)\((\text{SiBu-t})_4\) led to a hexastannaprismane instead (see Section III).

2. Cyclo-oligomers with E–X–E bridges

Typical candidates prone to oligomerize via formation of E–X–E bridges are tetrylenes bearing at least one substituent with free electron pairs, such as halide, alkoxide and amide or, alternatively, bearing substituents that may form strong three-centre two-electron bonds such as hydride. Many tetrylenes with two such groups (EX\(_2\)) have been known for a long time and in many cases form cyclo-oligomers, but are beyond the scope of this
**TABLE 10. Parameters (bond length in pm, angle in deg) of E−X−E bridged oligomers of tetrylenes [R−E−X] (E = Ge, Sn, Pb)**

<table>
<thead>
<tr>
<th>Germynes</th>
<th>R</th>
<th>X</th>
<th>Ge−R</th>
<th>Ge−X</th>
<th>Ge−X′</th>
<th>R−Ge−X</th>
<th>R−Ge−X′</th>
<th>Ge−X−Ge′</th>
<th>X−Ge−X′</th>
<th>References</th>
<th>Remarks</th>
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</thead>
<tbody>
<tr>
<td>Mcp^b</td>
<td>Br</td>
<td>220</td>
<td>270.6</td>
<td>313.3</td>
<td>98.2</td>
<td>98.9</td>
<td>93.8</td>
<td>85.5</td>
<td></td>
<td>71</td>
<td>dimer</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Stannylenes</th>
<th>R</th>
<th>X</th>
<th>Sn−R</th>
<th>Sn−X</th>
<th>Sn−X′</th>
<th>R−Sn−X</th>
<th>R−Sn−X′</th>
<th>Sn−X−Sn′</th>
<th>X−Sn−X′</th>
<th>References</th>
<th>Remarks</th>
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<tr>
<td>Btp</td>
<td>H</td>
<td>221</td>
<td>189(3)</td>
<td>195(3)</td>
<td>92</td>
<td>94</td>
<td>109</td>
<td>71</td>
<td>98.3</td>
<td>81.7</td>
<td>56</td>
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<tr>
<td>Btm</td>
<td>Cl</td>
<td>222</td>
<td>260.1</td>
<td>268.5</td>
<td>92.3</td>
<td>102.1</td>
<td>99.6</td>
<td>80.4</td>
<td>101.6</td>
<td>78.4</td>
<td>92</td>
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<tr>
<td>C(SiMe_2Ph)_3</td>
<td>Cl</td>
<td>230</td>
<td>259.2</td>
<td>277.9</td>
<td>99.1</td>
<td>111.1</td>
<td>101.6</td>
<td>78.4</td>
<td>110.9</td>
<td>92</td>
<td>dimer</td>
</tr>
<tr>
<td>C(SiMe_3)_2(SiMe_2OMe)</td>
<td>Cl</td>
<td>229</td>
<td>253.8</td>
<td>295.2</td>
<td>103.1</td>
<td>99.5</td>
<td>99.6</td>
<td>80.4</td>
<td>102.3</td>
<td>77.7</td>
<td>92</td>
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<tr>
<td>c-C_4S_2(XIa)^c</td>
<td>N=C(NMe_2)_2</td>
<td>229</td>
<td>218</td>
<td>219</td>
<td>93.8</td>
<td>94.3</td>
<td>102.3</td>
<td>77.7</td>
<td>93</td>
<td>dimer</td>
<td></td>
</tr>
<tr>
<td>c-C_4S_2(SiMe_3)(XIb)^c</td>
<td>N=C(NMe_2)_2</td>
<td>238</td>
<td>218</td>
<td>218</td>
<td>93.1</td>
<td>95.7</td>
<td>102.8</td>
<td>77.2</td>
<td>93</td>
<td>dimer</td>
<td></td>
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</tbody>
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<table>
<thead>
<tr>
<th>Plumbylenes</th>
<th>R</th>
<th>X</th>
<th>Pb−R</th>
<th>Pb−X</th>
<th>Pb−X′</th>
<th>R−Pb−X</th>
<th>R−Pb−X′</th>
<th>Pb−X−Pb′</th>
<th>X−Pb−X′</th>
<th>Reference</th>
<th>Remarks</th>
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<tbody>
<tr>
<td>C(SiMe_2Ph)_3</td>
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<td>242</td>
<td>272.4</td>
<td>283.5</td>
<td>99.0</td>
<td>110.8</td>
<td>100.6</td>
<td>79.4</td>
<td>92</td>
<td>dimer</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>C(SiMe_2Ph)_3</td>
<td>Cl</td>
<td>244</td>
<td>272.9</td>
<td>296.3</td>
<td>98.5</td>
<td>112.0</td>
<td>92.9</td>
<td>87.1</td>
<td>94</td>
<td>dimer</td>
<td>monoclinic</td>
</tr>
<tr>
<td>C(SiMe_3)_2(SiMe_2OMe)</td>
<td>Cl</td>
<td>237</td>
<td>268.1</td>
<td>286.8</td>
<td>103.4</td>
<td>100.9</td>
<td>97.7</td>
<td>82.3</td>
<td>92</td>
<td>dimer</td>
<td>Pb−O 259.8</td>
</tr>
<tr>
<td>Tsi</td>
<td>Cl</td>
<td>235(mean)</td>
<td>271−274</td>
<td>—</td>
<td>99−104</td>
<td>—</td>
<td>90.3 (t); 115.7; 112.0</td>
<td>92</td>
<td>87.7; 91.2</td>
<td>92</td>
<td>trimer</td>
</tr>
<tr>
<td>Btp</td>
<td>Br</td>
<td>233</td>
<td>278.9</td>
<td>301.6</td>
<td>95.4</td>
<td>—</td>
<td>94.8; 94.4</td>
<td>52</td>
<td>85.1; 85.6</td>
<td>dimer</td>
<td></td>
</tr>
</tbody>
</table>

^a The symbols Ge′ and X′ indicate atoms of the REX moieties linked to the present one by X or Ge bridges, respectively.

^b Mcp = methylcyclopentadienyl.

^c For the structure of substituents XIa, b, see Chart 3.
chapter since they have no E–C bond. There are only a dozen heteroleptic species with at least one hydrocarbyl substituent which meet the mentioned requirement; nine of them are bridged by halide, two by imido groups, and very recently one species was reported comprising bridging hydride.
This unique hydride of two-valent tin, BtpSnH\textsuperscript{(58)}, had been synthesized by Power's group via the reaction of BtpSnCl with LiAlH\textsubscript{4}. While the analogous lead derivative BtpPbBr\textsuperscript{(59)} is reduced by LiAlH\textsubscript{4} and yields a plumblyne dimer BtpPbPbBtp\textsuperscript{95} (Section III), BtpSnCl undergoes a substitution reaction, and a dark blue solution of the monomeric hydride \textsuperscript{(58)} is formed. By crystallization from benzene orange crystals of the dimer, \textsuperscript{(58)}\textsubscript{2} are obtained (equation 5). The X-ray crystal data were of sufficient quality to locate the bridging hydride. Within twice the standard deviation all Sn–H bonds are of equal length (189(3) and 195(3) pm, respectively). The terphenyl groups occupy trans positions at the planar ring, with tilt angles of 93.3°. All remaining dimers adopt similar trans-bridged structures (Table 10). While all halides have almost planar rings with asymmetric bridges (approximate \(C_1\) symmetry), i.e. tetrylene entities may still be recognized, the two imido-substituted species comprise planar rings with symmetric bridges (approximate \(C_{2h}\) symmetry); see Scheme 3.

For all asymmetric cases the constituting tetrylene moieties within the dimers are not only recognized by the shorter E–X bond, but also by the smaller C–Sn–X angle. Whether oligomers are formed at all, and which kind of oligomer is more stable should be mainly governed by the interplay of the bulk of the hydrocarbyl group and the length of the E–X bond, whereas the question whether symmetric or asymmetric bridges are formed should depend on both steric and electronic effects. Thus, while BtpSnI\textsuperscript{39}\textsuperscript{18} is monomeric, the related chloride with the smaller Btm group BtmSnCl\textsuperscript{(59)} forms dimers in the solid state\textsuperscript{56}, as does BtpPbBr \textsuperscript{60} in which a longer E–C bond and a smaller halide again allow for interactions of the parent tetrylenes\textsuperscript{52}. A very unsymmetrical bridge (Pb–Br 278.7 and 300.3 pm, both mean values) is found for \textsuperscript{(60)}\textsubscript{2}, however. Very unsymmetrical bridges are also found for the dimers of the tetrylenes (Me\textsubscript{3}Si)\textsubscript{2}[(MeO)Me\textsubscript{2}Si]C–E–Cl \textsuperscript{(61)}, (a) E = Sn, (b) E = Pb\textsuperscript{92}, where competing O → E intramolecular interactions are present. As expected from the relative strength of the O → E bonds and the E–Cl bond, a
by far looser dimer is found for the stannylene 61a (Figure 13, left): the E−X bond lying approximately in line with the O → E interaction is longer by 41.4 ((61a)₂) and 18.7 pm ((61b)₂), respectively, than the other E−X bond. The differences in the E−X bond lengths are less pronounced, 18.4 and 11.1 pm, respectively, for the related stannylene dimer [(PhMe₂Si)₃CSnCl]₂(62a)₂ and one polymorph of [(PhMe₂Si)₃CPbCl]₂(62b)₂ with no donor functionality within the substituent. The second polymorph (62b)₂' exhibits again more strongly differing Pb−Cl bonds (23.4 pm), however. Perhaps interactions with a phenyl group of the hydrocarbyl substituent are responsible for this fact, since in (62b)₂ — in contrast to (62b)₂' a phenyl group would be in the right orientation, i.e. opposite to one (the longer) Pb−Cl bond of the Pb₂Cl₂ ring (Figure 13, right).

There is only one R−E−X trimer known so far: [(Me₃Si)₃CPbCl]₃(63)₃. Whereas most trimers known from other fields of chemistry comprise six-membered rings in either a planar or a chair conformation, the Pb₃Cl₃ ring in (63)₃ adopts a very unusual boat-type structure with approximate Cs symmetry as depicted in Figure 14. All Pb−Cl bond lengths are the same within twice their standard deviation, 271(2) to 274(2) pm, thus lying in between the values found for the shorter and longer bonds within RPbCl dimers. Different are the angles around the Cl atoms, however: whereas those for the two ClB atoms at the ‘bottom’ of the boat are large (112° and 116°), the one at the ‘top’ ClT is much smaller (90°). No reasons are obvious, neither for the boat conformation itself nor for the differing environments of the Cl atoms.

![Molecular structure of the chloro(alkyl)stannylene 61a (left) and of chloro(alkyl)plumbylene 62b' (right) in the crystal, both forming asymmetric halogen-bridged dimers due to competitive intramolecular Lewis acid/Lewis base interactions. These are depicted as dashed lines (---) and the longer E−Cl bonds as thin solid lines.](image)
III. MULTIPLE-BONDED SYSTEMS

A. Introduction

Since 1996 when the earlier volume of this book was published, the field of multiple-bonded systems containing heavier tetrel atoms has been developed intensely. The main focus has shifted from Si to the heavier elements Ge, Sn and Pb. Even for the heaviest element of this series, Pb, several species have been synthesized meantime, comprising (at least formal) double and even triple bonds. The structural details revealed by experiment and quantum chemistry, however, challenge long-established models of bonding, and especially the well-established relationships of bond order, bond strength and bond length. It showed that multiple bonds may be much longer and weaker than single bonds. Numerous published theoretical papers deal with this topic2–4,96,97, and it is beyond the scope of the present chapter to deal with the details of these theoretical analyses, especially since several excellent reviews have been published recently5b–g. Only the most important results will be summarized briefly.

Alkenes and alkynes represent the prototypic models for doubly and triply bonded species, respectively. The C=C double and triple bond within these systems is much shorter and stronger than the corresponding C–C single bond in alkanes. A very simple relationship between bond order \((n)\) and bond length \(d_n\) (equation 6) had been given by Pauling and may be also extended to fractional bond orders in conjugated systems98. Consequently, the C–C double (triple) bond as well as other classical homonuclear double (triple) bonds are by 21 pm (34 pm) shorter than the related single bond.

\[
d_n = d_1 - 71 \text{ pm} \cdot \log(n) \quad (d_1 = \text{bond order for } n = 1) \tag{6}
\]

The inspection of bond lengths determined by absolute structure methods or \textit{ab initio} calculations for compounds with homonuclear multiple bonds reveals that a similar relationship is valid only for boron and the heavier members of group 15 and 16. Nitrogen and oxygen display a much stronger shortening of about 30 and 27 pm, respectively,
going from single to double bonds, since in N—N or O—O single-bonded species crowding of lone-pairs on these relatively small atoms causes strong repulsive interactions, which are significantly diminished if the number of substituents or lone-pairs is reduced by going from single- to double-bonded species. For the heavier tetrels Ge and Sn, on the other hand, the shortening is much less pronounced than for carbon; for Sn and Pb even a \textit{lengthening} for the E—E bond may be observed going from singly- to doubly-bonded systems. Moreover, most digermenes and distannenes and all diplumbenes are in equilibrium with their carbene homologous fragments (tetrylenes) ER\textsubscript{2} in solution. The seemingly paradoxical observation that a higher bond order does not necessarily imply a shorter and stronger bond is traced back to the different electronic ground states of the parent tetrylenes compared to the parent carbenes. While carbenes typically have triplet ground states or at least a very low lying triplet state, all known higher homologues possess a singlet ground state, due to energetically and spatially stronger separation of valence s- and p-orbitals\textsuperscript{96}. Only triplet tetrylenes can directly form classical double bonds by making two covalent interactions with their singly occupied valence orbitals, whereas the analogous interaction of singlet species (in the same orientation) would lead to strong Pauli repulsion between doubly occupied orbitals (Scheme 4). Therefore, a promotion step is necessary in all those cases where the tetrylene fragment possesses a singlet ground state. However, the more energy is required for the initial promotion (2 \cdot \Delta E_{ST} where \Delta E_{ST} is the singlet–triplet energy difference, since \textit{two} tetrylene fragments must be promoted), the more the overall bond energy \( E_{\text{total}} \) is reduced. A critical point is reached if the double-bond formation from these triplet species (snapping process\textsuperscript{22}) gains less energy (\( E_{\sigma+\pi} \)) than the promotion costs; then, for obvious reasons, no classical double bond may form (equation 7).

\begin{equation}
E_{\sigma+\pi} > 2 \cdot \Delta E_{ST} \iff \Delta E_{ST} < 1/2E_{\sigma+\pi}
\end{equation} (7)
However, even in cases where equation 7 does not hold, i.e. $E_{\sigma+\pi} < 2 \cdot \Delta E_{ST}$, a bonding interaction between two tetrylene fragments is possible, and a double bond may be formed: no classical double bond, of course, but a double donor–acceptor bond (double dative bond). This idea was already proposed by Lappert and coworkers in 1976 when they succeeded in the synthesis of the first stable distannene $\text{Bsi}_2\text{Sn}=\text{SnBsi}_2$\textsuperscript{42} and found that the compound has no planar, but a trans-bent distorted $\text{C}_2\text{Sn}=\text{SnC}_2$ skeleton. A double donor–acceptor bond may form, if the tetrylene fragments, prior to interaction, are tilted in an appropriate way, such that the lone-pair of one fragment may interact with the empty $p$-orbital of the other (Scheme 4). The resulting bond energy depends — as it always does for dative bonding — on the difference in orbital energies between the interacting orbitals; the larger the difference, the weaker the bond. A model widely accepted and used nowadays to predict quantitatively the limits for the stability of both types of double-bonded systems, classical and dative ones, is the CGMT model\textsuperscript{13}. As a simple quantum-chemical model it not only provides equation 7 for the existence of classical double bonds, but also equation 8 for the existence of double donor–acceptor bonds.

$$E_{\sigma+\pi} > \Delta E_{ST} \iff \Delta E_{ST} < E_{\sigma+\pi}$$

Since, in general, the promotion energy $\Delta E_{ST}$ of the two tetrylene fragments of the double-bonded system increases going down group 14, and since the expected $E-E(\sigma+\pi)$ bond strength decreases in the same direction, it is obvious that the tendency to form classical double bonds will be reduced going from C to Pb. According to the calculated or estimated values for $\Delta E_{ST}$ or $E(\sigma+\pi)$ of the parent hydrido derivatives (EH\textsubscript{2} and E\textsubscript{2}H\textsubscript{4}), one would expect that of the heavier group 14 elements, only Si (and perhaps Ge) should be able to form classical double bonds. Double donor–acceptor bonds should be observed for Ge and Sn, whereas plumbylenes PbR\textsubscript{2}, finally, should remain monomers. Calculations at high \textit{ab initio} levels reveal, however, some degree of distortion from planarity already for Si\textsubscript{2}H\textsubscript{4}, although the potential surface is very shallow in the questionable region. Moreover, these calculations predict that even diplumbene Pb\textsubscript{2}H\textsubscript{4} is a stable dimer, but with a very low dissociation energy of about 25 to 40 kJ mol\textsuperscript{−1}, depending on the employed quantum-chemical method. (Note that the comparison of dissociation energies for compounds with double donor–acceptor bonds with the values of related singly-bonded species is very problematic, since in the former case a bond is broken \textit{heterolytically} to relatively low-energy closed-shell monomers, whereas in the latter case a \textit{homolytic} bond breakage occurs giving usually high-energy radical species.) It should be noted at this point that there are several other minima on the hypersurfaces of the heavier tetrylene dimers (Scheme 5); for three of them (B–D) it is not (or not exclusively) the lone-pair of one tetrylene unit that is serving as Lewis base to the other unit, but a E–H bond, finally leading to hydrogen-bridged species with three-centre two-electron E···H···E bonds. Isomer E is a tetryltetrylene, a mixed valence species (cf 27) and F is no minimum at all for the parent E\textsubscript{2}H\textsubscript{4} derivatives; it may be observed, however, with substituents other than hydrogen (see below). The relative energies of the isomers are dependent on the element E and, if other substituents than H are introduced, on the nature of the employed substituent.

All synthetically accessible alkene homologues bear other than hydrogen substituents, therefore additional influences on the double bond are present by the nature of the substituent pattern. It was shown that the promotion energy $E_{ST}$ may be strongly influenced by the chosen substituent on E: the lower the electronegativity, the smaller $E_{ST}$, and vice versa\textsuperscript{88,99}. Finally, one should consider that for synthetically accessible tetrylenes, steric effects (large substituents) may also lead to changes in $\Delta E_{ST}$ — by altering bond lengths and the valence angle at E — and may reduce or enhance the dissociation energy of R\textsubscript{2}E=ER\textsubscript{2} by additional van der Waals interactions within the periphery of the molecule.
The CGMT model was intended to describe (non-cyclic) homonuclear and heteronuclear double-bonded systems. However, in the meantime other multiple-bonded species have also been synthesized, as will be seen in the following. They also often exhibit structural features which are not familiar from the analogous carbon derivatives, and are not yet fully understood. Some of them are, however, related to the phenomena discussed above and may be understood on a similar base. I will not go into details in these cases, but will refer to recent literature when available.

In the following sections alkene homologues will be discussed first, i.e. species exhibiting a double bond between two heavier tetrel atoms. Then we will switch to molecules comprising double bonds between heavier tetrels and carbon, and finally relatives of ketones and imines will be discussed. Structural information about all structurally characterized compounds are found in following tables: digermenes (Table 11), distannenes (Table 12), diplumbenes (Table 13), cyclic species (Table 14), germenes and stannenes (Table 15) and heteroketones as well as heteroimines (Table 16).

B. Alkene Homologues (Ditetrenes)

According to the CGMT model the skeleton of ditetrenes \( R_2E = ER_2 \) bearing organyl or related non-donor substituents may exhibit at least two possible ideal conformations:

(I) planar conformation \( (D_{2h} \) symmetry) \( \rightarrow \) a classical double bond.

(II) \( \text{trans-} \)bent conformation \( (C_{2v} \) symmetry) \( \rightarrow \) a double dative bond (characterized by a \( \text{trans-} \)bent angle \( \kappa \) as defined in Scheme 6).

Depending on the nature of \( R \), various structural changes or distortions are observed:

(a) lengthening of the \( E=E \) bond,
(b) torsion about the \( E=E \) bond (characterized by the twist angle \( \tau \) defined in Scheme 6),
(c) formation of a zwitterionic form (single dative bond) \( R_2Sn \rightarrow SnR'_2 \).

For diplumbenes and distannenes — in accordance with the presence of the weakest \( E=E \) bond of group 14 and a shallow potential curve for \( E-E \) stretching — a distortion of type (a) is predominantly found due to steric strain or electronic destabilization, the lengthening of the \( E=E \) bond being more pronounced for \( E = Pb \). For few cases, for instance if very sterically demanding silyl substituents are present which strengthen the
4. Recent advances in structural chemistry

\[ \kappa = \frac{\tau_1 + \tau_2}{2} \]

**Scheme 6.** Definition of two characteristic parameters describing the conformation of ditetrenes. \( \kappa \) is the tilt angle of the \( R_2E \) plane towards the \( E-E \) bond; \( \tau \) is the twist angle, defined as arithmetic mean of the (signed) torsion angles \( \tau_1 \) and \( \tau_2 \), thus giving the distortion from an ideal \( \textit{trans} \)-bent conformation \((\tau_1 = -\tau_2)\)

Sn=Sn bond electronically, a relatively short bond and a large torsion angle \( \tau \) have been observed. Finally, three distannenes exhibit the zwitterionic conformation which has not been observed for other ditetrenes to date. The digermenes possessing the strongest \( E=E \) bond among the discussed ditetrenes frequently display distortion mode (b), whereas lengthening of the bond is not as pronounced as for the heavier congeners.

1. Digermene

The first ever structurally characterized digermene, Lappert's \( \text{Bsi}_2\text{Ge}=\text{GeBsi}_2 \) (64), is the only tetraalkyldigermene known to date\(^{100}\). It exhibits the expected undistorted \( \textit{trans} \)-bent conformation \((k = 32^\circ; \tau = 0)\) and the longest \( \text{Ge}=\text{Ge} \) bond (234.7 pm) among tetraorganyldigermene, being, however, still markedly shorter than \( \text{Ge}^\equiv\text{Ge} \) single bonds in digermanes \((\text{Ge}_2\text{H}_6: 240.3 \text{ pm}^{101a}; \text{Ge}_2\text{Ph}_6: 243.7 \text{ pm}^{101b})\). Three out of four tetraaryldigermene (Table 11) exhibit slightly distorted \( \textit{trans} \)-bent structures and significantly shorter \( \text{Ge}=\text{Ge} \) bonds (221.3–230.1 pm) than 64. The \( \textit{trans} \)-bent angles \( k \) for the two derivatives with the shortest \( \text{Ge}=\text{Ge} \) bond \( \text{Dep}_4\text{Ge}_2 \) (65)\(^{102}\) and \( \text{Tip}_4\text{Ge}_2 \) (66)\(^{103}\) with 12.2° and 12.3°, respectively, are markedly smaller than that for 64. Thus bond lengths and conformation are close to those values expected for a classical, planar \( \text{Ge}=\text{Ge} \) bond, indicating that digermene are near the borderline to classical double-bond systems, as also derived from the CGMT model. Both the other two tetraaryldigermene, \( \text{Bmp}_4\text{Ge}_2 \) (67)\(^{104}\) and \( \text{Mes(Dip)}\text{Ge}=\text{Ge(Dip)}\text{Mes} \) (68)\(^{105}\), show some unexpected features. (67), bearing the most sterically demanding substituents among this series, is (not unexpectedly) strongly twisted about the \( \text{Ge}=\text{Ge} \) bond \((\tau = 21.2^\circ)\), but, in spite of a longer \( \text{Ge}=\text{Ge} \) bond (225.2 pm), it seemingly adopts a planar conformation. The large thermal parameters of the Ge atoms indicate dynamic or static disordering, however, and so perhaps the presence of the expected \( \textit{trans} \)-bent conformation. The remaining species, the only unsymmetrically substituted tetraaryldigermene 68, was obtained as the unexpected \( Z \)-isomer and exhibits an only slightly twisted \( \text{Ge}=\text{Ge} \) double bond \((\tau = 3.4^\circ)\).

In spite of sterically very demanding substituents, both structurally characterized tetrasyldigermene\(^{106}\) (Table 11) show nearly planar conformations with \( \textit{trans} \)-bent angles \( k \) of 6–7° only. The observed \( E=E \) bond lengths (226.7; 229.8 pm) are, however, significantly longer than those found for 65 and 66, thus leading to the conclusion that the extent of \( \textit{trans} \)-bent distortion is mainly governed by the electronic effects of the substituents: electropositive substituents, such as silyl groups, diminish the promotion energy \( E_{ST} \) and thus favour small \( \textit{trans} \)-bent angles or even the planar form;
TABLE 11. Parameters (bond length in pm, angle in deg) of digermenes R$_1$R$_2$Ge$_4$ GeR$_1$R$_2$

<table>
<thead>
<tr>
<th>R$_1$</th>
<th>R$_2$</th>
<th>E=E</th>
<th>E−R</th>
<th>R−E−R</th>
<th>$\kappa$</th>
<th>$\tau$</th>
<th>Reference</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Det</td>
<td>Det</td>
<td>221.2</td>
<td>196; 196</td>
<td>115.4</td>
<td>12.0</td>
<td>10.8</td>
<td>102</td>
<td></td>
</tr>
<tr>
<td>Tip</td>
<td>Tip</td>
<td>221.3</td>
<td>196; 196; 196; 197</td>
<td>117.0</td>
<td>12.3</td>
<td>1.1</td>
<td>103</td>
<td></td>
</tr>
<tr>
<td>Bmp</td>
<td>Bmp</td>
<td>225.2</td>
<td>201; 201; 202</td>
<td>128.0</td>
<td>0.6</td>
<td>21.2</td>
<td>104</td>
<td></td>
</tr>
<tr>
<td>Mes</td>
<td>Dip</td>
<td>230.1</td>
<td>197</td>
<td>109.9</td>
<td>35.4</td>
<td>3.4</td>
<td>105</td>
<td></td>
</tr>
<tr>
<td>Bsi</td>
<td>Bsi</td>
<td>234.6</td>
<td>198; 204</td>
<td>112.5</td>
<td>32.2</td>
<td>0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>XIIa (Si, N)$^a$</td>
<td>245.4</td>
<td>243.8 (Si); 186 (N)</td>
<td>102.9</td>
<td>41.3</td>
<td>36.8</td>
<td>107</td>
<td></td>
<td></td>
</tr>
<tr>
<td>XIIb (Si, N)$^a$</td>
<td>245.3</td>
<td>243.2 (Si); 184 (N)</td>
<td>101.4</td>
<td>47.3</td>
<td>0</td>
<td>19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>i-Pr$_2$MeSi (Si)</td>
<td>226.7</td>
<td>240.0; 240.6</td>
<td>117.0</td>
<td>7.1</td>
<td>0</td>
<td>106</td>
<td></td>
<td></td>
</tr>
<tr>
<td>i-Pr$_3$Si (Si)</td>
<td>229.8</td>
<td>242.7; 244.3</td>
<td>115.2</td>
<td>16.4</td>
<td>0</td>
<td>106</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Btp</td>
<td>Cl</td>
<td>244.3</td>
<td>200 (C)</td>
<td>109.1</td>
<td>49.0</td>
<td>0</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>Btp</td>
<td>Na</td>
<td>239.4</td>
<td>207 (C)</td>
<td>—</td>
<td>—</td>
<td>108</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetragermabutadiene</td>
<td>234.4</td>
<td>Ge$^1$; 199; Ge$^2$: 200</td>
<td>107.8</td>
<td>109.6</td>
<td>33.2</td>
<td>31.1</td>
<td>4.8</td>
<td>110</td>
</tr>
<tr>
<td>Tip$_4$Ge$_4$</td>
<td>235.7</td>
<td>Ge$^3$: 200; Ge$^4$: 199</td>
<td>109.4</td>
<td>108.9</td>
<td>35.3</td>
<td>31.1</td>
<td>6.4</td>
<td>22.5$^a$</td>
</tr>
</tbody>
</table>

$^a$For the definition of substituents XII a,b see Chart 3; atomic symbols in parentheses denote the type of atom binding to Ge.
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electronreceptive substituents enhance the promotion energy and thus favour large trans-
bent angles. The bond length, however, depends on at least two factors: (a) the type of
substituent — electropositive groups will shorten and electronegative groups will lengthen
the bond — and (b) the steric demand of the substituent — small groups will allow for a
short bond while large groups will stretch the bond and may cause twisting. This proposal,
which must be corroborated by more experimental evidence, of course, is supported by
the observation that alkenes may be twisted or suffer bond stretching, but never show any
trans-bent distortion, even if very large substituents are present.

The structures of three heteroleptic digermenes, 69 – 71, have been reported. In 69 each
Ge bears a terphenyl group and a Cl atom, in 70 and 71 tris(amino)silyl and
amino substituents are present at each Ge. While 69 and 70 are E-isomers, 71 adopts
the unusual Z-form. The electronegative chloro or amino groups cause large trans-bent
angles between 39° and 47° and long Ge=Ge bonds between 244.3 and 246.0 pm.

![Graphical representation of 69, 70, and 71]

The dianionic digermene [BtpGe=GeBtp]2− (72a) and the respective distannene
[BtpSn=SnBtp]2− (72b) were synthesized by Power and coworkers by reduction of the
appropriate aryl(chloro)germylene BtpGeCl (34) and aryl(chloro)stannylene BtpSnCl with
an excess alkali metal in benzene, respectively. Doubly metal-bridged [BtpE=EBtp]2−
units are observed in the solid state (72b: Figure 15). The cations are coordinated by the
aromatic rings of the Tip fragments of the utilized terphenyl ligand and the
π-electrons of the dianion. Since the formation of the double bond in these RE=ER anions needs no s-p
promotion, 72a and 72b can be regarded as systems with almost classical double bonds, as
are the isoelectronic neutral dipnictenes RY=YR (Y = As, Sb). The Ge=Ge and Sn=Sn
bonds (239.4 pm and 277.6 pm, resp.) in 72a and 72b are about 10 pm longer than
the respective As=As and Sb=Sb bond distances observed for dipnictenes. Despite
similar covalent radii for Ge and As as well as for Sn and Sb, this can be traced back to
electrostatic repulsion between adjacent negative charges in 72a and 72b.
Very interestingly, if equimolar amounts of alkali metal are used for the reduction of the aryl(chloro)stannylene, radical anions (which will be discussed later) are formed.

2. Distannenes

The distannenes show the greatest variety of structures among the ditetrenes (Table 12) although, in accordance with the CGTM model, and apart from the dianion 72b\(^{108}\) for which this model does not apply, no distannene with a planar skeleton is known. Most organyl- and silyl-substituted distannenes adopt undistorted or only slightly distorted \(\text{trans}\)-bent structures; Hyp\(_2\)Sn=SnHyp\(_2\) \(^{73}\), which is the only tetrasilyldistannene known, is strongly twisted, however. Since an Sn=Sn bond is generally weaker than a respective Ge=Ge bond, a greater variation in bond lengths is observed among the \(\text{trans}\)-bent structures for Sn=Sn, ranging from 270.2 pm for Mes(Hyp)Sn=Sn(Hyp)Mes (74)\(^{54}\) to 363.9 pm for Ar\(_2\)F\(^{\text{Sn}}\)=SnAr\(_2\)F (75)\(^{27b}\). The influence of the electronegativity of the substituent can be impressively demonstrated by comparing the structural parameters of tetraaryldistannenes with those of the respective heteroleptic diaryldihypersilyldistannenes (Table 12). The substitution of two aryl groups for two hypersilyl groups generally results in much shorter Sn=Sn bonds and smaller tilt angles \(\kappa\). Having the most electronegative substituents among the series, Ar\(_2\)F\(^{\text{Sn}}\) (12) forms only a loose dimer (75) with a Sn−Sn distance of 363.9 pm. The substitution of two Ar\(^F\) in 75 for two strongly electropositive hypersilyl groups shortens the Sn=Sn bond by about 80 pm (!) to give 283.3 pm in the respective heteroleptic derivative Hyp(Ar\(^F\))Sn=Sn(Ar\(^F\))Hyp (76)\(^{59}\). Similar differences are found for the couple Bmp\(_2\)Sn=SnBmp\(_2\) (77)\(^{111}\)/Hyp(Bmp)Sn=Sn(Bmp)Hyp (78)\(^{60}\) (77 has no simple \(\text{trans}\)-bent structure; see below). Finally 74, the species bearing the smallest aryl group among all diaryl-di...(continued).
<table>
<thead>
<tr>
<th>R$^1$</th>
<th>R$^2$</th>
<th>Compound</th>
<th>Sn=Sn</th>
<th>Sn−R$^b$</th>
<th>R−Sn−R</th>
<th>$\kappa$</th>
<th>$\tau$</th>
<th>Reference</th>
<th>Remarks</th>
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<tr>
<td>Bsi</td>
<td>Bsi</td>
<td>79</td>
<td>276.8</td>
<td>221; 223</td>
<td>109.2</td>
<td>41</td>
<td>0</td>
<td>100</td>
<td>Bmp$_2$Sn → SnBmp$_2$</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td>zwitterionic</td>
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<td>Bmp</td>
<td>Bmp</td>
<td>77</td>
<td>291.0</td>
<td>227; 227</td>
<td>114.4</td>
<td>64.4</td>
<td>10.7</td>
<td>111</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>219; 222</td>
<td>114.6</td>
<td>21.3</td>
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<tr>
<td>Ar$^F$</td>
<td>Ar$^F$</td>
<td>75</td>
<td>363.9</td>
<td>228; 229</td>
<td>95.1</td>
<td>45</td>
<td>0</td>
<td>27b</td>
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</tr>
<tr>
<td></td>
<td>Hyp</td>
<td>76</td>
<td>283.3</td>
<td>226 (C)</td>
<td>103.8</td>
<td>41.5</td>
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<td>59</td>
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</tr>
<tr>
<td></td>
<td>Hyp</td>
<td>74</td>
<td>270.2</td>
<td>218 (C)</td>
<td>105.5</td>
<td>39.4</td>
<td>0</td>
<td>54</td>
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</tr>
<tr>
<td></td>
<td>Hyp</td>
<td>73</td>
<td>282.5</td>
<td>266.7 (Si); 267.8 (Si)</td>
<td>120.5</td>
<td>28.6</td>
<td>62.7</td>
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<tr>
<td>Bmp</td>
<td>Hyp</td>
<td>78</td>
<td>279.1</td>
<td>222 (C)</td>
<td>109.0</td>
<td>44.9</td>
<td>0</td>
<td>60</td>
<td>E-isomer</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>C$_2$Sn → SnC$_2$</td>
<td>80$^a$</td>
<td>300.9</td>
<td>221 (C, donator, mean)</td>
<td>89.5</td>
<td>1.4</td>
<td>14.0</td>
<td>115</td>
<td>zwitterionic</td>
<td>$\lambda^6, \lambda^3$ Sn atoms</td>
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<td></td>
<td></td>
<td></td>
<td>223 (C', acceptor, mean)</td>
<td>90.0</td>
<td>81.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>227 (N → Sn)</td>
<td>94.6</td>
<td>83.8</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>C$_2$Sn → SnCl$_2$</td>
<td>81$^a$</td>
<td>296.1</td>
<td>220 (C, donator, mean)</td>
<td>100.1</td>
<td>0.1</td>
<td>87.0</td>
<td>112</td>
<td>zwitterionic</td>
<td>$\lambda^5, \lambda^3$ Sn atoms</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>245 (Cl, acceptor, mean)</td>
<td>94.6</td>
<td>83.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>241 (N → Sn)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_2$Sn → SnN$_2$</td>
<td>82$^a$</td>
<td>304.9</td>
<td>218 (C, donator, mean)</td>
<td>110.4</td>
<td>18.1</td>
<td>12.0</td>
<td>113</td>
<td>zwitterionic</td>
<td>$\lambda^5, \lambda^3$ Sn atoms</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>208 (N, acceptor, mean)</td>
<td>88.1</td>
<td>81.3</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>254 (N →)</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>308.7</td>
<td>219 (C, donator, mean)</td>
<td>110.7</td>
<td>16.8</td>
<td>6.5</td>
<td>2 independent molecules</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>209 (N, acceptor, mean)</td>
<td>86.9</td>
<td>81.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>255 (N →)</td>
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<td></td>
</tr>
<tr>
<td>Btp</td>
<td>K</td>
<td>72$^b$</td>
<td>277.6</td>
<td>227 (C)</td>
<td></td>
<td></td>
<td></td>
<td>108</td>
<td>doubly bridged</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>357.9; 359.1 (K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>R−E=E ; 107.5</td>
</tr>
</tbody>
</table>

$^a$See text; $^b$atomic symbols in parentheses denote the type of atom binding to Sn.
bond (270.2 pm) found so far, even shorter than in Lappert’s Bsi$_2$Sn=SnBsi$_2$ (79)\(^8\). The substitution of aryl for hypersilyl also allowed the synthesis of the first diplumbenes, as shown below. Nevertheless, tetrahypersilyldistannene (73), in spite of comprising four electropositive groups, has no extraordinary short Sn=Sn bond (282.5 pm). However, due to the enormous steric demand of the four hypersilyl groups it adopts a distorted trans-bent structure with a small tilt angle ($\kappa = 28.6^\circ$), but very large torsion angle $\tau$ of 62.7$^\circ$ (Figure 16).

The other four known distannenes all adopt a novel zwitterionic structure with a single dative bond, i.e. one stannylene fragment serves as electron-pair donor (Lewis base), the other as acceptor (Lewis acid): R$_2$Sn $\rightarrow$ SnR$'_2$, hence they are not distannenes within a stricter definition.

For three of these compounds (80–82)\(^{112,113}\) this particular structure type may be expected, since herein two different stannylene moieties (R $\neq$ R$'$) having different acceptor abilities interact. The remaining example is the tetra(aryl)distannene Bmp$_2$Sn=SnBmp$_2$ (77)\(^{111}\) (Figure 17) with four identical substituents (R = R$'$)\(^{114}\). It is not understood to date why 77 adopts this particular conformation, although steric reasons may be responsible. According to the different ‘dative bond orders’, the Sn–Sn bond distances for the zwitterionic compounds are significantly longer than for those with
FIGURE 16. Molecular structure of distannene 73 in the crystal. Projection along the Sn=Sn bond illustrating the large twist angle $\tau = 62.7^\circ$.

FIGURE 17. Molecular structure of zwitterionic distannene 77 in the trans-bent conformation, the values ranging from 291.0 pm (77) to 308.7 pm (82). In compounds 80–82 one or two additional intramolecular nitrogen donors block the acceptor orbital of one Sn atom, thus making the respective stannylene unit a pure electron donor. This is demonstrated in Figure 18 for 81. Hence, these distannenes are closely related to the adducts of Lewis bases such as carbenes or ylids to stannylenes, as described in Section II. The acceptor stannylenes comprise SnC$_2$ (80), SnCl$_2$ (81) or SnN$_2$.
central units. The acceptor orbital of these fragments is oriented perpendicular to the SnR₂ planes, whereas the donor orbital of the Lewis-basic tetrylene R₂Sn should lie approximately within the plane, formed by the tin atoms and the α-atom of the R groups. Therefore, the respective tilt angles κ should be near 90° (ER₂) and 0° (ER₂), respectively. The observed deviations from these ideal values may be due to the steric demands of the R and R’ groups.

3. Diplumbenes

For a long time it was thought that plumbylenes, in contrast with their lighter congeners, would show no tendency to dimerise to doubly-bonded species. The first \textit{ab initio} calculations inspecting the hypersurface of Pb₂H₄ also seemed to exclude the possibility of even a \textit{trans}-bent diplumbene A (Scheme 5); H₂Pb=PbH₂ was calculated to be actually a saddle point\textsuperscript{2c}. Instead, a doubly hydrogen-bridged isomer B was calculated to be the global minimum, whereas several other isomers were calculated as at least local minima (Scheme 5). Later, calculations at higher levels confirmed structure B as a global minimum, but they revealed that \textit{trans}-bent diplumbene A is also a local minimum on the hypersurface. After all, the calculated dissociation energy for H₂Pb=PbH₂ is very small (about 20–40 kJ mol\textsuperscript{−1})\textsuperscript{2a,b,59}.

It was not until 1998 that the first plumbylene dimer had been isolated and structurally characterized: the heteroleptic diaryl-dihypersilyl-substituted \textit{trans}-bent species \(\text{[Hyp}(\text{ArF})\text{Pb]}\text{₂} (83\text{a})\textsuperscript{59}. It is generated via an at first unexpected ligand exchange reaction between the homoleptic species Hyp₂Pb (21) and Ar₂Sn (12), the originally intended mixed ditetrene Hyp₂Pb=SnAr₂\textsuperscript{F} being a probable intermediate of the reaction. It was
demonstrated later that such exchange reactions generally occur when Hyp$_2$Sn (20) or Hyp$_2$Pb (21) react with other diaryl- or dialkyltetrylenes$^{41,60,116}$. The presence of electropositive substituents, which leads to significant shortening of Sn=Sn bonds for the respective distannenes, seems here to favour the formation of plumbylene dimers. The observed Pb−Pb distance of 353.7 pm for 83a is, however, much longer than the calculated double bond length for the parent Pb$_2$H$_4$ [281.9 (DFT)$^{2a} \sim 295.0$ pm(CCSD)$^{59}$]. Two reasons — both related to the employed aryl group — become obvious when the structure is analysed in detail. (a) The strongly electronegative ArF group, by its electronic influence, strongly disfavours the formation of tetrylene dimers, and (b) the lone-pairs of the fluorine atoms of the CF$_3$ groups compete with the only weak Lewis-basic plumbylene lone-pair for the acceptor orbital of the second plumbylene moiety (short F···Pb contacts are formed; see Section II).

<table>
<thead>
<tr>
<th>R,R′</th>
<th>Pb=Pb</th>
<th>Pb−R or Pb−R′</th>
<th>R−Pb−R′</th>
<th>κ</th>
<th>τ</th>
<th>Reference</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tip, Tip</td>
<td>305.2</td>
<td>229; 229</td>
<td>102.3</td>
<td>51.3</td>
<td>16.0</td>
<td>117</td>
<td>Mg(THF)$_4$Br$_2$ adduct Pb···Br 315.7</td>
</tr>
<tr>
<td>Mes, Mes</td>
<td>335.5</td>
<td>230; 232</td>
<td>97.4</td>
<td>58.5</td>
<td>0</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>Mes, Hyp</td>
<td>290.3</td>
<td>231 (C)</td>
<td>102.5</td>
<td>46.0</td>
<td>0</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>Tip, Hyp</td>
<td>299.0</td>
<td>230 (C)</td>
<td>108.9</td>
<td>42.7</td>
<td>0</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>ArF, Hyp</td>
<td>353.7</td>
<td>237 (C)</td>
<td>96.6</td>
<td>40.8</td>
<td>0</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td>Bmp, Hyp</td>
<td>337.0</td>
<td>236 (C)</td>
<td>106.0</td>
<td>46.5</td>
<td>0</td>
<td>116</td>
<td></td>
</tr>
</tbody>
</table>

Atomic symbols in parentheses denote the type of atom binding to Pb.

FIGURE 19. Molecular structure of heteroleptic diplumbene 83b comprising the shortest Pb=Pb double bond observed so far
Thus, the next logical step was the replacement of ArF by other groups which are less electronegative and bear no donor groups. To date, the synthesis of three further heteroleptic diplumbenes with trans-bent geometry (Table 13)\textsuperscript{51,54,116} had been reported; the species with the shortest Pb=Pb bond so far — with 290.3 pm now in the range of the calculated values for Pb\(_2\)H\(_4\) — is the mesityl derivative Mes(Hyp)Pb=Pb(Hyp)Mes \textsuperscript{83b} (Figure 19)\textsuperscript{54}. Again ligand exchange led to the formation of \textsuperscript{83b}, but here mesitylcopper CuMes was used as reaction partner for PbHyp \(_2\) (21). The synthesis of a first homoleptic trans-bent diplumbene Tip\(_2\)Pb=PbTip\(_2\) \textsuperscript{84} by reaction of TipMgBr with PbCl\(_2\) showed, however, that the existence of diplumbenes is not restricted to species comprising silyl groups. As can be seen again by comparing the observed Pb=Pb bond length (305.2 pm) with that of the appropriate heteroleptic species Tip(Hyp)Pb=Pb(Hyp)Tip \textsuperscript{83c} (299.0 pm), the formation of diplumbenes is at least favoured by the utilization of such electropositive substituents. \textsuperscript{84} is the only diplumbene known which comprises a twisted Pb=Pb double bond (\(\tau = 16^\circ\)). If instead MesMgBr is reacted with PbCl\(_2\), again the expected diplumbene Mes\(_2\)Pb=PbMes\(_2\) \textsuperscript{85} is formed, but from the obtained solution it was isolated as a unique Mg(thf)\(_4\)Br\(_2\) adduct (Figure 20)\textsuperscript{51}. Herein the Pb=Pb bond is markedly lengthened to 335.5 pm by competing interaction of the p-orbitals on both Pb atoms with bromide anions. Replacing mesityl for 2,4,6-triethylphenyl finally leads to a complex \textsuperscript{51} of two separated plumbylene fragments which are bridged by one Mg(thf)\(_4\)Br\(_2\) molecule (see above)\textsuperscript{50}.

The data for all these diplumbenes are given in Table 13.

\section*{4. Cyclic ditetrenes and their derivatives}

When the earlier edition of this book was in preparation, no cyclic digermene or distannene was known. Meanwhile, several cyclotrigermenes and mixed Si/Ge heterocycles with Si=Si or Si=Ge bond have been synthesized by Sekiguchi’s group. The
only cyclotristannene c-Sup₄Sn₃ (86) was obtained by isomerization of a tristannallene¹¹⁸ and will be discussed together with this unique cumulated compound in the next section.

\[
\begin{align*}
(t-Bu)₂Si & \quad \text{Si(Bu-t)₃} \\
(t-Bu)₂Si & \quad \text{Sn} \quad \text{Sn} \quad \text{Sn} \\
(t-Bu)₂Si & \quad \text{Si(Bu-t)₃}
\end{align*}
\]

(86)  

(87)  (a) \( R = (t-Bu)₃Si \)  
(b) \( R = (t-Bu)₃Ge \)  

(88) \( R = \text{Hyp (a), (t-Bu)₃Ge, Tm₃Ge, Mes} \)

The two symmetrically substituted cyclotrigermenes \(((t-Bu)₃E)₄Ge₃ \) 87a and 87b are formed from GeCl₂·dioxane and the appropriate alkali metal tetryl \(( t-Bu )₃EM (M = Li, Na)²²⁹\). Unsymmetrically substituted derivatives 88 were obtained by addition of different alkali metal silyls or germyls to salts of the cyclotrigermium cation 89¹²⁰ (of equation 10 below). The heteronuclear disilagermirenes 90a and 90b were finally prepared by reduction of a \(( t-Bu )₂MeSiSiBr₃/( t-Bu )₂MeSi)GeCl₂ mixture²¹¹. At first the 1-disilagermirene 90a is isolated from the reaction mixture and may then be photochemically isomerized to 90b (equation 9).

\[
\begin{align*}
(t-Bu)₂MeSi & \quad \text{Si(Bu-t)₂Me} \\
(t-Bu)₂MeSi & \quad \text{Ge} \quad \text{Si(Bu-t)₂Me} \\
(t-Bu)₂MeSi & \quad \text{Si(Bu-t)₂Me}
\end{align*}
\]

(90a)  

\[
\begin{align*}
(t-Bu)₂MeSi & \quad \text{Si} \quad \text{Si(Bu-t)₂Me} \\
(t-Bu)₂MeSi & \quad \text{Ge} \quad \text{Si(Bu-t)₂Me} \\
(t-Bu)₂MeSi & \quad \text{Si(Bu-t)₂Me}
\end{align*}
\]

(90b)  

The structural parameters from the crystal structures of the two cyclotrigermenes 87a and 87b are very similar, the Ge=Ge bond length of 224.1 and 226.0 pm, respectively, being somewhat shorter than in silyl-substituted acyclic digermenes (227.0–229.8 pm). The endocyclic Ge−Ge bonds with 250.6 and 252.2 pm are by far longer than those in the acyclic derivatives (239.9–244.3 pm). Since the Ge₃ ring lies on a crystallographic mirror plane, both Ge atoms of the Ge=Ge bond have a planar coordination (in agreement with a short Ge=Ge bond). In sharp contrast to this finding, the double-bonded germanium atoms in the asymmetrically substituted cyclotrigermene 88a show pyramidal coordination (cis-bent) and a somewhat longer Ge=Ge bond of 226.4 pm. A pronounced trans-bent conformation is found, however, for 2-disilagermirene 90b. Apart from the torsion angle including the double-bonded atoms and the connected Si atoms of 40.3(5)°, which is a little larger than for the 1-sila-isomer (37.0°), no reliable data can be given for 90b, due to disordering of Si and Ge. Isomer 90a is well ordered in the crystal, the Si=Si bond being 214.6 pm and the Si−Ge bonds being 241.5 and 242.0 pm.
Treatment of the cyclotrimerene 87a with trityl tetraarylborates yields salts containing the corresponding cyclotrimerenium cation 89\textsuperscript{122,123}. Its structural parameters are very similar among the different salts. The Ge–Ge bond lengths fall into a narrow range between 232.6 and 233.5 pm, thus lying in between typical single and double bond values, being indicative of a delocalized 2\(\pi\)-aromatic system. The Ge atoms exhibit almost planar coordination, although, depending on the counter-anion present, the out-of-plane positioning of the connected silicon atoms may reach up to 30 pm.

Power reported the synthesis of a cyclogermanyl radical Btm\textsubscript{3}Ge\textsubscript{3} \textsuperscript{(91)\textsuperscript{124}} by dehalogenation of the heteroleptic terphenyl(chloro)germylene BtmGeCl \textsuperscript{(35)} (see above) by KC\textsubscript{8}. Unfortunately, the X-ray crystal structure analysis revealed severe disordering for the Ge atoms, therefore no reliable structural data are available to date. Nevertheless, the ESR spectrum of the compound indicate the localization of the unpaired electron on one Ge atom.

Crystallographic data on the cyclic compounds are given in Table 14.

C. Other Systems with Multiple Bonds between Heavier Tetrel Atoms

In recent years a couple of other compounds featuring multiple bonds between tetrel atoms have been synthesized, perhaps showing and defining one of the future courses of tetrel chemistry. Among them are the first examples of cumulated and conjugated double bonds and the very first E–E triple bond, or, strictly speaking, a \textit{formal} analogue of alkynes\textsuperscript{97,125}, comprising a REER skeleton. Anionic and radical species with no stable analogue in carbon chemistry were also found to be (kinetically) stable for its heavier congeners.
The first structurally authenticated heteronuclear double bond between heavier tetrals was prepared by Sekiguchi’s group via cycloaddition of phenylacetylene across the Ge=Si double bond of the appropriate disilagermirene 90b (equation 11). The bicyclic intermediate rearranges quickly to form the 1,2,3-germadisilol 92, comprising formally conjugated C=C and Ge=Si bonds. Despite the almost planar geometry of the ring, conjugation was...
TABLE 14. Parameters (bond length in pm, angle in deg) of cyclotrigermenes, cyclotristannenes and cyclotrigermenium cations

<table>
<thead>
<tr>
<th>Cyclotrigermenes</th>
<th>Cyclotristannene</th>
<th>Cyclotrigermenium cations</th>
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<tr>
<td><strong>R$^1$</strong></td>
<td><strong>R$^2$</strong></td>
<td><strong>Ge−R$^1$</strong></td>
</tr>
<tr>
<td>(t-Bu)$_3$Si</td>
<td>(t-Bu)$_3$Si</td>
<td>244.7</td>
</tr>
<tr>
<td>(t-Bu)$_3$Ge</td>
<td>(t-Bu)$_3$Ge</td>
<td>249.0</td>
</tr>
<tr>
<td>(t-Bu)$_3$Si</td>
<td>(t-Bu)$_3$Si</td>
<td>251.0</td>
</tr>
<tr>
<td>Hyp</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(t-Bu)$_3$Si</td>
<td>(t-Bu)$_3$Si</td>
<td>not reported</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(<strong>R$^1$</strong> is attached to −E=E and <strong>R$^2$</strong> to −E−E.)</td>
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<td></td>
</tr>
</tbody>
</table>
neither detected by spectroscopic means nor supported by the structural data, however\textsuperscript{126}. The Ge=Si bond length of 225.0 pm meets the expectation\textsuperscript{127}, being 17 pm shorter than the Ge−Si single bond in the same molecule. The [2 + 2] cycloaddition of a second phenylacetylene moiety furnishes finally a novel bicyclic system 93 (equation 12) with a Ge−Si single bond (Ge−Si: 243.2 pm); note that for a conjugated system, a [4 + 2] cycloaddition would have been expected rather than a [2 + 2] cycloaddition. Other novel bicyclic systems have been obtained by analogous reaction of the unsymmetrically substituted cyclotrimerenines\textsuperscript{88,128}.

\begin{center}
\begin{tikzpicture}

\node (tip2ge) at (0,0) {\textbf{Tip}_2\text{Ge}};
\node (ge2tip2) at (0,-1) {\textbf{GeTip}_2};
\node (ge4tip4) at (0,-2) {\textbf{Ge}_4\text{Tip}_4};
\node (ge6tip6) at (0,-3) {\textbf{Ge}_6\text{Tip}_6};

\draw[->,thick] (tip2ge) -- (ge2tip2);
\draw[->,thick] (ge2tip2) -- (ge4tip4);
\draw[->,thick] (ge4tip4) -- (ge6tip6);

\node (mesbr) at (1,-2) {\textbf{MesBr}};
\node (tip3li) at (1,0) {\textbf{Tip}3\text{Li}};
\node (tip2ge2) at (1,-1) {\textbf{Tip}_2\text{Ge}};

\draw[->,thick] (tip2ge) -- (mesbr);
\draw[->,thick] (tip2ge) -- (tip3li);
\draw[->,thick] (tip2ge) -- (tip2ge2);

\node (tip2ge3) at (2,-2) {\textbf{Tip}_2\text{Ge}};
\node (ge4tip42) at (2,-3) {\textbf{Ge}_4\text{Tip}_4};

\draw[->,thick] (tip2ge3) -- (ge4tip42);

\end{tikzpicture}
\end{center}

\textbf{SCHEME 7. Synthesis of 94 and 96}

Conjugated bonds are indeed found within the tetragermabutadiene Tip\textsubscript{6}Ge\textsubscript{4} (94) synthesized by Weidenbruch’s group\textsuperscript{110}. It was obtained by an analogous route to that of the respective tetrasilabutadiene Tip\textsubscript{6}Si\textsubscript{4} (95) (Scheme 7)\textsuperscript{129}. Like is lighter congener 95 the tetragermabutadiene 94 has 2,3-ditipyl cis-configuration. For steric reasons the Ge\textsubscript{4} skeleton is not planar, but shows a dihedral angle of 22.5° — much smaller than that observed for 95 (51°). The Ge−Ge distances are 235.7 and 234.4 pm and thus markedly longer than in the parent digermene 66 (221.3 pm), but still lying in the range for double bonds, while the central Ge−Ge bond with 245.8 pm lies in the range of normal single bonds. The main evidence for conjugative interactions between the two Ge=Ge bonds comes from the large bathochromic shift of the long-wave visible absorption to 560 nm, giving a deep blue solution; ordinary digermenes are yellow or orange, showing much lower shifts than 500 nm\textsuperscript{106,130}. Both digermene fragments of 94 exhibit a pronounced trans-bent conformation with respective $\kappa$-values of 31.1 and 35.4°, values much larger than for other known digermenes ($<22.3^\circ$).
Slight changes in the reaction conditions furnished via an elusive reaction path a salt with a very unusual cyclic $C_5$ symmetric tetragermaallyl anion 96 (Scheme 7)\textsuperscript{110}. Two different Ge–Ge bond lengths are found within the planar ring system, one of them (Ge$_{A}$–Ge$_{B}$ and Ge$_{A}$–Ge$_{B}'$) with 236.8 pm clearly indicating multiple-bond character, whereas the other (Ge$_{B}$–Ge$_{C}$ and Ge$_{B}$–Ge$_{C}'$) with 251.2 pm is typical for an elongated single bond. A markedly longer Ge–Ge multiple bond of 242.2 pm is found for the open-chain trigemaallyl-type anion [Btm$_3$Ge$_3$]$^-$ 97, being a reduction product from the respective cyclogermyl radical 91\textsuperscript{124}. The anion 97 with two two-coordinated Ge atoms may also be addressed as bisgermylene, one terphenyl group and two germlyidene moieties serving as substituents to a germanide anion. Whereas the terminal Ge atoms exhibit C–Ge–Ge angles of 111.3°, typical for sterically congested germynes, the Ge$_3$C$_3$ skeleton is almost planar and a very wide Ge–Ge–Ge angle (159.2°) is observed, implying delocalization of the negative charge by π-bonding to the adjacent Ge atoms. Consequently, the observed Ge–Ge distances (242.2 pm) are somewhat shorter than expected for Ge–Ge single bonds in congested digermanes\textsuperscript{131}.

![Diagram](97)

Terphenyl(chloro) and terphenyl(bromo)tetrylenes Ar–E–X (Ar = Btp; X = Cl, Br) have been used by Power’s group to synthesize a series of multiply-bonded dinuclear species with a varying amount of multiple-bond character\textsuperscript{95,132–134}. They originally intended to synthesize alkyne homologues ArGe≡GeR and ArSn≡SnAr by intermolecular reductive elimination of alkali metal halides from BtpGeCl (34) and BtpSnCl, respectively. Presumably such compounds may have formed at first, but due to the presence of low-lying empty p-orbitals (or $\pi^\ast$-orbitals) on E, they came up with reduced anionic species. In the case of E = Ge only a doubly reduced compound with Ge=Ge double bond (72a) was isolated (see above). The analogous Sn derivative 72b is obtained when using an excess of an alkali metal.

![Diagram](98)

If a stoichiometric amount of alkali metal is used instead, in the case of E = Sn singly reduced species, the radical anion [Btp$_2$Sn$_2$]$^-$ (98) is formed as the predominant product. Depending on the employed alkali metal and donor-solvent present, three different crystalline compounds were obtained and structurally characterized: 98a and 98b built from isolated ions\textsuperscript{132} and 98c comprising contact ion pairs with a Na–Sn bond\textsuperscript{133}. The
structural parameters of the solvates are, however, very similar, only the Sn—Sn—C angles are somewhat larger for 98c, probably for steric reasons. Thus the direct interaction of the anion and the cation seems to have only little influence on the structure of 98c (Figure 21). The observed Sn—Sn distances of 278.2 to 282.4 are in the same region as for sterically encumbered distannenes and are shorter than in encumbered distannanes. While the Sn—Sn distances match both possible bonding schemes: 98′ having a dative double bond augmented by a one-electron π-bond or 98 having a single bond augmented by a one-electron π-bond, the small Sn—Sn—C angles of 95.2°–98° show a major contribution of hybrid 98 (Scheme 8).

Switching from alkali metal to LiAlH₄ as reducing agent for Btp—E—X the first alkyne analogue could be finally isolated and structurally characterized, not for E = Ge and Sn, however, but for E = Pb. While in the Sn case the novel Sn(II) hydride BtpSnH (58) was isolated instead (see Section II), the putative Pb(II) hydride is not stable and dehydrogenates, finally yielding BtpPb≡PbBtp (99)°5.

The structural features of the dark green diplumbyne 99, a very long Pb—Pb bond of 318.8 pm and a very small C—Pb—Pb angle of 94.3°, favour more the description

FIGURE 21. Molecular structure of the contact ion-pair in sodium salt 98c comprising the radical anion [Btp₂Sn₂]⁻
as a diplumbylene with a lone-pair on each Pb atom (Scheme 9, hybide 100′) than as a diplumbylene with a Pb≡Pb triple bond (hybide 100). The double dative bonds, which may be used for the description of ditetrynes\(^4,97,125\), are expected to be weakest for \(E = Pb\); therefore, one can look forward with eager expectation to what future experiments will reveal for the other tetrels, especially for Si and Ge. However, even Pb is capable of forming relatively strong and short triple bonds, as was shown by the structure of a Pb\(_2\) dianion, recently synthesized and structurally characterized by Rutsch and Huttner as the transition metal complex \([\text{Ph}_4\text{P}]_2[\text{Pb}_2[\text{W(CO)}_5]_4]\) (101). In this complex a \([\text{Pb}_2]^–\) unit is found which is isoelectronic to Bi\(_2\). Other than for diplumbynes, but similar to the dianions \([\text{BtpE} = \text{EBtp}]^–\)\(^72a\) and \(72b\) (see above), the bond energy is not reduced by a preceding promotion step, since the low-energy s-orbital may stay doubly occupied and thus is not involved in bonding. Consequently, the observed Pb≡Pb distance of 281 pm in 101, despite putative coulomb repulsion, is very short.

Four interesting compounds derive from the reaction of Sn(NTms\(_2\))\(_2\) (26) with supersilylsodium NaSi(Bu-\(t\))\(_3\) (NaSup): Wiberg and coworkers reported that, depending on the solvent and the reaction conditions, a heterocumulene, a cyclotristannene or two striking cage compounds are obtained. At a low temperature in pentane tetra(supersilyl)tristannaallene Sup\(_2\)Sn=Sn=SnSup\(_2\) (102) is formed in about 20\% yield\(^118\). It could be isolated as dark blue crystals at \(-25^\circ\text{C}\). If allowed to stay for a longer period at room temperature, it rearranges quantitatively to the isomeric dark red-brown tetrasupersilylcyclotristannene (86) [half-life: 9.8 h at 25 °C(C\(_6\)D\(_6\)).]

In contrast to allenes R\(_2\)C=\(\equiv\)C\(_2\), which for most cases are almost linear, the tristannaallene 102 adopts a bent structure with an Sn—Sn—Sn angle of 155.9° (Figure 22). Both terminal Sn atoms display pyramidal coordination with tilt angles \(\kappa\) of 48° and 42.9° for Sn1 and Sn3, respectively. The two stannylene moieties are twisted with respect to each other by 66.7°. Both Sn=Sn double bonds with 268.4(1) and 267.5(1) pm are shorter than the shortest bond found so far for distannenes in Hyp(Mes)Sn=Sn(Mes)Hyp (74) (270.2 pm)\(^54\), probably owing to the presence of electropositive substituents and small steric repulsion across the double bond. The repulsion between adjacent supersilyl groups is large, however, leading to Si—Sn—Si angles of about 134°.

An even shorter Sn=Sn double bond is found for the cyclotristannene 86\(^118\): though the quality of the diffraction data is poor, the Sn=Sn distance could be determined with sufficient accuracy to be 259 pm (mean value). Moreover, the Sn atoms have an almost planar surrounding, thus based on these parameters cyclotristannene 86 is the only example of classical double bonding within an R\(_2\)Sn=SnR\(_2\) fragment. Due to steric reasons the Sn=Sn single bonds with 286 pm (mean value) are relatively long.

If cyclotristannene 86 is heated to 100 °C for several days or if the solvent of the initial reaction mixture is replaced by \(t\)-BuOMe, hexasupersilyl hexastannaprismane Sup\(_6\)Sn\(_6\) 103, the first hexastannaprismane is obtained\(^136\). The Sn–Sn bonds range from 291 to 294 pm and match those Sn–Sn bonds in encumbered distannanes. Very striking is the orientation of the supersilyl groups towards the Sn–Sn–bonds within the triangular faces of the prismane: the projection along the 3-fold axis of the prismane (Figure 23) reveals an
FIGURE 22. Molecular structure of tristannaallene 102 with non-linear Sn$_3$ backbone

FIGURE 23. Sn$_6$Si$_6$ core of hexastannaprismane 103: projection along the 3-fold axis

orientation of the three substituents at each face that resembles the proposed arrangements of the substituents in cyclotriplumbanes$^{88}$ or in one triangular face of the tetrameric thallium(I) alkyl (TsiTl)$_4$ (104)$^{137}$. At this point, it is an open question whether a similar electronic structure is responsible for these distortions in 103 and 104.
If the thf-solvate of NaSup is employed in the reaction with Sn(NTms₂)₂ (26), a further cage compound is obtained: the salt [(thf)₂Na]₂[Sn₈Sup₆] (105)\textsuperscript{138}. In the solid state a contact triple ion is observed, consisting of a cubic Sn₈ cage where all, but two opposite corners, are substituted by supersilyl groups (Figure 24). The free corners bind the two sodium ions; the observed Na—Sn distance of 310 pm is only slightly longer than that
found for Hyp$_3$Sn−Na(η$^6$-toluene) 106$^{139}$ (Figure 25; Na−Sn: 307 pm), but markedly shorter than that within the ion pair [(thf)$_3$Na][Sn$_2$Btp$_2$] (98c) (324 pm). The Sn−Sn bonds in stannacubane 105 range from 287 to 292 pm and are somewhat shorter than in prismane 103.

**D. Multiple Bonds to Carbon: Germenes, Stannenes and Plumbenes**

While the chemistry of silenes R$_2$Si=CR$_2$ has been well developed, structural information about germenes R$_2$Ge=CR$_2$ and stannenes R$_2$Sn=CR$_2$ is still scarce, and no plumbene R$_2$Pb=CR$_2$ had been isolated to date.

Although several germenes have been described$^{148}$, only one simple germene, i.e. a derivative bearing non-functionalized organyl substituents, the fluorenylidene derivative Mes$_2$Ge=C$_{13}$H$_8$ (107), with mesityl groups on Ge, has been structurally characterized so far$^{140}$. The Ge=C bond is by about 18 pm shorter than the standard Ge−C single bond, which is close to 198 pm, but about 21 pm shorter than in the corresponding sterically crowded germane Mes$_2$Ge(H)−C$_{13}$H$_9$ (108) (201 pm)$^{140}$. Thus the shortening is almost the same as for the couple C−C/C=C and the one derived from Pauling’s logarithmic estimation (equation 6).

A somewhat longer and twisted bond ($\tau = 35.7^\circ$) is found for the cryptodiborylcarbene adduct 109 to bis[bis(trimethylsilyl)amino]germylene$^{141}$. The value of 182.7 pm is still in accordance with the presence of a Ge=C double bond, but sharply contrasting the much larger values found for the Ge−C bonds in the carbene adducts 110a−c$^{79−81}$ which are even longer than the Ge−C single bond in the crowded germane 108. Moreover, the Ge atoms within these adducts are strongly pyramidalized, whereas the Ge atom in 109 is almost planar ($\kappa$: Ge: 1.7$^\circ$; C: 4.7$^\circ$). The bonds in 110a−c should therefore be addressed as dative C → Ge interactions (the respective carbenes are obviously pure donor carbenes).
TABLE 15. Parameters (bond length in pm, angle in deg) of compounds with heteronuclear double bonds to carbon $R^1R^2E=CR_3^2$ ($E=$ Ge, Sn)

<table>
<thead>
<tr>
<th>$R^1$</th>
<th>$R^2$</th>
<th>$R^3_{a}$</th>
<th>E</th>
<th>E=Y</th>
<th>$E-R^1_{E-R^2}$</th>
<th>$E-R^2_{E-R^2}$</th>
<th>$R^1-E=CR_3^2_{E-C}$</th>
<th>$\kappa$</th>
<th>$\tau$</th>
<th>Reference</th>
<th>Remarks</th>
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</thead>
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<tr>
<td>Mes</td>
<td>Mes</td>
<td>XIII</td>
<td>Ge</td>
<td>180</td>
<td>194</td>
<td>115.0</td>
<td>122.7</td>
<td>3.1 (Ge); 2.1 (C)</td>
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<td>(Tms)$_2$N</td>
<td>(Tms)$_2$N</td>
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<td>Ge</td>
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<td>181</td>
<td>115.9</td>
<td>122.1</td>
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<tr>
<td>Tip$^b$</td>
<td>Tbt$^b$</td>
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<td>192</td>
<td>112.9</td>
<td>116.4</td>
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<td>Tip$^c$</td>
<td>Tip$^c$</td>
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<td>C=C 131.4; Ge=C=C 159.2</td>
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<td>Bmp$^d$</td>
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<td>130.7</td>
<td>113.7</td>
<td>2.8 (Ge); 1.9 (C)</td>
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<td>Bmp</td>
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<td>Ge</td>
<td>177</td>
<td>202</td>
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<td>Sn</td>
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<td>122.2</td>
<td>4.4 (Sn); 4.5 (C)</td>
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<td>147</td>
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<td>XIV</td>
<td>Sn</td>
<td>203</td>
<td>218</td>
<td>105.4</td>
<td>120.0</td>
<td>13.2 (Sn); 9.7 (C)</td>
<td>11.9</td>
<td>145</td>
<td>cryptocarbenne adduct</td>
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</table>

$^a$ For the definition of substituent $XIII$ and $XIV$, see chart 3.
$^b$ Compound 111.
$^c$ Compound 112.
$^d$ Compound 113a.
A further germene structurally characterized is 111\textsuperscript{142}, the reaction product of CS\textsubscript{2} and the germylene Tbt(Tip)Ge, comprising a cyclic 1,2,3-dithiagermetandiy unit as carbene fragment. It exhibits the shortest Ge=C bond (177.0 pm) of all molecules with a Ge=C double bond, even shorter than the corresponding bond in the recently characterized 1-germaallene 112\textsuperscript{143}, a germene with a Ge=C bond to a sp-hybridized carbon atom. The Ge=C=C fragment of this cumulated multiply-bonded system is bent with a Ge−C−C angle of 159.2°, and the GeC\textsubscript{2} plane of the germylene fragment is markedly tilted towards the Ge=C bond (κ = 32.6°) (Figure 26), both observations indicating a somewhat different bonding mode compared to homonuclear allenes R\textsubscript{2}C=C=CR\textsubscript{2}. The central Si−C−C plane of the C(Tms)Ph carbene unit of 112 is orientated almost perpendicular to the GeC\textsubscript{2} plane of the germylene unit, as it is found for most allenes, however. Very recently two 1,6-digermahexadienynes 113\textsubscript{a} and 113\textsubscript{b}, comprising two germene units linked by an acetylene bridge, were synthesized\textsuperscript{144}. The conjugation of the germene moieties could be proven by UV−Vis spectroscopy. The structure determination of 113\textsubscript{a} indeed revealed an almost coplanar Ge\textsubscript{2}C\textsubscript{4} backbone (Figure 27) and short Ge=C bonds of 181.9 pm (although somewhat longer than for the fluorenylidene germane 107), however the main structural evidence for conjugation being the very short C(sp)−C(sp\textsuperscript{2}) single bond (140.7 pm).
Although simple stannenes such as the violet ditipyl fluorenylidestannane 114 had been synthesized\textsuperscript{149}, the only structurally characterized compounds which exhibit proper structural features for stannenes are the three cryptodiborylcarbene adducts 115a–c\textsuperscript{145–147}. In spite of large to medium twist angles (60.9°, 36.5° and 11.9°, respectively) between the carbene and the stannylene moieties, short Sn–C bonds of 203–204 pm are observed, being substantially shorter than Sn–C single bonds (\textit{ca} 215 pm) or C → Sn dative bonds in donor carbene adducts (>230 pm). Quantum-chemical calculations lead to similar or even shorter bond lengths for the parent species H\textsubscript{2}Sn=CH\textsubscript{2} depending on the method used: 206.3 pm (MCSCF)\textsuperscript{2b} or 194.5 pm (DFT)\textsuperscript{2a} with slightly \textit{trans}-bent or planar skeleton, respectively. According to these calculations even plumbenes should be accessible; DFT methods predict a planar structure for H\textsubscript{2}Pb=CH\textsubscript{2} with a Pb=C bond of 204.5 pm, thus again having a substantially shorter bond than Pb–C single-bonded species.
E. Heavier Homologues of Ketones $R_2E=Y$ ($E=\text{Ge--Pb}; Y=\text{O--Te}$)

Whereas aldehydes and ketones are one of the most important classes of organic compounds containing multiple bonds, no species with a $E=O$ double bond with $E=\text{Si, Ge, Sn, Pb}$ could be isolated as a pure compound in the condensed phase\textsuperscript{148b,161}. The germanone $\text{Tbt(Tip)}\text{Ge}=\text{O}$ \textsuperscript{116} prepared by Tokitoh’s group could be detected in solution only. At room temperature, however, by insertion of the $\text{Ge}=\text{O}$ bond into a $\text{C}–\text{Si}$ bond of an $\text{ortho}$-$\text{Bsi}$ substituent of the employed $\text{Tbt}$ ligand, it rearranges quickly to a mixture of diastereomeric benzogermacyclobutanes (equation 13)\textsuperscript{162}.

The first structural characterization of homologues of ketones (strictly speaking, of ureas), where $E$ and $Y$ are elements of the later rows of the periodic table, were reported in 1989 by Veith and coworkers. By sulfurization of the bis(aminogermylene) \textsuperscript{117}, the germanethione \textsuperscript{118} (Ge–Se: 206.3 pm) that is stabilized by intramolecular $\text{N}→\text{Ge}$ complexation was obtained (equation 14)\textsuperscript{163}. Several analogous or similar...
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<tr>
<th>R¹</th>
<th>R²</th>
<th>E</th>
<th>Y</th>
<th>E−R¹</th>
<th>E−R²</th>
<th>E=Y</th>
<th>E=Y−R³</th>
<th>Reference</th>
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</thead>
<tbody>
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<td>Bsi</td>
<td>Bsi</td>
<td>Ge</td>
<td>(N)₂SiMes₂</td>
<td>197</td>
<td>116.3</td>
<td>168.1</td>
<td>137.3</td>
<td>150</td>
<td>two Ge=N units C₂ symmetry</td>
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<tr>
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<td>Bsi</td>
<td>Ge</td>
<td>NSi(Bu-t)₂N₃</td>
<td>195</td>
<td>122.9</td>
<td>170.4</td>
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For the definition of substituents VI and XV, see charts 2 and 3, respectively.
species comprising the structural fragment N₂Ge=Y were synthesized afterwards and structurally characterized. Real ketone homologues R₂E=Y (R = hydrocarbyl), however, with no further stabilization by Lewis bases, were reported by Okazaki and Tokitoh only in 1993. They used the extremely sterically demanding 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group for protecting the reactive E=Y bond from dimerisation; one should note that the chalcogen atom itself bears no substituent, thus it must be protected by the substituents bonded to the tetrel.

Two different routes were developed: (a) chalcogenation of appropriate (transient) tetrylenes Tbt(Ar)E and (b) dechalcogenation of chalcogenametallolanes Tbt(R)EY₄ (equation 15). Thus, several species with Ge=S, Ge=Se, Ge=Te or Sn=Se bonds were synthesized and structurally characterized so far (Table 16). All compounds have similar structures [see, for example, Tbt(Tip)Ge=Te (119) in Figure 28] with E=Y multiple bonds much shorter (by ca 20 pm) than the respective single bonds; the values from diffraction experiments match very well the calculated values (B3LYP) for the parent species H₂E=Y. 

Meller and Leung and their coworkers succeeded in preparing heteroketones stabilized by intramolecular interactions to Lewis-basic centres, such as 120 and 121,
by chalcogenation of appropriate tetrylenes. In this manner even a compound with Sn=Te double bond (122) could be characterized. The observed E=Y(E = Ge, Sn; Y = Se, Te) bonds are significantly elongated compared with the calculated values, since the N → E dative interactions weaken the E−Y π-bond by competing with the chalcogen for the empty p-orbital of the tetrylene fragment. As could be expected by the intrinsic strength of these N → E dative interactions, this lengthening is more pronounced for Ge than for Sn.

For E = Pb, neither base-stabilized nor base-free derivatives have been isolated so far. The plumbanethione 123 could be indeed prepared by desulfurization of the respective tetrathiaplumbolane at −78 °C and trapped with several reagents, but has not been isolated to date. Instead, at ambient conditions the plumbylene 124 and the head-to-tail dimer, the 1,3,2,4-dithiadiplumbetane 125, is obtained (equation 16).

\[ \text{Tbt} \quad \text{Pb} \quad \text{Tbt} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{R} = \text{Ph, NMe}_2 \]

\[ \text{Tbt} \quad \text{Pb} \quad \text{S} \quad \text{Tbt} \]

\[ (123) \]

\[ \text{Tbt} \quad \text{Pb} \quad \text{S} \quad \text{Tbt} \]

\[ (124) \]

\[ \text{Tbt} \quad \text{Pb} \quad \text{S} \quad \text{Pb} \quad \text{S} \quad \text{Tbt} \]

\[ (125) \]
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**F. Other Multiple-bonded Compounds**

Examples of compounds with heavier tetrals multiply-bonded to other main-group elements are still scarce. Only a handful of species have been structurally characterized with double bonds between Ge or Sn and pnictogenes $R_1 R_2 E = X R_3$ and even less with hydrocarbyl substituents on $E$ (Table 16). No such derivative is known for $E = Pb$ and no example with $X = As$, Sb and Bi. Iminogermanes $R_1 R_2 Ge NR_3$ and iminostannanes are usually prepared by reaction of an azide $R_3 N_3$ with the appropriate tetrylene $R_2 E$ or the corresponding dimer, while phosphagermenes $R^2 R^1 Ge PR_3$ (126a, 126b)\textsuperscript{152,153},

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**FIGURE 29.** Molecular structure of heteroketone 122 comprising intramolecular $N \rightarrow Sn$ interactions

**FIGURE 30.** Molecular structure of phosphagermene 126b with planar coordinated Ge.
the only species structurally characterized with both E and X being the heavier elements of their respective groups, have been prepared by salt elimination reactions. All known compounds feature almost planar coordination geometry at E (see, for example, 126b\textsuperscript{153}; Figure 30), bent geometry at X and short E–X bonds, again about 20 pm shorter than typical single-bonded species. Using a bis(azide), even a bis(iminogermane) (127)\textsuperscript{150} could be prepared; its structural parameters match those of other iminogermanes.

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Recent advances in structural chemistry


148. For recent reviews, see:


CHAPTER 3

Theoretical studies of organic germanium, tin and lead compounds

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I. LIST OF ABBREVIATIONS

AIMP \textit{Ab Initio} Model Potential
AO Atomic Orbital
ASE Aromatic Stabilization Energy
BDE Bond Dissociation Energy
BO Born–Oppenheimer
B3LYP Becke’s 3-parameter fit using the correlation functional by Lee, Yang and Parr
CASSCF Complete Active Space Self-Consistent Field
CC Coupled-Cluster Theory
CCSD(T) Coupled-Cluster Theory with Singles, Doubles and Noniterative Approximation of Triples
CI Configuration Interaction
CIPSI Configuration Interaction by Perturbation with Multiconfigurational Zero-Order Wave Function Selected by Iterative Process
CISD Configuration Interaction with Singles and Doubles
DFT Density Functional Theory
ECP Effective Core Potential
GGA Generalized Gradient Approximation
HF Hartree–Fock
HOMO Highest Occupied Molecular Orbital
KS Kohn–Sham
LANL Los Alamos National Laboratory
LCAO Linear Combination of Atomic Orbitals
LDA Local Density Approximation
LUMO Lowest Unoccupied Molecular Orbital
MNDO Modified Neglect of Diatomic Differential Overlap
MCSCF Multiconfiguration Self-Consistent Field
MO Molecular Orbital
MP Møller–Plesset Perturbation Theory
NICS Nuclear Independent Chemical Shift
PE Photoelectron
PES Potential Energy Surface
QCISD Quadratic Configuration Interaction with Singles and Doubles
QCISD(T) Quadratic Configuration Interaction with Singles, Doubles, and Noniterative Approximation of Triples
SAC-CI Symmetry Adapted Cluster–Configuration Interaction
SVP Split-Valence basis set plus Polarisation functions
ZORA Zero-Order Regular Approximation
ZPE Zero-Point Energy

II. INTRODUCTION

The enormous progress in the development of theoretical methods and the dramatic increase in computer power have made it possible for quantum chemical investigations of heavy-atom molecules to become a standard research tool in chemistry in the last decade. While the 1980s can be considered as the age where application of \textit{ab initio} methods to classical organic molecules which contain elements of the first and second full rows of the periodic system were routinely done in organic chemistry, the 1990s saw the conquest of inorganic compounds with all elements of the periodic system including transition metals by accurate quantum chemical methods. Numerous theoretical studies have been reported
in the last 10 years about compounds which contain atoms that were once considered to be elusive for reliable theoretical calculations.

Two methods are mainly responsible for the breakthrough in the application of quantum chemical methods to heavy atom molecules. One method consists of pseudopotentials, which are also called effective core potentials (ECPs). Although ECPs have been known for a long time,

ECPs not only significantly reduce the computer time of the calculations compared with all-electron methods, they also make it possible to treat relativistic effects in an approximate way which turned out to be sufficiently accurate for most chemical studies. Thus, ECPs are a very powerful and effective method to handle both theoretical problems which are posed by heavy atoms, i.e. the large number of electrons and relativistic effects.

The second method which dramatically changed the paradigm of the dominant computational method in chemistry is density functional theory (DFT). The introduction of gradient corrected functionals into quantum chemistry altered the view that DFT is not reliable enough for the calculation of molecules. After initial resistance by the theoretical establishment it is now generally accepted that DFT is the most cost-effective quantum chemical method which usually gives reliable results for molecules in the electronic ground state. DFT has specific problems like any approximate method which should be known. Some of them are different from problems in ab initio theory and some of them are the same. In the next section we will shortly address the most important features of the present DFT methods and their strength and weakness.

The goal of this chapter is to give a summary of the most important results of quantum chemical studies in the field of organic germanium, tin and lead compounds which have been reported since 1990. The first volume in this series, published in 1989, covered the chemistry of organic germanium, tin and lead compounds, and included a chapter by Basch and Hoz (BH) which covered the theoretical work in this field up to 1989. Therefore, we have focused on more recent work in order to show the progress which has been made in the last decade. However, our chapter is written in a different way than the previous one by Basch and Hoz, who discussed the nature of the E−C bond (E = Ge, Sn, Pb) while presenting results for compounds with the formula H3E−Y where Y is a ligand. Theoretical research in the field has been greatly extended recently to compounds which have different molecular connectivities than H3E−Y. In particular, molecules which have multiple bonds of Ge to Pb have been reported. The review is an attempt to cover all theoretical work published in the field since 1990. This includes publications about combined experimental and theoretical studies. We wish to draw the attention of the reader to a recently published related review about theoretical aspects of compounds containing Si, Ge, Sn and Pb by Karni et al. A review about experimental and theoretical studies of main group analogues of carbenes, olefines and small ring compounds was published by Driess and Grützmacher.

The great diversity of the published work in the field made it difficult to find a simple ordering scheme for presenting the results. We decided to present first a summary of theoretical studies about relevant parent compounds of group-14 elements which makes it possible to compare the structures and the nature of the bonding of the elements Ge, Sn and Pb with C and Si. We have chosen the divalent carbene analogues EH2 and EX2 (X = halogen) and the tetravalent compounds EH4, EX4 and H3E−EH3. We also discuss recent work about the ethylene analogues E2H4 and E2X4 and the protonated species E2H5+. 
The section about parent compounds includes also theoretical work about the group-14 homologues of acetylene $E_2H_2$, cyclopropenium cation $E_3H_3^+$ and benzene $E_6H_6$. Although these molecules do not strictly belong to the class of organometallic compounds, they are important for an understanding of the molecules which have $E-C$ bonds.

The section about organometallic compounds of Ge, Sn and Pb was divided into neutral closed-shell molecules, which comprise the largest part of the chapter, cations and anions and finally radicals. The section about closed-shell molecules is further divided into papers which report about structures and properties of molecules with multiple and those with single bonds of Ge, Sn and Pb, and work that concentrates on the elucidation of reaction mechanisms. We included all studies which report about compounds of the heavier elements Ge to Pb even when the main focus of the work was on the lighter atoms C and Si or other elements. Thus, some work which is discussed here will also be found in the chapter which focuses on Si compounds.

III. THEORETICAL METHODOLOGY

Because this chapter is a follow-up of previous work in the field it is not necessary to repeat the basics of *ab initio* methods. This has been done in detail by Basch and Hoz, who also discuss the most important atomic properties of Ge, Sn and Pb. We also recommend the theoretical section in the chapter by Apeloig about organosilicon compounds in this series who gave an excellent overview about the most important aspects of *ab initio*, semiempirical and force-field methods. The reader will find there an explanation of the most common standard methods which will be mentioned in this review without further explanation. We will focus in the following on those theoretical and computational aspects of methods which are particularly important for heavy-atom molecules that have been advanced in the last decade, i.e. ECPs and DFT. We also briefly discuss relativistic effects. We point out that semiempirical methods and force field parameters are available for the elements Ge, Sn and Pb. However, the application of the two methods has not gained much popularity and not many papers have been published in the field. Most reports are restricted to special problems.

The following is a very short outline of the basic ideas of the relevant theoretical methods and aims at giving experimental chemists an understanding of the underlying principles. For those readers who wish to learn more about present methods in computational chemistry, we recommend the textbook *Introduction to Computational Chemistry* by Jensen. An excellent book about the theory and application of DFT given from a chemist’s point of view is *A Chemist’s Guide to Density Functional Theory* by Koch and Holthausen. Two reviews are available which discuss the application of ECPs to heavy atom molecules. We also mention the *Encyclopedia of Computational Chemistry* which contains a large number of reviews written by experts about nearly all aspects of the field.

A. Density Functional Theory

It is perhaps helpful to introduce the fundamental concepts of DFT by comparing it with *ab initio* methods which are based on Hartree–Fock theory. The basic idea of the latter is that the many-electron wave function of a molecule is approximated by a set of one-electron functions which give the energy of a single electron in the field of (i) fixed nuclei and (ii) the average of the remaining electrons. The former approximation is known as the Born–Oppenheimer (BO) approximation. It holds also in DFT. The error caused by the BO model is negligible in most cases for molecules in their electronic ground state. The second approximation introduces correlation energy. It is the difference between the nonrelativistic
electron–electron interactions in HF theory which are calculated using an average field of the electronic charge distribution and the sum of the exact, i.e. individual electron–electron interactions. There are several methods in \textit{ab initio} theory which can be used to calculate correlation energy. The most popular ones are Møller–Plesset perturbation theory (MP), coupled-cluster theory (CC) and configuration interaction (CI).

The central equations in \textit{ab initio} theory are the Hartree–Fock equations:

$$F \phi_i = \epsilon_i \phi_i$$ \hspace{1cm} (1)

The Fock operator $F$ contains terms for the kinetic energy, the nuclei–electron attraction and the averaged electron–electron repulsion. The values $\epsilon_i$ are the energies of the electrons which, after proper addition, give the Hartree–Fock (HF) total energy $E^{\text{HF}}$ of the molecule. The one-electron functions $\phi_i$ (molecular orbitals) give in a simplified view the 3-dimensional distribution of the electron $i$ in space. The total wave function of all electrons can be constructed from the $\phi_i$ via the so-called Slater determinant. Each $\phi_i$ is expressed in terms of a linear combination of atomic orbitals (LCAO). The size of the basis set determines the calculated energy $E^{\text{HF}}$ of the molecule. The correlation energy $E^{\text{corr}}$ is estimated in a separate calculation after the HF equations have been solved. The nuclear repulsion energy $E^{N-N}$ is calculated classically using the fixed positions of the nuclei. The total energy of the molecule is then given by the sum of three terms:

$$E^{\text{tot}} = E^{\text{HF}} + E^{\text{corr}} + E^{N-N}$$ \hspace{1cm} (2)

Thus, the accuracy of a (nonrelativistic) \textit{ab initio} calculation is determined by two factors, i.e. the size and quality of the basis set and the method by which correlation energy has been calculated. The accuracy can systematically be improved by choosing better basis sets and better methods for calculating correlation energy.

The working equations in DFT look very similar to the Hartree–Fock equations. They are called Kohn–Sham (KS) equations$^{6,15,17}$:

$$F^{\text{KS}} \phi_i = \epsilon_i \phi_i$$ \hspace{1cm} (3)

The difference between equations 1 and 3 is the form of the operator $F$. The Kohn–Sham operator $F^{\text{KS}}$ is constructed with the goal that the resulting one-electron functions $\phi_i$ yield a total ground-state electron density distribution of the molecule which is correct. Hohenberg and Kohn showed that the total energy of a molecule in the electronic ground state is uniquely determined by the electron density$^{6a}$. It follows that the electron density which is calculated via equations 3 gives directly the correct total energy $E^{\text{tot}}$ via proper summation of the one-electron energies $\phi_i \epsilon_i$, unlike the HF equations 1 which give the HF energy $E^{\text{HF}}$. Thus, the operator $F^{\text{KS}}$ contains a term for the correlation energy.

The problem with the conceptually simple form of the KS equations is the choice of the functionals which determine the operator $F^{\text{KS}}$ in equations 3. While the HF operator $F$ is known but yields only approximate energies, the operator $F^{\text{KS}}$ gives the correct energy but the functional is not known. The form of $F^{\text{KS}}$ can only be guessed! The popularity of DFT in molecular quantum chemistry which came in the last decade is because the guesses have been very successful. New types of functionals have been suggested for $F^{\text{KS}}$ which yield a much higher accuracy than earlier functionals.

Before we discuss in brief the new functionals, we wish to comment on the one-electron functions $\phi_i$ in equations 3 and the basis sets used in DFT. The functions $\phi_i$ have originally been calculated with the purpose of describing the total electron density in terms of one-electron functions. It was recently suggested that the Kohn–Sham orbitals $\phi_i$ can also be
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used for qualitative MO models in the same way as HF orbitals were employed in the past\textsuperscript{18}. Thus, orbital interaction diagrams can be constructed and frontier orbital analyses of chemical reactivity can be carried out using Kohn–Sham orbitals which are calculated by DFT methods\textsuperscript{19}. KS orbitals have the advantage over HF orbitals in that their energies are an approximation to the total energy of the molecule, while the latter give only the HF energy. The shape of the KS orbitals $\phi_i$ is very similar to the shape of HF orbitals $\varphi_i$, but the occupied orbitals $\phi_i$ are higher in energy than the occupied $\varphi_i$ and the unoccupied $\phi_i$ are lower in energy than the vacant $\varphi_i$.

A fortunate finding of test calculations was that the same basis sets of Gaussian-type functions which are used as standard basis sets in \textit{ab initio} calculations can be used for DFT calculations. It was also found that the same ECPs which have been optimized for \textit{ab initio} methods can be employed for DFT methods\textsuperscript{20}. Users of the program package Gaussian may, e.g., simply choose DFT/6-31G(d) instead of HF/6-31G(d) or MP2/6-31G(d). The only choice which one has to make is the DFT functional.

Mathematical expressions for the functionals which are found in the Kohn–Sham operator $F^{\text{KS}}$ are usually derived either from the model of a uniform electron gas or from a fitting procedure to calculated electron densities of noble gas atoms\textsuperscript{15}. Two different functionals are then derived. One is the exchange functional $F_x$ and the other the correlation functional $F_c$, which are related to the exchange and correlation energies in \textit{ab initio} theory. We point out, however, that the definition of the two terms in DFT is slightly different from \textit{ab initio} theory, which means that the corresponding energies cannot be directly compared between the two methods.

In order to run a DFT calculation the user has to choose a combination of $F_x$ and $F_c$, which together define the DFT method to be employed. Mathematical expressions for $F_x$ and $F_c$ were first derived as a function of the electron density $\rho(r)$. This is called the Local Density Approximation (LDA). A significant improvement in the accuracy of the calculated results was achieved when not only the electron density $\rho(r)$ but also its gradient $\nabla \rho(r)$ was used for deriving mathematical expressions for $F_x$ and $F_c$. This is called the Generalized Gradient Approximation (GGA), which gives gradient corrected functionals. They are sometimes called nonlocal functionals which is a misnomer, because the gradient $\nabla \rho(r)$ is also a local function.

The situation at present is that the nonlocal exchange functional suggested by Becke (B) in 1988\textsuperscript{21} has been established as a standard expression in DFT calculations. The choice of the best correlation functional is less obvious than the choice of the exchange functional. The presently most popular correlation functionals are those of Perdew (P86)\textsuperscript{22}, Lee et al. (LYP)\textsuperscript{23}, Perdew and Wang (PW91)\textsuperscript{24} and Vosko et al. (VWN)\textsuperscript{25}.

The situation in choosing proper combinations of exchange and correlation functionals became a bit confusing in the early 1990s when different functionals were combined and the resulting energy expression was given by a multiparameter fit of the functionals to a set of well-established experimental values, i.e. the so-called G2 set\textsuperscript{26}. The most commonly used functional combination of this type is the 3-parameter fit of Becke (B3)\textsuperscript{27}. A widely used variant of the B3 hybrid functional termed B3LYP\textsuperscript{28}, which is slightly different from the original formulation of Becke, employs the LYP expression for the nonlocal correlation functional $F_c$. It seems that the B3LYP hybrid functional is at present the most popular DFT method for calculating molecules. Other widely used combinations of functionals are BP86, which gives particularly good results for vibrational frequencies\textsuperscript{29}, BPW91 and BLYP. It should be noted that the development of new functionals is presently an area of active research. New DFT procedures may soon come and replace the above functionals as standard methods. The present state of development in the field has been the topic of a special issue of the \textit{Journal of Computational Chemistry}\textsuperscript{30}. It is a wise idea
to estimate the accuracy of a functional for a particular problem at the beginning of a research project, by running some test calculations before the final choice of the DFT is made. The disadvantage of DFT compared with conventional \textit{ab initio} methods is that the DFT calculations cannot systematically be improved toward better results by going to higher levels of theory.

1. Basis sets, effective core potentials and relativistic effects

As said above it is possible to use the same Gaussian-type standard basis sets of \textit{ab initio} theory for DFT calculations. Concerning the quality of the basis set which is necessary to obtain reliable results, it is advisable to use for Ge at least a split-valence basis set which should be augmented by a d-type polarization function such as 6-31G(d). Better basis sets of triple-zeta quality with more polarization functions up to 6-311G(3df) have been developed for Ge which belong to the standard basis sets in Gaussian 98\textsuperscript{31}. Other basis sets for Ge are available, e.g., from the compilations of Huzinaga et al.\textsuperscript{32} and Poitier et al.\textsuperscript{33} and from the work of Ahlrichs et al.\textsuperscript{34}.

All-electron basis sets are also available for the heavier atoms Sn and Pb, but relativistic effects become so important for these elements that they must be considered in the theoretical method. This is the reason why most workers choose for Sn and Pb quasi-relativistic ECPs with valence-only basis sets which significantly reduce the computational costs while at the same time the most important relativistic effects are considered. The error introduced by the approximate treatment of relativity and replacement of the core electrons by a pseudopotential is for most chemical questions negligible compared with the truncation of the basis set and the approximate calculation of correlation energy\textsuperscript{4,5}. ECPs may actually be used also for Ge and even for Si and C. It is uncommon to employ ECPs for the lighter elements carbon and silicon, but calculations of germanium compounds frequently use ECPs rather than all-electron basis sets. Relativistic effects may be neglected for the calculation of energies and geometries of germanium compounds if chemical accuracy is sufficient.

The program package Gaussian 98\textsuperscript{31} has three different ECPs as standard for heavy atom calculations. One popular set of ECPs has been developed by Hay and Wadt (HW) and includes parameters for Si to Pb\textsuperscript{35}. Standard versions of the HW ECPs in Gaussian 98\textsuperscript{31} have minimal basis sets (LANL2MB) and double-zeta basis sets (LANL2DZ). Additional d-type polarization functions for the HW ECPs have been published in the literature\textsuperscript{36} but they must be added by hand to the basis sets. The user should know, however, that the HW ECPs for Si and Ge are nonrelativistic, while only the ECPs for Sn and Pb include scalar-relativistic effects\textsuperscript{35}. Another important point is that the valence basis sets of HW have only three Gaussian functions for the s and p orbitals, written as (3/3). The LANL2DZ keyword splits them into (21/21), which has the same quality as the 3-21G all-electron basis set for the valence electrons. Four Gaussian functions are needed for the valence s and p orbitals in order to achieve the same quality as 6-31G after contraction to (31/31). This is provided by the ECPs of Stevens et al.\textsuperscript{37,38} and the ECPs of the Stuttgart/Dresden group\textsuperscript{39,40}. The ECPs of the two groups are also available as standard options in Gaussian 98\textsuperscript{31}. The Stuttgart/Dresden group is particularly active in developing ECPs for all elements of the periodic system. An overview of the pseudopotentials which are available from the group is given on their web site\textsuperscript{41}. Other ECPs for main group elements which include functions for the heavier group-14 elements have been published by the group of Christiansen\textsuperscript{42–45}, by Gomez and Pacios\textsuperscript{46} and by Bouteiller et al.\textsuperscript{47}. The former group also developed ECPs for a larger valence space which explicitly includes outermost core electrons. An overview of the
most widely used ECPs is given in Table 1. It should be noted that it is possible to use nonstandard ECPs in Gaussian 98 through the general basis set option. Finally, we mention the so-called \textit{ab initio} model potentials (AIMP) which have been developed and advocated by Huzinaga and coworkers. The main difference between ECPs and AIMPs is that the latter have the correct nodal structure of the valence orbitals, while the ECPs are smoothed out in the core region. This means, e.g., that an ECP 4s valence orbital of Ge is nodeless, while the 4s orbital of an AIMP has three nodes. Test calculations have shown that the results of the two methods are very close to each other if a similar size basis set is used. For a detailed discussion of ECPs and AIMPs see References 4 and 5.

Relativistic effects may be also considered by other methods than pseudopotentials. It is possible to carry out relativistic all-electron quantum chemical calculations of molecules. This is achieved by various approximations to the Dirac equation, which is the relativistic analogue to the nonrelativistic Schrödinger equation. We do not want to discuss the mathematical details of this rather complicated topic, which is an area where much progress has been made in recent years and where the development of new methods is a field of active research. Interested readers may consult published reviews. A method which has gained some popularity in recent years is the so-called Zero-Order Regular Approximation (ZORA) which gives rather accurate results. It is probably fair to say that

\begin{table}[h]
\centering
\begin{tabular}{llllll}
\hline
Authors & Reference & Atoms & Method$^a$ & Type$^b$ & Valence basis set$^c$ \\
\hline
Stevens et al. & 37 & Li–Ar & ECP & NR & [4/4] \\
Stevens et al. & 38 & K–Rd & ECP & R & [5/5]$^d$ \\
Christiansen and coworkers & 42 & Li–Ar & ECP & R & [4/4] \\
Christiansen and coworkers & 46 & B–Kr$^q$ & ECP & R & [311/311]$^p$ \\
Bouteiller and coworkers & 47 & Li–Kr & ECP & NR & [4/4] \\
\hline
\end{tabular}
\caption{Overview of common pseudopotentials for main group elements}
\end{table}

\begin{itemize}
\item $^a$ECP = effective core potential, AIMP = \textit{ab initio} model potential.
\item $^b$NR = nonrelativistic, R = relativistic.
\item $^c$Number of valence s and p Gaussian functions [s/p].
\item $^d$The valence basis set for group 1 and group 2 elements is [4/4].
\item $^e$The valence basis set for group 16 and group 17 elements is [4/5].
\item $^f$For group 1 and 2 the valence basis set is [5/4].
\item $^g$Valence basis set for group 13–18 elements which has the \((n – 1)\) d electrons in the valence shell.
\item $^h$Valence basis set for group 1 and 2 elements is [5/5].
\item $^i$Valence basis set for Tl–Rn.
\item $^j$Valence basis set for Cs and Ba including the outermost 5s, 5p and 5d electrons.
\item $^k$The s and p valence basis sets were optimized for the contraction scheme 311.
\item $^l$Valence basis set for Li–Ne.
\item $^m$Valence basis set for Na–Ar.
\item $^n$Valence basis set for K–Kr.
\item $^o$Valence basis set for Rb–Xe.
\item $^p$Only main group elements of groups 13–17.
\item $^q$Only main group elements of groups 13–18.
\end{itemize}
approximate relativistic all-electron calculations of molecules achieve a similar accuracy to relativistic ECPs but at higher computational costs. The advantage of approximate all-electron methods is that the results may in principle become improved by going to higher levels of theory.

**IV. QUANTUM CHEMICAL STUDIES OF GROUP-14 COMPOUNDS**

In the following we review quantum chemical work about organic germanium, tin and lead compounds which has been published since 1990. The presentation of the results is organized as follows. First, we discuss in brief some relevant theoretical work about parent compounds of Ge to Pb. Then we summarize calculations of organometallic compounds. The latter section is divided into studies of neutral closed-shell molecules, charged species and radicals. E is used for any of the group-14 elements C to Pb.

**A. Parent Compounds**

Although the chapter focuses on calculations of organometallic compounds of group-14 elements Ge, Sn and Pb, we also review recent theoretical work about parent compounds of the elements which show the differences between the structures and energies of the carbon and silicon compounds and the heavier analogues of germanium, tin and lead. This part covers papers which report about theoretical studies of EH2, EX2, EH4, EX4, E2H6, E2H4, E2H5+, E2X4, E2H2, E3H5+ and E6H6 (X = halogen) that have been published since 1990.

1. **EH2 and EX2 (X = halogen)**

Table 2 shows calculated geometries and theoretically predicted energy differences between the (1A1) singlet state and (3B1) triplet state of the divalent group-14 compounds EH2, EF2 and ECl2. CH2 is the only EX2 species which has a triplet ground state. The energy difference between the triplet and singlet state in favor of the latter shows the order C << Si < Ge ~ Sn < Pb. Chlorine and particularly fluorine strongly favor the singlet state over the triplet state of EX2.

Benavides-Garcia and Balasubramanian studied also the dibromides and diiodes of Ge, Sn and Pb. The latter work gives also results for the monohalogen systems GeHCl, GeHBr and GeHI. The geometries and singlet–triplet excitation energies are intermediate between the values of the germanium dihydrides and dihalogens. The authors calculated also the positive ions ECl2+, EBr2+ and EI2+ (E = Sn to Pb) in the 2A1 ground state and 2B1 excited state.

The electronic ground states of EH2 for E = Si to Pb and the hydrogenation energy yielding EH4 have been calculated by Barandiarán and Seijo and by Dyall. Table 3 shows the theoretically predicted reaction energies for the reaction EH4 → EH2 + H2. The calculations predict that the reaction becomes less endothermic from Si to Pb in intervals of ca 20 kcal mol⁻¹. The hydrogenation of PbH2 is nearly thermoneutral. The reaction energies of H2 loss from EH4 and MeEH3 have been calculated by Hein et al. The results are discussed in the next section (see Table 6).

The spectroscopic constants of the dihydrides SiH2, GeH2 and SnH2 and their cations and anions have been calculated by Mineva et al. The neutral dihydrides and their donor–acceptor complexes with various AH3 and AH2 species have been the subject of a theoretical work by Schöller and Schneider. Table 4 shows the calculated bond energies of the complexes. It becomes obvious that the bond strength of the EH2 complexes has the order SiH2 > GeH2 > SnH2. The donor–acceptor complex of GeH2 with water has also been calculated by Nowek and Leszczynski.
TABLE 2. Calculated geometries and relative energies (kcal mol\(^{-1}\)) of the \(^1A_1\) and \(^3B_1\) states of EX\(_2\)(X = H, F, Cl); distances \(R\) in (Å), angles \(A\) in (deg)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Ge</th>
<th>Sn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>EH(_2)(^a)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(R) (E−X)</td>
<td>1.150</td>
<td>1.555</td>
<td>1.620</td>
<td>1.793</td>
<td>1.880</td>
</tr>
<tr>
<td>(A) (X−E−X)</td>
<td>100.1</td>
<td>93.4</td>
<td>92.3</td>
<td>92.4</td>
<td>91.5</td>
</tr>
<tr>
<td><strong>Singlet (^1A_1)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(R) (E−X)</td>
<td>1.116</td>
<td>1.511</td>
<td>1.559</td>
<td>1.734</td>
<td>1.827</td>
</tr>
<tr>
<td>(A) (X−E−X)</td>
<td>129.8</td>
<td>118.3</td>
<td>118.9</td>
<td>116.8</td>
<td>115.2</td>
</tr>
<tr>
<td>(ΔE_{S−T}^b)</td>
<td>10.6</td>
<td>−16.8</td>
<td>−24.1</td>
<td>−23.7</td>
<td>−39.1</td>
</tr>
<tr>
<td><strong>EF(_2)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(R) (E−X)</td>
<td>1.279</td>
<td>1.598</td>
<td>1.742</td>
<td>1.889</td>
<td>2.091</td>
</tr>
<tr>
<td>(A) (X−E−X)</td>
<td>104.7</td>
<td>99.5</td>
<td>97.0</td>
<td>95.7</td>
<td>98.2</td>
</tr>
<tr>
<td><strong>Singlet (^1A_1)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(R) (E−X)</td>
<td>1.303</td>
<td>1.596</td>
<td>1.732</td>
<td>1.878</td>
<td>2.060</td>
</tr>
<tr>
<td>(A) (X−E−X)</td>
<td>118.3</td>
<td>114.0</td>
<td>112.8</td>
<td>111.8</td>
<td>118.9</td>
</tr>
<tr>
<td>(ΔE_{S−T}^b)</td>
<td>−46.3</td>
<td>−71.0</td>
<td>−75.3</td>
<td>−73.7</td>
<td>−88.4</td>
</tr>
<tr>
<td><strong>ECl(_2)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(R) (E−X)</td>
<td>1.756</td>
<td>2.073</td>
<td>2.191</td>
<td>2.363</td>
<td>2.542</td>
</tr>
<tr>
<td>(A) (X−E−X)</td>
<td>109.4</td>
<td>101.7</td>
<td>100.5</td>
<td>98.4</td>
<td>100.8</td>
</tr>
<tr>
<td><strong>Singlet (^1A_1)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(R) (E−X)</td>
<td>1.730</td>
<td>2.049</td>
<td>2.040</td>
<td>2.336</td>
<td>2.599</td>
</tr>
<tr>
<td>(A) (X−E−X)</td>
<td>125.5</td>
<td>118.2</td>
<td>118.6</td>
<td>116.0</td>
<td>139.9</td>
</tr>
<tr>
<td>(ΔE_{S−T}^b)</td>
<td>−20.5</td>
<td>−55.2</td>
<td>−60.3</td>
<td>−60.0</td>
<td>−69.7</td>
</tr>
</tbody>
</table>

\(^a\)Reference 55.
\(^b\)Reference 58. Negative values indicate that the singlet state is more stable than the triplet state.
\(^c\)Reference 56.
\(^d\)Reference 57.
\(^e\)Reference 59.

TABLE 3. Reaction energies \(ΔE\) (kcal mol\(^{-1}\)) without ZPE corrections for XH\(_4\) \(→\) XH\(_2\) + H\(_2\)\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>DHF(^b)</th>
<th>PT(^c)</th>
<th>QR-AIMP(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X=Si</td>
<td>62.3 (−0.6)</td>
<td>62.6 (−0.3)</td>
<td></td>
</tr>
<tr>
<td>X=Ge</td>
<td>42.4 (−3.1)</td>
<td>42.6 (−2.9)</td>
<td>41.7 (−2.1)</td>
</tr>
<tr>
<td>X=Sn</td>
<td>23.2 (−7.7)</td>
<td>26.6 (−4.3)</td>
<td>21.6 (−6.6)</td>
</tr>
<tr>
<td>X=Pb</td>
<td>−6.2 (−27.4)</td>
<td>7.1 (−13.5)</td>
<td>−2.2 (−18.7)</td>
</tr>
</tbody>
</table>

\(^a\)Numbers in parentheses give the relativistic effects. See also Table 6.
\(^b\)Dirac–Hartree–Fock calculations, Reference 61.
\(^c\)Relativistic correction included by perturbation theory, Reference 61.
\(^d\)Quasi-relativistic \(ab\) initio model potential calculations, Reference 60.
3. Theoretical studies of organic germanium, tin and lead compounds

### TABLE 4. Binding energies (kcal mol\(^{-1}\)) for \(\text{H}_2\text{E} - \text{AH}_m\) adduct formation of silylene, germylene and stannylene with various \(\text{AH}_3\) and \(\text{AH}_2\) units\(^a\)

<table>
<thead>
<tr>
<th>(\text{AH}_m)</th>
<th>(\text{EH}_2 = \text{SiH}_2)</th>
<th>(\text{GeH}_2)</th>
<th>(\text{SnH}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{NH}_3)</td>
<td>24.6</td>
<td>20.9</td>
<td>19.4</td>
</tr>
<tr>
<td>(\text{PH}_3)</td>
<td>20.9</td>
<td>16.3</td>
<td>12.5</td>
</tr>
<tr>
<td>(\text{AsH}_3)</td>
<td>16.3</td>
<td>13.0</td>
<td>10.2</td>
</tr>
<tr>
<td>(\text{SbH}_3)</td>
<td>17.1</td>
<td>14.0</td>
<td>10.8</td>
</tr>
<tr>
<td>(\text{BiH}_3)</td>
<td>11.3</td>
<td>9.5</td>
<td>7.4</td>
</tr>
<tr>
<td>(\text{OH}_2)</td>
<td>13.2</td>
<td>11.5</td>
<td>11.6</td>
</tr>
<tr>
<td>(\text{SH}_2)</td>
<td>12.4</td>
<td>10.3</td>
<td>9.0</td>
</tr>
<tr>
<td>(\text{SeH}_2)</td>
<td>12.5</td>
<td>10.6</td>
<td>9.3</td>
</tr>
<tr>
<td>(\text{TeH}_2)</td>
<td>14.7</td>
<td>12.3</td>
<td>10.4</td>
</tr>
</tbody>
</table>

\(^a\)Reference 64.

The \(^1\text{A}_1\) state of \(\text{EH}_2\) with \(\text{E} = \text{C}\) to \(\text{Pb}\) has been calculated in the context of theoretical studies by Trinquier which focused on the structures and isomers of the heavier analogues of the ethyl cation \(\text{E}_2\text{H}_5^+\)\(^66\). The author reports calculated proton affinities of \(^1\text{A}_1\) \(\text{EH}_2\) and \(\text{E}_2\text{H}_4\) which are discussed below in Section IV.A.3.

2. \(\text{EH}_4\), \(\text{EX}_4\) \((\text{X} = \text{halogen})\) and \(\text{E}_2\text{H}_6\)

The structures and properties of group-14 tetrahydrides \(\text{EH}_4\) have been the subject of several comparative theoretical studies in the last decade\(^61,67–69\). Table 5 shows calculated values of the \(\text{E} - \text{H}\) bond distances \(R_e\), total bond dissociation energies of the four \(\text{E} - \text{H}\) bonds \(D_0\) and the force constants of the totally symmetric stretching mode \(k_e\) which were published by Wang and Schwarz\(^67\). The authors investigated also the tetrachlorides \(\text{ECl}_4\) and these results are also shown in Table 5. The bond energies and force constants of the \(\text{EH}_4\) species follow the trend \(\text{C} > \text{Si} > \text{Ge} > \text{Sn} > \text{Pb}\). The \(D_0\) and \(k_e\) values of the \(\text{ECl}_4\) molecules show that the heavier tetrahalides \(\text{SiCl}_4\) to \(\text{PbCl}_4\) have a similar bond strength to the tetrahydrides, while \(\text{CCl}_4\) has a significantly weaker bond than \(\text{CH}_4\).

The stability and vibrational spectra of \(\text{EH}_4\) and the methyl-substituted analogues \(\text{MeEH}_3\) have been the subject of a high-level theoretical study at the CCSD(T) level.

### TABLE 5. Calculated bond distances \(R_e(\text{Å})\), total bond dissociation energies \(D_0\) (kcal mol\(^{-1}\)) which include ZPE corrections and force constants of the totally symmetric mode \(k_e\) (N cm\(^{-1}\)) of the molecules \(\text{EH}_4\) and \(\text{ECl}_4\), using relativistic gradient-corrected DFT\(^a\)

<table>
<thead>
<tr>
<th>(\text{CH}_4)</th>
<th>(\text{SiH}_4)</th>
<th>(\text{GeH}_4)</th>
<th>(\text{SnH}_4)</th>
<th>(\text{PbH}_4)</th>
<th>(\text{CCl}_4)</th>
<th>(\text{SiCl}_4)</th>
<th>(\text{GeCl}_4)</th>
<th>(\text{SnCl}_4)</th>
<th>(\text{PbCl}_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_e)</td>
<td>1.10</td>
<td>1.49</td>
<td>1.55</td>
<td>1.73</td>
<td>1.78</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(D_0)</td>
<td>418.56</td>
<td>321.47</td>
<td>281.81</td>
<td>245.14</td>
<td>202.71</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(k_e)</td>
<td>20.40</td>
<td>11.00</td>
<td>9.81</td>
<td>7.96</td>
<td>7.22</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(R_e)</td>
<td>1.84</td>
<td>2.08</td>
<td>2.20</td>
<td>2.39</td>
<td>2.48</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(D_0)</td>
<td>262.20</td>
<td>321.01</td>
<td>265.66</td>
<td>248.83</td>
<td>198.33</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(k_e)</td>
<td>12.80</td>
<td>11.10</td>
<td>8.80</td>
<td>7.52</td>
<td>6.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Reference 67.
by Hein et al.\textsuperscript{62}. Table 6 shows the theoretically predicted reaction energies for \( \text{H}_2 \) loss. Note that the calculated reaction energies which include ZPE effects clearly predict that \( \text{PbH}_4 \) is unstable with regard to \( \text{PbH}_2 + \text{H}_2 \). However, the reaction has a large activation barrier. Figure 1 shows the calculated reaction profiles for the reactions \( \text{EH}_4 \rightarrow \text{EH}_2 \). All \( \text{EH}_4 \) molecules have large activation energies for \( \text{H}_2 \) loss. Table 6 shows that methyl substitution lowers the relative stability of the tetravalent molecules \( \text{MeEH}_3 \) compared with \( \text{EH}_2 + \text{CH}_4 \). The thermodynamic stability of \( \text{EH}_4 \) toward loss of \( \text{H}_2 \) calculated by different theoretical methods was already shown in Table 3. The values there and in Table 6 are very similar.

**TABLE 6.** Calculated reaction energies and ZPE corrections (kcal mol\(^{-1}\)) for hydrogen loss from \( \text{EH}_4 \) and \( \text{H}_3\text{ECH}_3 \)\textsuperscript{a}

<table>
<thead>
<tr>
<th>E</th>
<th>( \text{EH}_4 \rightarrow \text{EH}_2 + \text{H}_2 )</th>
<th>( \text{H}_3\text{ECH}_3 \rightarrow \text{EH}_2 + \text{CH}_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SCF</td>
<td>MP2</td>
</tr>
<tr>
<td>Si</td>
<td>68.3</td>
<td>68.6</td>
</tr>
<tr>
<td>Ge</td>
<td>44.9</td>
<td>45.8</td>
</tr>
<tr>
<td>Sn</td>
<td>23.9</td>
<td>23.0</td>
</tr>
<tr>
<td>Pb</td>
<td>−2.2</td>
<td>−1.6</td>
</tr>
</tbody>
</table>

\( \text{aReference 62.} \)

![FIGURE 1. Calculated reaction profile (at CCSD(T) including ZPE corrections) for \( \text{H}_2 \) loss from \( \text{EH}_4 \) molecules. Reprinted with permission from Reference 62. Copyright 1993 American Chemical Society](image-url)
3. Theoretical studies of organic germanium, tin and lead compounds

Several theoretical studies compared properties of EH$_4$ molecules for different group-14 elements E. Oliveira et al. calculated the IR intensities, polar tensors and core electron energies of EH$_4$ and the deuteriated species ED$_4$ with E = C to Sn$^{70}$. The work includes also results for the fluorosilanes and fluorogermaines. NMR spin–spin coupling constants of EH$_4$ with E = C to Sn have been calculated by different groups$^{71–73}$. Theoretically predicted magnetic shielding constants of SnH$_4$ and SnX$_4$ (X = Cl to I) have been reported by Kaneko et al.$^{74}$.

The homonuclear and heteronuclear homologues of ethane H$_3$E–E’H$_3$ (E, E’ = C to Pb) have been studied in an extensive investigation by Schleyer et al.$^{75}$. The focus of the paper is the size and origin of the energy barrier for rotation about the E–E’ bond. Table 7 shows the calculated E–E’ distances of the staggered energy minimum conformations and of the eclipsed conformations and the theoretically predicted rotational barriers. The energy barrier for rotation about the E–E’ bond becomes smaller when the atom E or E’ becomes heavier, but it does not vanish even for E, E’ = Pb. The analysis of the different factors which contribute to the energy barrier led the authors to conclude that the origin of the barrier is not steric repulsion between the hydrogen atoms. The lower energy of the staggered conformation is rather due to the stabilizing hyperconjugative interaction between the filled E–H σ-orbital and the vacant E’–H σ*-orbital$^{75}$.

The equilibrium geometries of H$_3$E–EH$_3$ for E = C to Ge have been calculated at very high levels of theory by Leszczynski et al.$^{76}$. Trinquier investigated in a detailed theoretical study the stabilities of the methylene–methane type complexes H$_2$E–H–EH$_3$ with respect to isomerization to the more stable H$_3$E–EH$_3$ isomers and to dissociation into EH$_2$ + EH$_4$$^{77}$. Table 8 shows the calculated relative energies of the molecules and fragments. Figure 2 exhibits the calculated reaction profiles for the rearrangement of the isomers. It becomes obvious that the H$_2$E–H–EH$_3$ isomers of E = C, Si are very shallow minima on the potential energy surface which will be very difficult to observe.

<table>
<thead>
<tr>
<th>E</th>
<th>E’</th>
<th>$R_{st}$ (Å)</th>
<th>$R_{ec}$ (Å)</th>
<th>$\Delta E_{rot}$ (kcal mol$^{-1}$)</th>
<th>$R_{st}$ (Å)</th>
<th>$R_{ec}$ (Å)</th>
<th>$\Delta E_{rot}$ (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>C</td>
<td>1.542</td>
<td>1.556</td>
<td>2.751</td>
<td>1.526</td>
<td>1.539</td>
<td>2.776</td>
</tr>
<tr>
<td>C</td>
<td>Si</td>
<td>1.883</td>
<td>1.893</td>
<td>1.422</td>
<td>1.883</td>
<td>1.893</td>
<td>1.388</td>
</tr>
<tr>
<td>C</td>
<td>Ge</td>
<td>1.990</td>
<td>1.999</td>
<td>1.104</td>
<td>1.996</td>
<td>2.004</td>
<td>0.986</td>
</tr>
<tr>
<td>C</td>
<td>Sn</td>
<td>2.188</td>
<td>2.193</td>
<td>0.498</td>
<td>2.178</td>
<td>2.184</td>
<td>0.520</td>
</tr>
<tr>
<td>C</td>
<td>Pb</td>
<td>2.275</td>
<td>2.278</td>
<td>0.204</td>
<td>2.242</td>
<td>2.246</td>
<td>0.321</td>
</tr>
<tr>
<td>Si</td>
<td>Si</td>
<td>2.342</td>
<td>2.355</td>
<td>0.949</td>
<td>2.355</td>
<td>2.364</td>
<td>0.823</td>
</tr>
<tr>
<td>Si</td>
<td>Ge</td>
<td>2.409</td>
<td>2.420</td>
<td>0.613</td>
<td>2.425</td>
<td>2.433</td>
<td>0.682</td>
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<tr>
<td>Si</td>
<td>Sn</td>
<td>2.610</td>
<td>2.617</td>
<td>0.581</td>
<td>2.610</td>
<td>2.616</td>
<td>0.476</td>
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<tr>
<td>Si</td>
<td>Pb</td>
<td>2.695</td>
<td>2.701</td>
<td>0.486</td>
<td>2.640</td>
<td>2.645</td>
<td>0.358</td>
</tr>
<tr>
<td>Ge</td>
<td>Ge</td>
<td>2.499</td>
<td>2.513</td>
<td>0.664</td>
<td>2.499</td>
<td>2.506</td>
<td>0.528</td>
</tr>
<tr>
<td>Ge</td>
<td>Sn</td>
<td>2.662</td>
<td>2.667</td>
<td>0.445</td>
<td>2.669</td>
<td>2.675</td>
<td>0.408</td>
</tr>
<tr>
<td>Ge</td>
<td>Pb</td>
<td>2.741</td>
<td>2.745</td>
<td>0.395</td>
<td>2.705</td>
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<td>0.315</td>
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<tr>
<td>Sn</td>
<td>Sn</td>
<td>2.850</td>
<td>2.855</td>
<td>0.412</td>
<td>2.843</td>
<td>2.847</td>
<td>0.350</td>
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<tr>
<td>Sn</td>
<td>Pb</td>
<td>2.928</td>
<td>2.930</td>
<td>0.309</td>
<td>2.869</td>
<td>2.873</td>
<td>0.286</td>
</tr>
<tr>
<td>Pb</td>
<td>Pb</td>
<td>3.012</td>
<td>3.015</td>
<td>0.214</td>
<td>2.897</td>
<td>2.900</td>
<td>0.230</td>
</tr>
</tbody>
</table>

$^{a}$Reference 75.
$^{b}R_{st}$ and $R_{ec}$ are the E–E’ distances for the staggered and eclipsed conformations, respectively.
TABLE 8. Calculated relative energies (kcal mol$^{-1}$) of E$_2$H$_6$ species$^a$

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Ge</th>
<th>Sn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>2EH$_3$$^b$</td>
<td>93.5</td>
<td>69.6</td>
<td>64.2</td>
<td>58.5</td>
<td>50.8</td>
</tr>
<tr>
<td>EH$_4$ + EH$_2$</td>
<td>110.9</td>
<td>53.3</td>
<td>41.4</td>
<td>33.6</td>
<td>17.9</td>
</tr>
<tr>
<td>H$_3$E--H--EH$_2$</td>
<td>109.8</td>
<td>48.5</td>
<td>36.3</td>
<td>23.8</td>
<td>8.8</td>
</tr>
<tr>
<td>H$_3$E--EH$_3$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

$^a$At the MP4 level. From Reference 77.
$^b$The energy of two EH$_3$ radicals with respect to H$_3$E--EH$_3$ at the MP2 level.

FIGURE 2. Calculated reaction profile at MP4 for the rearrangement of H$_3$E--EH$_3$ to H$_3$E--H--EH$_2$ complexes. Reproduced by permission of The Royal Society of Chemistry from Reference 77
3. Theoretical studies of organic germanium, tin and lead compounds

The barriers for rearrangements of the complexes to the more stable classical isomers become larger for the heavier elements Ge to Pb.

3. $E_2H_4$, $E_2H_5^+$ and $E_2X_4$ ($X = \text{halogen}$)

It is well known that compounds with multiple bonds between the heavier group-14 elements are much less stable than their carbon homologues. Although numerous olefin analogous compounds of the general formula $R_2EER_2$ could be isolated in the recent past, they usually require substituents which sterically or electronically protect the $E-E$ bond against nucleophilic and electrophilic attack. Theoretical work has been published which addresses the question about the structure and bonding situation in the parent compounds $H_2E=E'H_2$ and explains the different behavior of the heavier analogues where $E$ and/or $E' = \text{Si to Pb}.$

Jacobsen and Ziegler calculated the hetero- and homonuclear analogous olefins $H_2E=CH_2$ and $H_2E=EH_2$ ($E = C$ to Pb) at the DFT level and they analyzed the bonding situation of the molecules with an energy decomposition method. The calculations predict that the heteronuclear compounds $H_2E=CH_2$ have a planar geometry, while the heavier homonuclear compounds $H_2E=EH_2$ with $E = \text{Si to Pb}$ have a trans-bent geometry as shown in Figure 3. Table 9 shows relevant results of the work. The bonding angle $\Phi$ increases and the energy difference between the planar ($D_{2h}$) structure and the bent ($C_{2h}$) equilibrium structure becomes higher along the sequence Si < Ge < Sn < Pb. The $E=E$ and $E=C$ bond dissociation energies are much lower than the $C=C$ BDE.

Jacobsen and Ziegler concluded from the analysis of the bonding situation that the $H_2E=CH_2$ and $H_2E=EH_2$ species have double bonds, because the intrinsic $\pi$-bonding, which in case of the trans-bent species arises from the $b_0(\pi)$ orbitals, makes an important contribution to the overall bond strength. The authors suggest that the weaker bonds of the heavier analogues come from two factors. One is the high excitation energy of the $(^1A_1)$ ground state of the $EH_2$ fragments to the $^3B_1$ excited state which is the electronic reference state for the double bonding in $H_2EEH_2$. The second important factor is the high intra-atomic and interatomic Pauli repulsion which is said to be mainly responsible for the change in the geometry from planar to trans-bent form.

The $\pi$-bond strength of $H_2E=E'H_2$ ($E = \text{Ge, Sn}$; $E' = C$ to Sn) was the subject of a theoretical investigation at the MP2 and MCSCF+CI level by Windus and Gordon. These authors estimated the strength of the $\pi$-bonding by evaluating the rotational barriers and by investigating thermochemical cycles. The results are shown in Table 10. Both methods give nearly the same results for the strength of the $\pi$-bonds, which have the energy order $C > \text{Si} \sim \text{Ge} > \text{Sn}$. Note that according to the data given in Table 10, Sn has about the same $\pi$-bond strength in $H_2Sn=EH_2$ independent of the other group-14 element $E$.

The bonding situation in homonuclear systems $E_2H_4$ with a linkage $H_2E-EH_2$ and isomeric forms where the $EH_2$ fragments are bonded to each other through one or two

![FIGURE 3. Definition of the bending angle $\Phi$ of the trans-bent forms of $H_2E=EH_2$ with $E = \text{Si to Pb}$. See Table 9](image)
<table>
<thead>
<tr>
<th>H₂E=EH₂</th>
<th>Symmetry</th>
<th>Distances</th>
<th>Angles</th>
<th>Energies</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>E=E'</td>
<td>E−H</td>
<td>E'−H</td>
</tr>
<tr>
<td>H₂C=CH₂</td>
<td>D₂h</td>
<td>1.323</td>
<td>1.093</td>
<td></td>
</tr>
<tr>
<td>H₂Si=SiH₂</td>
<td>C₂h</td>
<td>2.150</td>
<td>1.483</td>
<td></td>
</tr>
<tr>
<td>H₂Si=CH₂</td>
<td>D₂h</td>
<td>2.127</td>
<td>1.478</td>
<td></td>
</tr>
<tr>
<td>H₂Ge=GeH₂</td>
<td>C₂v</td>
<td>1.687</td>
<td>1.480</td>
<td>1.092</td>
</tr>
<tr>
<td>H₂Ge=CH₂</td>
<td>D₂h</td>
<td>2.245</td>
<td>1.538</td>
<td></td>
</tr>
<tr>
<td>H₂Sn=SnH₂</td>
<td>C₂v</td>
<td>2.205</td>
<td>1.521</td>
<td></td>
</tr>
<tr>
<td>H₂Sn=CH₂</td>
<td>D₂h</td>
<td>1.770</td>
<td>1.526</td>
<td>1.090</td>
</tr>
<tr>
<td>H₂Pb=PbH₂</td>
<td>C₂v</td>
<td>2.569</td>
<td>1.727</td>
<td></td>
</tr>
<tr>
<td>H₂Pb=CH₂</td>
<td>D₂h</td>
<td>2.501</td>
<td>1.698</td>
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</tr>
<tr>
<td></td>
<td>C₂v</td>
<td>1.945</td>
<td>1.698</td>
<td>1.089</td>
</tr>
<tr>
<td></td>
<td>C₂h</td>
<td>2.819</td>
<td>1.794</td>
<td></td>
</tr>
<tr>
<td></td>
<td>D₂h</td>
<td>2.693</td>
<td>1.771</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₂v</td>
<td>2.045</td>
<td>1.774</td>
<td>1.090</td>
</tr>
</tbody>
</table>

*Bond distances in Å, bond angles in deg. From Reference 80.

*Bond angle; for definition see Figure 3.
3. Theoretical studies of organic germanium, tin and lead compounds

TABLE 10. Theoretical $\pi$-bond strengths (kcal mol$^{-1}$) of H$_2$E–E'H$_2$ molecules in their equilibrium geometry$^a$

<table>
<thead>
<tr>
<th>E</th>
<th>E'</th>
<th>Thermocycle</th>
<th>Rotation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>C</td>
<td>33</td>
<td>32.2</td>
</tr>
<tr>
<td>Ge</td>
<td>Si</td>
<td>26</td>
<td>25.7</td>
</tr>
<tr>
<td>Ge</td>
<td>Ge</td>
<td>28</td>
<td>25.4</td>
</tr>
<tr>
<td>Sn</td>
<td>C</td>
<td>21</td>
<td>20.9</td>
</tr>
<tr>
<td>Sn</td>
<td>Si</td>
<td>21</td>
<td>21.5</td>
</tr>
<tr>
<td>Sn</td>
<td>Ge</td>
<td>23</td>
<td>21.6</td>
</tr>
<tr>
<td>Sn</td>
<td>Sn</td>
<td>20</td>
<td>19.7</td>
</tr>
</tbody>
</table>

$^a$Estimated by thermodynamical cycles and by calculations of the rotational barrier. From Reference 81.

TABLE 11. Nature of the E$_2$H$_4$ stationary points on the potential energy surface$^{a,b}$

<table>
<thead>
<tr>
<th>E</th>
<th>C</th>
<th>G Min</th>
<th>TS</th>
<th>SP 2</th>
<th>TS</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>G</td>
<td>Min</td>
<td>Min</td>
<td>Min</td>
<td>Min</td>
</tr>
<tr>
<td>Si</td>
<td>TS</td>
<td>G Min</td>
<td>Min</td>
<td>Min</td>
<td>Min</td>
</tr>
<tr>
<td>Ge</td>
<td>TS</td>
<td>Min</td>
<td>G Min</td>
<td>Min</td>
<td>Min</td>
</tr>
<tr>
<td>Sn</td>
<td>TS</td>
<td>TS G</td>
<td>Min</td>
<td>Min</td>
<td>Min</td>
</tr>
<tr>
<td>Pb</td>
<td>TS</td>
<td>TS G</td>
<td>Min</td>
<td>Min</td>
<td>Min</td>
</tr>
</tbody>
</table>

$^a$Reference 65b.

$^b$G Min, global energy minimum; Min, energy minimum; TS, transition state; SP 2, second-order saddle point.

TABLE 12. Calculated relative energies (in kcal mol$^{-1}$) of E$_2$H$_4$ units$^a$

<table>
<thead>
<tr>
<th>Structure</th>
<th>Symmetry</th>
<th>C$_2$H$_4$</th>
<th>Si$_2$H$_4$</th>
<th>Ge$_2$H$_4$</th>
<th>Sn$_2$H$_4$</th>
<th>Pb$_2$H$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 EH$_2$(^1$A_1$)</td>
<td>C$_s$</td>
<td>192.0</td>
<td>53.7</td>
<td>35.9</td>
<td>33.2</td>
<td>28.7</td>
</tr>
<tr>
<td>H$_3$E=EH ($^1$A')</td>
<td>65.3$^b$</td>
<td>79.1</td>
<td>9.8</td>
<td>2.4</td>
<td>7.0</td>
<td>17.5</td>
</tr>
<tr>
<td>HE H=EH</td>
<td>$^2$E, cis</td>
<td>140.3</td>
<td>25.2</td>
<td>11.6</td>
<td>2.3</td>
<td>2.0</td>
</tr>
<tr>
<td>H$_2$E=EH</td>
<td>$^2$E, trans</td>
<td>164.7</td>
<td>22.5</td>
<td>9.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H$_2$E=EH</td>
<td>$^2$E, trans-bent</td>
<td>0</td>
<td>0</td>
<td>3.2</td>
<td>18.5</td>
<td>43.7</td>
</tr>
</tbody>
</table>

$^a$At the CIPSI level. From Reference 65b.

$^b$(^3$A'$) triplet state.

E–H–E bridges have been studied in a series of papers by Trinquier and Malrieu$^{65b,82–85}$. Table 11 shows the nature of the stationary points which have been found on the Hartree–Fock potential energy surfaces of E$_2$H$_4$$^{65b}$. Table 12 gives the relative energies at the CIPSI correlated level using the HF-optimized geometries of the different isomers. Because Si$_2$H$_4$ is found to be planar at the HF level, the calculated energy at the correlated level gives the planar form as the lowest energy structure. Geometry optimization of Si$_2$H$_4$ at correlated levels gives the trans-bent form as lowest-energy species which has a small barrier for becoming planar$^{10}$. The trans-bent form is the energetically lowest-lying isomer of Ge$_2$H$_4$ while the most stable structures of Sn$_2$H$_4$ and Pb$_2$H$_4$ are the
trans-bridged forms. The trans-bent form of Sn₂H₄ is a higher-lying isomer while the trans-bent form of Pb₂H₄ is a transition state and not a minimum on the PES. A later study by Trinquier revealed that yet another low-lying isomer which has a direct E–E linkage and one E–H–E bridge exists as minimum on the Sn₂H₄ and Pb₂H₄ potential energy surface. The latter isomers were calculated to lie 8 and 15 kcal mol⁻¹ higher than the doubly-bridged forms of Sn₂H₄ and Pb₂H₄₈².

Figure 4 shows a qualitative model which was suggested for the chemical bonding in the planar and trans-bent species H₂EH₂. The σ/π bonding in the planar structures arises according to this model from the interactions of the EH₂ fragments in the \(^3\)B¹ triplet state, while the bonding in the trans-bent form are explained in terms of donor–acceptor interactions between the EH₂ moieties in the \(^1\)A₁ state. Trinquier and Malrieu proposed a criterion which links the singlet–triplet energy difference Δ\(E_{ST}\) of EH₂ with the occurrence of the trans-bent form and the doubly bridged form\(^{85}\). They suggested that a trans-bent form should become more stable than the planar structure if the sum of the Δ\(E_{ST}\) values is higher than half of the total (σ + π) EE bond energy, i.e. if the following condition is met:

\[ \Sigma \Delta E_{ST} \geq \frac{1}{2} E_{\sigma+\pi} \]

The doubly bridged form was predicted to exist only as long as the following condition holds:

\[ \Delta E_{ST} \geq \frac{1}{2} E_{\sigma+\pi} \]

Table 13 shows the estimated energies and the expected structures of the E₂H₄ systems\(^{65b}\). The predictions made by the qualitative model are generally in agreement with the calculated energy minima on the E₂H₄ potential energy surfaces\(^{65b,82}\).

A related theoretical study by Trinquier focused on trends in electron-deficient bridged compounds of A₂H₆ (A = B, Ga), E₂H₄ (E = C to Pb) and E₂H₆²⁺ (E = C, Si)\(^{83}\). Bridged and unbridged forms of the ethyl cation and its heavier analogues E₂H₅⁺ (E = Si
3. Theoretical studies of organic germanium, tin and lead compounds

TABLE 13. Estimated singlet-triplet separations $\Delta E_{ST}$ in EH$_2$ versus E=E bond energies$^a$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta E_{ST}$</th>
<th>$4E_{\sigma+\pi}$</th>
<th>$2E_{\sigma+\pi}$</th>
<th>Expected structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$C=CH$_2$</td>
<td>$-9$</td>
<td>43</td>
<td>86</td>
<td>planar</td>
</tr>
<tr>
<td>H$_2$Si=SiH$_2$</td>
<td>18–21</td>
<td>18–19</td>
<td>35–38</td>
<td>trans-bent (borderline)</td>
</tr>
<tr>
<td>H$_2$Ge=GeH$_2$</td>
<td>22</td>
<td>15–17</td>
<td>30–35</td>
<td>trans-bent</td>
</tr>
<tr>
<td>H$_2$Sn=SnH$_2$</td>
<td>23</td>
<td>15–17</td>
<td>30–35</td>
<td>trans-bent</td>
</tr>
<tr>
<td>H$_2$Pb=PbH$_2$</td>
<td>41</td>
<td>12–15</td>
<td>25–30</td>
<td>doubly bridged</td>
</tr>
</tbody>
</table>

$^a$All values in kcal mol$^{-1}$. From Reference 65b.

to Pb) have also been studied by the same author$^{66}$. Figure 5 exhibits the investigated structures. Table 14 shows the theoretically predicted relative energies of the stationary points on the E$_2$H$_5^+$ potential energy surface. The nonclassical form which has a H$_2$E=EH$_2$ moiety bridged by H$^+$ is the global minimum on the C$_2$H$_5^+$ and Si$_2$H$_5^+$ PES. The classical form H$_2$Si=SiH$_2$ is nearly degenerate with the nonclassical isomer, however. The classical form is the lowest lying isomer of Ge$_2$H$_5^+$. The most stable structures of Sn$_2$H$_5^+$ and Pb$_2$H$_5^+$ have a geometry where an EH$^+$ moiety is bonded to EH$_4$ through two hydrogen atoms of the latter species. The same paper reports also calculated proton affinities of EH$_2$ and E$_2$H$_4$. Table 15 shows the theoretical results at the MP4 level. The proton affinities of EH$_2$ show a regular trend C > Si > Ge > Sn > Pb, while the values of the E$_2$H$_4$ species first increase but then decrease. Note that the values for E$_2$H$_4$ refer to the energetically lowest lying forms of the molecules$^{66}$.

Trinquiert and Barthelat calculated also the structures and energies of different isomers of E$_2$F$_4$ with E = C to Pb$^{56}$. The planar $\pi$-bonded structure F$_2$E=EF$_2$ was found to be

![Classical ($C_s$)](image1)

![Nonclassical ($C_{2v}$)](image2)

![Doubly Bridged ($C_4$)](image3)

![Singly Bridged ($C_s$)](image4)

FIGURE 5. Calculated E$_2$H$_5^+$ species by Trinquier$^{66}$. Relative energies are given in Table 14
TABLE 14. Calculated relative energies (kcal mol\(^{-1}\)) of \(E_2H_5^+\) systems shown in Figure 5\(^a\)

<table>
<thead>
<tr>
<th>Molecules(^b)</th>
<th>C</th>
<th>Si</th>
<th>Ge</th>
<th>Sn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_2H_5^+ + )H(^+)</td>
<td>172.3</td>
<td>208.7</td>
<td>207.3</td>
<td>204.9</td>
<td>190.8</td>
</tr>
<tr>
<td>(EH_3^+ + XH_2)</td>
<td>150.7</td>
<td>65.4</td>
<td>55.3</td>
<td>55.5</td>
<td>50.6</td>
</tr>
<tr>
<td>(EH^+ + XH_4)</td>
<td>151.3</td>
<td>41.4</td>
<td>32.3</td>
<td>29.7</td>
<td>26.1</td>
</tr>
<tr>
<td>Doubly bridged (Cs)</td>
<td>102.9</td>
<td>12.0</td>
<td>5.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Singly bridged (Cs)</td>
<td>117.2</td>
<td>16.6</td>
<td>7.8</td>
<td>3.7</td>
<td>1.5</td>
</tr>
<tr>
<td>Classical (Cs)</td>
<td>7.6(^c)</td>
<td>0.1</td>
<td>0</td>
<td>7.3</td>
<td>15.6</td>
</tr>
<tr>
<td>Nonclassical (C_{2v})</td>
<td>0</td>
<td>0</td>
<td>5.3</td>
<td>13.2</td>
<td>26.5</td>
</tr>
</tbody>
</table>

\(^a\)At the MP4 level. From Reference 66.
\(^b\)The fragments correspond to the preferred isomer for \(E_2H_4\), the \(^1A_1\) state for \(EH_2\) and the \(^1\Sigma^+\) state for \(EH^+\).
\(^c\)Eclipsed conformation.

TABLE 15. Calculated proton affinities (kcal mol\(^{-1}\)) of \(EH_2\) and \(E_2H_4\)\(^a\)

<table>
<thead>
<tr>
<th>(E)</th>
<th>(E_2H_2(1A_1))</th>
<th>(E_2H_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>220</td>
<td>166</td>
</tr>
<tr>
<td>Si</td>
<td>204</td>
<td>203</td>
</tr>
<tr>
<td>Ge</td>
<td>194</td>
<td>202</td>
</tr>
<tr>
<td>Sn</td>
<td>193</td>
<td>200</td>
</tr>
<tr>
<td>Pb</td>
<td>179</td>
<td>185</td>
</tr>
</tbody>
</table>

\(^a\)At MP4. From Reference 66.

TABLE 16. Calculated relative energies (kcal mol\(^{-1}\)) of \(E_2F_4\) species\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Ge</th>
<th>Sn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2EF_2(1A_1))</td>
<td>56.3</td>
<td>6.3</td>
<td>23.8</td>
<td>50.9</td>
<td>62.3</td>
</tr>
<tr>
<td>(F_2E-EF_2(3B))</td>
<td>44.0</td>
<td>38.8</td>
<td>74.6</td>
<td>102.4</td>
<td>134.4</td>
</tr>
<tr>
<td>(F_2E=EF_2)</td>
<td>0</td>
<td>50.5(^b)</td>
<td>97.3(^b)</td>
<td>133.1(^b)</td>
<td>212.2(^c)</td>
</tr>
<tr>
<td>(F_3E-)EF</td>
<td>38.9</td>
<td>0</td>
<td>32.1</td>
<td>60.0</td>
<td>88.7(^b)</td>
</tr>
<tr>
<td>(FE\leq F\leftarrow EF) (\begin{equation*} <em>{C</em>{2v}} \end{equation*})</td>
<td>(118.9(^b)</td>
<td>4.2</td>
<td>1.9</td>
<td>2.6</td>
<td>4.8</td>
</tr>
<tr>
<td>(\begin{equation*} <em>{C</em>{2h}} \end{equation*})</td>
<td>(118.8(^b)</td>
<td>3.7</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\)At CIPSI using HF optimized geometries. From Reference 55.
\(^b\)Not a true minimum.
\(^c\)First excited singlet state.

a true energy minimum for \(E = C\), a saddle point for \(E = Si, Ge, Sn\) and an energy minimum on the first excited singlet state for \(E = Pb\). The energetically lowest lying forms of the heavier analogues \(E_2F_4\) are \(F_3Si-SF\) for the silicon species, while doubly fluorine bridged structures were predicted to be the lowest lying forms of \(Ge_2F_4, Sn_2F_4\) and \(Pb_2F_4\)\(^c\). Table 16 shows the relative energies of the stationary point on the PES which were obtained at the CIPSI correlated level using HF optimized geometries. The calculated values of the fluorinated species may be compared with the energies of the analogous hydrogen system \(E_2H_4\) which are given in Table 12. Note that \(SnF_2\) and \(PbF_2\) are much more stabilized by forming the most stable dimer than \(SnH_2\) and \(PbH_2\), respectively, while
TABLE 17. Calculated reaction energies (kcal mol\(^{-1}\)) of \(E_2F_4\) and \(EF_2\) species\(^a, b\)

<table>
<thead>
<tr>
<th>(E)</th>
<th>(2EF_2 \rightarrow EF_4 + E)</th>
<th>(EF_4 + E \rightarrow E_2F_4)</th>
<th>(EF_2 + F_2 \rightarrow EF_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>+4.0</td>
<td>-53.5</td>
<td>-189.6</td>
</tr>
<tr>
<td>Si</td>
<td>+1.6</td>
<td>-12.9</td>
<td>-242.5</td>
</tr>
<tr>
<td>Ge</td>
<td>+37.6</td>
<td>-66.0</td>
<td>-167.7</td>
</tr>
<tr>
<td>Sn</td>
<td>+51.5</td>
<td>-108.0</td>
<td>-154.1</td>
</tr>
<tr>
<td>Pb</td>
<td>+105.8</td>
<td>-173.8</td>
<td>-70.9</td>
</tr>
</tbody>
</table>

\(^a\)At the HF level. From Reference 55.
\(^b\)Each species is in its ground state: \(E, 3P\); \(EF_2, 1A_1\), \(C_2F_4, \pi\)-bonded form; \(Si_2F_4, F_2Si-SiF\); other \(E_2F_4\): trans-bridged form.

CF\(_2\), SiF\(_2\) and GeF\(_2\) are less stabilized by dimerization than their dihydrides. Table 17 gives some relevant reaction energies of \(E_2F_4\) and \(EF_2\) species which were predicted by Trinquier and Barthelat\(^{56}\). The authors report also the energies for addition of \(F_2\) to \(EF_2\) which may be compared with the reactions energies for \(H_2\) addition to \(EH_2\) given in Tables 3 and 6. It is obvious that \(F_2\) addition to \(EF_2\) is much more exothermic than \(H_2\) addition to \(EH_2\) for all elements \(E\).

The homo- and heteroatomic ethylene homologues \(H_2EE'\)\(_2\) (\(E, E' = C, Si, Ge\)) have been calculated with quantum chemical methods in a theoretical paper by Horner et al. which focused on the strain energies of the three-membered cyclic compounds cyc-\(EE'\)\(_0\)\(_2\)H\(_6\) (\(E, E' = C, Si, Ge\))\(^{86}\). The authors estimated the strain energies of the rings by calculating the reaction enthalpies of homodesmotic reactions at the CCSD level using HF optimized geometries. They also give the theoretically predicted reaction enthalpies of the addition of \(E'\)\(_2\)\(_0\)\(_2\)H\(_2\) to \(cyc-EE'\)\(_0\)\(_2\)H\(_6\)\(^{86}\). The latter quantity was also estimated from a bond additivity scheme using standard energy values. Table 18 shows the calculated results. It becomes obvious that the ring strain of the three-membered rings \(E_2H_6\) increases with \(E = C < Si < Ge\). Of the ten rings studied, cyclogermirane cyc-\(GeC_2H_6\) is by far the least stable molecule with respect to dissociation, being only about 20 kcal mol\(^{-1}\) more stable than \(GeH_2 + ethylene\).

The reaction course for addition of the singlet \(EH_2\) and \(EF_2\) species with \(E = C\) to \(Sn\) to ethylene has been investigated with quantum chemical methods by Sakai\(^{87}\). The author calculated also the transition states for the addition reactions. A related work by Boatz et al. reported about the reactions of \(EH_2\) and \(EF_2\) (\(E = C\) to \(Sn\)) with acetylene yielding metallacyclopropenes\(^{88}\). The results of both studies are discussed below in the section on ‘reaction mechanisms’.

The ethylene and formaldehyde analogues \(H_2EEH_2\) and \(H_2EO\) (\(E = Si\) to \(Pb\)), respectively, have been the subject of a more recent theoretical work by Kapp et al. which was carried out at the DFT level\(^{89}\). The calculated results were in general agreement with the work by Trinquier except for \(H_2PbPbH_2\). In contrast to the latter author\(^{65b, 82}\) it was found that the trans-bent form of \(H_2PbPbH_2\) is a true energy minimum on the PES\(^{89}\). Table 19 gives theoretically predicted reaction energies of \(H_2EEH_2\) and \(H_2EO\). The \(H_2E-\)\(_2\)\(_0\)\(_2\)H\(_2\) bond energies are somewhat lower than those which are shown in Table 9 but the trend is the same. Note that the inclusion of relativistic effects has a strong influence on the results of the lead compounds.

The structures and relative energies of germasilene (\(H_2GeSiH_2\)) and its isomers silylgermylene (\(H_3SiGeH\)) and germylsilylene (\(H_3GeSiH\)) in the singlet and triplet states have been calculated in a theoretical work by Grev et al.\(^{90}\). The geometries were optimized at the TCSCF level while the energies were calculated at the CISD level. The
### TABLE 18. Energetics $\Delta E$ of the decomposition reactions cyc-XH$_2$YH$_2$ZH$_2$ → XH$_2$(singlet) + H$_2$Y ZH$_2$ and strain enthalpies of group 14 cyclotrimetallanes$^a$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta E$ (kcal mol$^{-1}$)</th>
<th>Strain enthalpy (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ab initio estimated</td>
<td>CCSD/DZ+d/CCSD/DZ+d</td>
</tr>
<tr>
<td>cyc-C$_3$H$_6$ → CH$_2$ + C$_2$H$_4$</td>
<td>98.6 (84.9)</td>
<td>101</td>
</tr>
<tr>
<td></td>
<td>28.1 (26.1)</td>
<td></td>
</tr>
<tr>
<td>cyc-Si$_3$H$_6$ → SiH$_2$ + Si$_2$H$_4$</td>
<td>62.3 (58.7)</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>34.5 (36.8)</td>
<td></td>
</tr>
<tr>
<td>cyc-Ge$_3$H$_6$ → GeH$_2$ + Ge$_2$H$_4$</td>
<td>47.1 (47.5)</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>37.3 (39.3)</td>
<td></td>
</tr>
<tr>
<td>cyc-SiC$_2$H$_6$ → SiH$_2$ + C$_2$H$_4$</td>
<td>43.2 (33.9)</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>35.2 (36.7)</td>
<td></td>
</tr>
<tr>
<td>cyc-SiC$_2$H$_6$ → CH$_2$ + CSiH$_4$</td>
<td>112.8 (101.6)</td>
<td>119</td>
</tr>
<tr>
<td></td>
<td>35.2 (36.7)</td>
<td></td>
</tr>
<tr>
<td>cyc-GeC$_2$H$_6$ → GeH$_2$ + C$_2$H$_4$</td>
<td>18.3 (9.3)</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>35.8 (38.1)</td>
<td></td>
</tr>
<tr>
<td>cyc-GeC$_2$H$_6$ → CH$_2$ + CGeH$_4$</td>
<td>107.3 (96.9)</td>
<td>116</td>
</tr>
<tr>
<td></td>
<td>35.8 (38.1)</td>
<td></td>
</tr>
<tr>
<td>cyc-CSi$_2$H$_6$ → SiH$_2$ + CSiH$_4$</td>
<td>60.3 (56.4)</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>37.0 (39.7)</td>
<td></td>
</tr>
<tr>
<td>cyc-CSi$_2$H$_6$ → CH$_2$ + Si$_2$H$_4$</td>
<td>120.3 (109.5)</td>
<td>129</td>
</tr>
<tr>
<td></td>
<td>37.0 (39.7)</td>
<td></td>
</tr>
<tr>
<td>cyc-CGe$_2$H$_6$ → GeH$_2$ + CGeH$_4$</td>
<td>44.5 (43.3)</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>39.2 (41.7)</td>
<td></td>
</tr>
<tr>
<td>cyc-CGe$_2$H$_6$ → CH$_2$ + Ge$_2$H$_4$</td>
<td>100.1 (91.0)</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td>39.2 (41.7)</td>
<td></td>
</tr>
<tr>
<td>cyc-CSiGe$_2$H$_6$ → GeH$_2$ + CSiH$_4$</td>
<td>42.9 (40.2)</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>38.2 (40.8)</td>
<td></td>
</tr>
<tr>
<td>cyc-CSiGe$_2$H$_6$ → SiH$_2$ + CGeH$_4$</td>
<td>62.3 (59.9)</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>38.2 (40.8)</td>
<td></td>
</tr>
<tr>
<td>cyc-CSiGe$_2$H$_6$ → CH$_2$ + SiGeH$_4$</td>
<td>110.2 (110.7)</td>
<td>118</td>
</tr>
<tr>
<td></td>
<td>38.2 (40.8)</td>
<td></td>
</tr>
<tr>
<td>cyc-GeSi$_2$H$_6$ → GeH$_2$ + Si$_2$H$_4$</td>
<td>52.5 (51.4)</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>35.6 (37.8)</td>
<td></td>
</tr>
<tr>
<td>cyc-GeSi$_2$H$_6$ → SiH$_2$ + Ge$_2$H$_4$</td>
<td>59.8 (58.8)</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>35.6 (37.8)</td>
<td></td>
</tr>
<tr>
<td>cyc-GeSi$_2$H$_6$ → CH$_2$ + Ge$_2$H$_4$</td>
<td>49.7 (49.7)</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>36.3 (38.6)</td>
<td></td>
</tr>
<tr>
<td>cyc-SiGe$_2$H$_6$ → SiH$_2$ + Ge$_2$H$_4$</td>
<td>57.3 (56.7)</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>36.3 (38.6)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$At CCSD/HF. Energy values in parentheses are HF/DZ+d results. From Reference 86.

### TABLE 19. Calculated B3LYP reaction energies (kcal mol$^{-1}$)$^a$ of reactions of E$_2$H$_4$ and EH$_2$ species$^b$

<table>
<thead>
<tr>
<th>E</th>
<th>H$_2$E=EH$_2$ + O$_2$ → cyclo-(H$_2$EO)$_2$ $^{c,d}$</th>
<th>2H$_2$E + O$_2$ → 2H$_2$E=O $^d$</th>
<th>H$_2$E=EH$_2$ → 2H$_2$E$^c$</th>
<th>2H$_2$E=O$^{-1}$ → cyclo-(H$_2$EO)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>-50.6</td>
<td>-222.6</td>
<td>160.2$^e$</td>
<td>11.78</td>
</tr>
<tr>
<td>Si</td>
<td>-193.3</td>
<td>-149.8</td>
<td>53.4</td>
<td>-96.9</td>
</tr>
<tr>
<td>Ge</td>
<td>-117.0</td>
<td>-68.0</td>
<td>32.7</td>
<td>-81.7</td>
</tr>
<tr>
<td>Sn</td>
<td>-101.0</td>
<td>-28.0</td>
<td>22.5</td>
<td>-95.5</td>
</tr>
<tr>
<td>n-Pb</td>
<td>-104.7</td>
<td>-25.1</td>
<td>24.5</td>
<td>-104.1</td>
</tr>
<tr>
<td>Pb</td>
<td>-38.8</td>
<td>25.2</td>
<td>10.5</td>
<td>-74.5</td>
</tr>
</tbody>
</table>

$^a$All energies include ZPE corrections.

$^b$Reference 89.

$^c$Calculated with the $C_{2h}$ minimum structures of the Si, Ge, Sn, n-Pb and Pb compounds (planarization barriers: 1.18, 6.54, 10.13, 7.17 and 22.79 kcal mol$^{-1}$, respectively).

$^d$Reactions with singlet oxygen are 38.6 kcal mol$^{-1}$ more exothermic.

$^e$Calculation with triplet CH$_2$.

$^f$n-Pb: lead computed with a nonrelativistic pseudopotential.

$\pi$-bond energy of germasilene is predicted to be 25 kcal mol$^{-1}$, essentially identical with those of H$_2$SiSiH$_2$ and H$_2$GeGeH$_2$. The bond dissociation energy, however, was found to decrease in the order Si=Si > Si=Ge > Ge=Ge and in each case was smaller than the bond energy of the corresponding single bonds in the saturated systems disilane, germysilane and digermane$^{90}$. Table 20 shows theoretical energy differences between isomers of the compounds which have been calculated or which were estimated by taking the differences between the $\pi$-bond energies $D_\pi$ and the bond energies $D(E-H)$. The two sets of data agree nicely with each other.
### Table 20.
Comparison of predicted and theoretically determined isomeric $0$ K enthalpy differences (kcal mol$^{-1}$)*

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H_{\text{predict}} = D_{\pi} + E_2(M'-H) - E_1(M-H)$</th>
<th>$\Delta H_{\text{ab initio}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{Ge} = \text{SiH}_2 \rightarrow \text{H}_2\text{Ge} - \text{SiH}$</td>
<td>$25 + 68.5 - 84.0 = 9.5$</td>
<td>9.4</td>
</tr>
<tr>
<td>$\text{H}_2\text{Ge} = \text{SiH}_2 \rightarrow \text{HGe} - \text{SiH}_3$</td>
<td>$25 + 57.4 - 90.6 = -8.2$</td>
<td>-6.3</td>
</tr>
<tr>
<td>$\text{H}_2\text{Si} = \text{GeH}_2 \rightarrow \text{H}_2\text{Ge} - \text{GeH}$</td>
<td>$25 + 57.4 - 84.0 = -1.6$</td>
<td>-2.0</td>
</tr>
<tr>
<td>$\text{H}_2\text{Si} = \text{SiH}_2 \rightarrow \text{H}_2\text{Si} - \text{SiH}$</td>
<td>$25 + 68.5 - 90.6 = 2.9$</td>
<td>6.4</td>
</tr>
<tr>
<td>$\text{H}_2\text{Si} = \text{CH}_2 \rightarrow \text{H}_2\text{Si} - \text{CH}$</td>
<td>$38 + 111.2 - 90.6 = 58.6$</td>
<td>45.2</td>
</tr>
<tr>
<td>$\text{H}_2\text{Si} = \text{CH}_2 \rightarrow \text{HSi} - \text{CH}_3$</td>
<td>$38 + 68.5 - 104.6 = 1.9$</td>
<td>3.6</td>
</tr>
<tr>
<td>$\text{H}_2\text{Ge} = \text{CH}_2 \rightarrow \text{HGe} - \text{CH}_3$</td>
<td>$31 + 57.4 - 104.6 = -16.2$</td>
<td>-17.6</td>
</tr>
</tbody>
</table>

*Reference 90.

### Figure 6.
Calculated geometries and relative energies (kcal mol$^{-1}$) of relevant Si$_2$H$_2$ and Ge$_2$H$_2$ isomers A–E. The linear forms E are not minima on the PES. Distances in Å, angles in deg. Data are from Reference 91 except for structure B of Ge$_2$H$_2$, which have been reproduced from Reference 92 by permission of Academic Press.

4. $E_2H_2$, $E_3H_3^+$ and $E_6H_6$

Quantum chemical investigations of the heavier group-14 analogues of acetylene aroused considerable interest because the calculations predicted that the energetically lowest lying Si$_2$H$_2$ and Ge$_2$H$_2$ isomers are very different from what is known about C$_2$H$_2$. Figure 6 shows the theoretically predicted stationary points on the $E_2H_2$ ($E = \text{Si, Ge}$) PES.
The results for the silicon and germanium species are very similar\(^{91-93}\). The doubly bridged structure \(A\) is the global energy minimum on the PES. The singly bridged isomer \(B\) and the energetically nearly degenerate vinylidene analogue \(C\) are 10–12 kcal mol\(^{-1}\) higher in energy than \(A\). The isomer with a H–E–E–H linkage \(D\) has a \textit{trans}-bent geometry which is 18–20 kcal mol\(^{-1}\) above \(A\). The linear form \(E\) is not a minimum on the PES of Si\(_2\)H\(_2\) and Ge\(_2\)H\(_2\). \(E\) is much higher (40–42 kcal mol\(^{-1}\)) in energy than \(A\).

The homonuclear species Ge\(_2\)H\(_2\) and the heteronuclear systems GeCH\(_2\) and GeSiH\(_2\) have been calculated in an extensive study by Boone and coworkers\(^{94}\). Figure 7 shows schematically the structural isomers which were investigated. Table 21 shows the calculated results. The doubly bridged isomer \(A\) is also the global energy minimum on the GeSiH\(_2\) PES. The vinylidene form H\(_2\)C–Ge is clearly the lowest lying isomer on the GeCH\(_2\) PES. Hydrogen-bridged structures of GeCH\(_2\) were not found as energy minima on the PES\(^{94}\). More recent calculations of GeCH\(_2\) isomers by Stogner and Grev agree with the previous results\(^{95}\).

Theoretical investigations of the heavier analogues Sn\(_2\)H\(_2\) and Pb\(_2\)H\(_2\) have recently been published\(^{96-98}\). Figure 8 shows the calculated potential energy surfaces of E\(_2\)H\(_2\) for E = Si to Pb at the MP2 level by Nagase and coworkers\(^{96}\). The qualitative features of the four systems are the same. The doubly bridged isomer \(A\) is also predicted as the global energy minimum of Sn\(_2\)H\(_2\) and Pb\(_2\)H\(_2\). The energy difference between the linear form HEEH and the most stable form \(A\) is particularly large for E = Pb. The latter isomer was also calculated by Han et al.\(^{97}\).

The potential energy surface of Pb\(_2\)H\(_2\) has recently been the subject of a detailed theoretical study at the DFT and MP2 level by Frenking and coworkers\(^{98}\). The geometries and relative energies of the calculated isomers are shown in Figure 9. The global energy minimum is the doubly-bridged isomer. The singly-bridged form \(B\) is a transition state at the DFT level, while it is an energy minimum at MP2\(^{98}\). The most important aspect of the work by Frenking and coworkers concerns the relative energies of the \textit{trans}-bent isomers \(D_1\) and \(D_2\). The former structure is the analogue of the \textit{trans}-bent form \(D\) which is shown in Figure 6. However, \(D_1\) lies energetically higher than another \textit{trans}-bent form.
<table>
<thead>
<tr>
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<th>Ge₂H₂</th>
<th>GeSiH₂</th>
<th>GeCH₂</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>B'</td>
</tr>
<tr>
<td>$E_{\text{rel}}$</td>
<td>0.00</td>
<td>8.69</td>
<td></td>
</tr>
<tr>
<td>$R(\text{Ge}−\text{Ge})$</td>
<td>2.365</td>
<td>2.234</td>
<td>2.365</td>
</tr>
<tr>
<td>$R(\text{Ge}−\text{H})$</td>
<td>1.745</td>
<td>1.789 (H₃)</td>
<td>1.528</td>
</tr>
<tr>
<td>$\Delta(\text{H}−\text{Ge}−\text{Ge})$</td>
<td>47.34</td>
<td>48.77 (H₃)</td>
<td>124.19</td>
</tr>
<tr>
<td>$\Delta(\text{Ge}−\text{Ge}−\text{H})$</td>
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<td>180</td>
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<tr>
<td>$E_{\text{rel}}$</td>
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<td>1.532 (H₃)</td>
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<td>51.11 (H₃)</td>
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<td>165.44 (H₃)</td>
<td>122.72</td>
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</table>

---

*d* At the MP2/TZV (2df, 2p) level of theory. From Reference 94. Bond distances $R$ in Å and bond angles in deg.

*b* Transition state.

*c* H₃ denotes bridging hydrogen, H₇ denotes terminal hydrogen.

*d* Structure B has a terminal Si−H bond and B' has a terminal Ge−H bond. Structure C has a GeH₂ moiety and C' has a SiH₂ moiety.

*e* Structure B has a terminal Ge−H bond and B' has a terminal C−H bond. Structure C has a GeH₂ moiety and C' has a CH₂ moiety.
FIGURE 8. Calculated PES of $M_2H_2$ species for $M = Si$ to $Pb$ at the MP2 level. Relative energies are given in kcal mol$^{-1}$. Reprinted from Reference 96 with permission from Elsevier Science

D2, which has an acute bond angle of ca $90^\circ$ (Figure 9). The analysis of the electronic structure of D1 and D2 showed that the HOMO of the former isomer is the Pb–Pb $\pi$-orbital, while the LUMO is a lead lone-pair type orbital. Structure D2 has the frontier orbitals reversed, i.e. the lead lone-pair orbital is the HOMO and the Pb–Pb $\pi$-orbital is the LUMO. This is shown in Figure 10. It means that lead has a valence shell with an electron sextet. Nevertheless structure D2 is lower in energy than D1. However, both structures D1 and D2 are not minima on the PES. The results were important, though, because the calculations showed that bulky substituents stabilize D2 so much that it not only becomes an energy minimum but even the global minimum on the PES$^{98}$.

The heavier analogues of the cyclopropenium cation $E_3H_3^+$ with $E = Si$ to Pb and other structural isomers of $E_3H_3^+$ have been calculated by Jemmis et al. at the DFT (B3LYP) level$^{99}$. Figure 11 shows the calculated isomers and the relative energies and nature of the stationary points on the PES. The classical cyclopropenium form 1(Si) is the most stable isomer of Si$_3$H$_3$. A second isomer which has a nonplanar C$_{3v}$ symmetry 2(Si) is 23.7 kcal mol$^{-1}$ higher in energy than 1(Si). The former isomer becomes clearly more stable than the cyclopropenium form in case of the germanium analogues. Structure 2(Ge) is 17.4 kcal mol$^{-1}$ lower in energy than 1(Ge). The bridged structures 2(Sn) and 2(Pb) are predicted to be the only minimum on the respective PES. The cyclopropenium forms of Sn$_3$H$_3^+$ and Pb$_3$H$_3^+$ are not minima on the PES$^{99}$.

The structures, stabilities and properties of the heavier analogues of benzene and other structural C$_6H_6$ isomers have been calculated for Si$_6$H$_6$ and Ge$_6$H$_6$ but not for Sn$_6$H$_6$ and Pb$_6$H$_6$. Matsunaga et al. optimized at the HF level the geometries of benzene and the planar analogues Si$_3$C$_3$H$_6$, Ge$_3$C$_3$H$_6$, Si$_6$H$_6$, Ge$_3$Si$_3$H$_6$ and Ge$_6$H$_6$ among other heteroatomic benzene analogues$^{100}$. Inspection of the vibrational frequencies showed that only the planar ($D_{3h}$) forms of Si$_3$C$_3$H$_6$ and Ge$_3$C$_3$H$_6$ are minima on the PES while the $D_{6h}$ geometries of Si$_6$H$_6$ and Ge$_6$H$_6$ and the $D_{3h}$ form of Ge$_3$Si$_3$H$_6$ are transition states of higher-order saddle points. A following paper by Matsunaga and Gordon reported about other isomeric forms of the molecules$^{101}$. The authors calculated the equilibrium geometries of the chair and boat forms of the EE’H$_6$ molecules (E, E’ = C, Si, Ge and
3. Theoretical studies of organic germanium, tin and lead compounds

FIGURE 9. Calculated geometries and relative energies of Pb₂H₂ species at B3LYP. Bond lengths are given in Å, angles in deg. The number of imaginary frequencies \( i \) indicates if the structure is an energy minimum \( (i = 0) \), a transition state \( (i = 1) \) or a higher-order saddle point \( (i = 2) \). Reproduced by permission of Wiley-VCH from Reference 98
**FIGURE 10.** Plots of the frontier orbitals of structures \( D_1 \) and \( D_2 \) of \( \text{Pb}_2\text{H}_2 \) (see Figure 9 for the notation). Reproduced by permission of Wiley-VCH from Reference 98

**FIGURE 11.** Calculated structures and relative energies (kcal mol\(^{-1}\)) of \( E_3\text{H}_3^+ \) isomers (\( E = \text{C to Pb} \)). The number of imaginary frequencies \( i \) is given in parentheses. Reprinted with permission from Reference 99. Copyright 1995 American Chemical Society
group13/15 elements) besides the planar structures. They also investigated the geometries and relative energies of the prismane analogue. Figure 12 shows the calculated isomers. Table 22 gives the relative energies of the stationary points on the PES. The prismane isomers of C₆H₆, Si₃C₃H₆ and Ge₃C₃H₆ are higher in energy than the planar isomers which are the global minima on the PES. The prismane analogues of Si₆H₆, Si₃Ge₃H₆ and Ge₆H₆ become the energetically lowest lying structures which are slightly more stable than the chair conformation of the 6-membered rings. The paper reports also about other heteroatomic C₆H₆ isomers with group13/group15 atoms in the ring.

The aromaticity of the planar (D₆h) and chair (D₃d) forms of Si₆H₆ and Ge₆H₆ and other heteroatom benzene analogues has been the subject of a theoretical study by Schleyer and coworkers. The authors used three different criteria for estimating the aromatic character of the molecules. They are: (i) the calculated NICS (Nuclear Independent Chemical Shift) values at the center of the ring, (ii) the ring size adjusted aromaticity index ρ which is based on the calculated magnetic susceptibility and

![Figure 12](image_url)

**FIGURE 12.** Calculated EₙEₖ₋ₙH₆ isomers (E, E' = C, Si, Ge) with planar, chair, boat and prismane structure. Relative energies are given in Table 22. The boat form is not an energy minimum on the PES. Reprinted with permission from Reference 101. Copyright 1994 American Chemical Society

<table>
<thead>
<tr>
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<th>Planar</th>
<th>Chair</th>
<th>Prismane</th>
</tr>
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<tbody>
<tr>
<td>C₆H₆</td>
<td>0.0</td>
<td>—</td>
<td>113.9</td>
</tr>
<tr>
<td>Si₃C₃H₆</td>
<td>0.0</td>
<td>—</td>
<td>35.3</td>
</tr>
<tr>
<td>Ge₃C₃H₆</td>
<td>0.0</td>
<td>—</td>
<td>27.2</td>
</tr>
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<td>Si₆H₆</td>
<td>0.0ᵇ</td>
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<td>-13.6</td>
</tr>
<tr>
<td>Si₃Ge₃H₆</td>
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<td>-4.8</td>
<td>-6.4</td>
</tr>
<tr>
<td>Ge₆H₆</td>
<td>0.0ᵇ</td>
<td>-10.7</td>
<td>-11.1</td>
</tr>
</tbody>
</table>

ᵃAt MP2 using HF optimized geometries. From Reference 101.
ᵇNot a minimum on the potential energy surface.
(iii) the calculated ASE (Aromatic Stabilization Energy) values which are based on the energies of homodesmotic reactions. The authors found that benzene is more aromatic than its sila and germa homologues on the basis of these three criteria even in $D_{6h}$ symmetry, but $\text{Si}_6\text{H}_6$ and $\text{Ge}_6\text{H}_6$ still have significant aromatic character even in their $D_{3d}$ equilibrium geometries.

B. Substituted Compounds

The previous sections discussed theoretical work of parent compounds of heavier group-14 elements which are homologues of important carbon reference compounds. In the next sections we will discuss in brief theoretical studies of organometallic molecules of germanium, tin and lead which were published since 1990.

1. Neutral closed-shell molecules

Most theoretical work on group-14 organometallic compounds was devoted to neutral closed-shell species. We divided the presentation of the papers into two parts. The first part focuses on theoretical studies of geometries and properties of molecules. The second part describes work where reaction mechanisms of chemical reactions of organometallic Ge-, Sn- and Pb-organic compounds have been investigated theoretically.

a. Structures and properties. i. Compounds with multiple bonds of Ge, Sn, Pb. Several theoretical papers which investigate compounds with multiple bonds of heavier group-14 elements Ge to Pb have been published recently. Most of them focus on germanium compounds. A theoretical study of Cotton et al. about multiple bonding between main group elements gave the experimental and calculated geometry using DFT (B3PW91) methods of $\text{Me}_2\text{Ge} \equiv \text{GeMe}_2$. Figure 13 shows the theoretically predicted and experimentally observed bond lengths and angles. The agreement is quite good.

Two papers by Khabashesku et al. report about theoretical and experimental work of various germenes $\text{R}_1\text{R}_2\text{Ge} \equiv \text{CH}_2$. One paper is a joint experimental/theoretical work about the gas-phase pyrolytic generation of $\text{Me}_2\text{Ge} \equiv \text{CH}_2$ from four-membered cyclic precursors. The authors give the calculated geometries of dimethylgermene $\text{Me}_2\text{Ge} \equiv \text{CH}_2$ (Table 23) and methylgermylene $\text{H}_3\text{C} \equiv \text{GeH}$ (Table 24) at different levels of theory. Comparison of the calculated vibrational spectra of the molecules and the experimental spectrum suggests that both species are formed in the pyrolysis. The second paper

![Figure 13. Optimized geometry of $\text{Me}_2\text{Ge} \equiv \text{GeMe}_2$ at B3PW91. Experimental values are given in parentheses. Bond lengths in Å, angles in deg. Reprinted with permission from Reference 106. Copyright 1998 American Chemical Society](image_url)
TABLE 23. Optimized geometry of 1,1-dimethyl-1-germene$^a$

<table>
<thead>
<tr>
<th>Bond length (Å)</th>
<th>Angle (deg)</th>
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<tbody>
<tr>
<td>Ge=C</td>
<td>Ge–C</td>
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<tr>
<td>HF/DZ+d</td>
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<tr>
<td>HF/6-311G(d,p)</td>
<td>1.765</td>
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<tr>
<td>MP2/DZ+d</td>
<td>1.772</td>
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<tr>
<td>B3LYP/6-311G(d,p)</td>
<td>1.780</td>
</tr>
</tbody>
</table>

$^a$Reference 107.

TABLE 24. Optimized geometry of methylgermylene$^a$

<table>
<thead>
<tr>
<th>Bond length (Å)</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge–C</td>
<td>Ge–H</td>
</tr>
<tr>
<td>HF/DZ+d</td>
<td>1.991</td>
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<tr>
<td>MP2/DZ+d</td>
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</tr>
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<td>B3LYP/6-311G(d,p)</td>
<td>2.012</td>
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</table>

$^a$Reference 107.

by Khabashesku et al. deals with five substituted germenes$^{108}$, Table 25 shows the optimized geometries, atomic partial charges and calculated dipole moments of H$_2$Ge=CH$_2$, MeHGe=CH$_2$, Me$_2$Ge=CH$_2$, FHGe=CH$_2$ and H$_2$Ge=CHF. The authors also calculated the reaction profiles of the head-to-head and head-to-tail dimerization of the germenes. The results will be discussed below in the section about reaction mechanisms.

Another combined experimental paper of Khabashesku et al. reported about pyrolytic generation of dimethylgermanone Me$_2$Ge=O and its dimer$^{109}$. The calculated geometries of the two compounds and the parent molecule H$_2$Ge=O are shown in Figure 14. The authors calculated the vibrational spectra of the organogermanium compounds. Comparison with the observed FTIR spectrum showed that both molecules are generated by pyrolysis from three different precursors. The observed frequency and the calculated force
TABLE 25. Optimized parameters of germene monomers at B3LYP/6–311G(d)\textsuperscript{a}

<table>
<thead>
<tr>
<th>Germene</th>
<th>Bond distances (Å)</th>
<th>Valence angles (deg)</th>
<th>Total net charge</th>
<th>Dipole moment (D)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Ge=C Ge–H Ge–R C–H C–R HGeC RGeC HGe RCGe Ge C</td>
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<td></td>
<td></td>
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<tr>
<td>H₂Ge=CH₂</td>
<td>1.778 1.525 1.082 122.5 121.4</td>
<td>+0.371 –0.496</td>
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<tr>
<td>MeHGe=CH₂</td>
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<tr>
<td>FHGe=CH₂</td>
<td>1.764 1.518 1.755 1.081 1.080 133.2 120.0 119.3 121.5</td>
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<tr>
<td>H₂Ge=CHF</td>
<td>1.794 1.518 1.518 1.085 1.353</td>
<td>117.9 122.3 124.3 123.4</td>
<td>+0.172 +0.036</td>
<td>1.624</td>
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</tbody>
</table>

\textsuperscript{a}At B3LYP/6-311G(d). From Reference 108.


constant and bond order of the Ge=O moiety in Me₂Ge=O was found to be lower than those in the parent germanone H₂Ge=O and in F₂Ge=O\textsuperscript{109}.

The geometries of the whole series of group-14 homologues of acetone Me₂E=O and the parent system H₂E=O (E = C to Pb) have been calculated at different levels of theory by Kapp et al.\textsuperscript{110}. The authors investigated also the relative energies of other isomers of the molecules and the structures and energies of the trimers (H₂EO)₃ as well as the hydrated species H₃EOH. Figure 15 shows the calculated species. The relative energies are given in Table 26. The theoretically predicted values show that the heavier monomeric H₂EO species with E = Si to Pb are higher in energy than the carbene-like isomers HEOH. The energy differences between the two isomeric forms of the silicon compound are rather small but they are much higher for E = Ge to Pb. It is interesting to note that the H₂EO
FIGURE 15. Calculated isomers of $\text{H}_2\text{EO}$, $\text{Me}_2\text{EO}$, $(\text{H}_2\text{EO})_3$ and $\text{H}_3\text{EOH}$ with $E = \text{C}$ to Pb. The relative energies are given in Table 26. Reprinted with permission from Reference 110. Copyright 1996 American Chemical Society.

The effect of bulky organic groups on the structures and relative stabilities of $\text{R}_2\text{Pb}_2$ isomers has been the subject of a theoretical study by Frenking and coworkers and was already mentioned above in the context of discussing $\text{Pb}_2\text{H}_2$ isomers. The authors...
calculated the phenyl-substituted systems Ph₂Pb₂ at the DFT (B3LYP) and MP2 levels of theory. Figure 16 shows the B3LYP optimized geometries and relative energies of stationary points on the PES. The doubly bridged isomer A(Ph) (see Figure 6 for the notation) remains the global energy minimum form. The DFT calculations give an asymmetrically bridged geometry which is shown in Figure 16. MP2 calculations give a symmetrically bridged structure with Pb–C distances of 2.579 Å. The trans-bent forms D₁(Ph) and D₂(Ph) are still higher in energy than A(Ph) (compare the results for Pb₂H₂ which are shown in Figure 9). The former two species are not minima on the PES. Geometry optimization at B3LYP of the sterically much more crowded molecule Ar₂PbPbAr₂ (Ar₂ = 2,6-Ph₂C₆H₃) gave the trans-bent form D₂(Ar₂) shown in Figure 16 as an energy minimum structure. The calculated bond lengths and angles of D₂(Ar₂) are in very good agreement with the values of the X-ray structure analysis of 2,6-Tip₂H₃C₆PbPbC₆H₃-2,6-Tip₂ (Tip = 2,4,6-(t-Pr)₃C₆H₂)\(^{111}\).  

The conformational profile of 2,3-digermabutadiene H₂C=GeH−HGe=CH₂ has been investigated by Jouany et al. and compared with the parent butadiene molecule at the MP4 level using HF optimized geometries\(^{112}\). The authors found that the conjugation about the central Ge–Ge bond is significantly decreased. The relatively long Ge−Ge bond reduces the steric hindrance which is causing the s-cis isomer of butadiene to distort into a nonplanar gauche form. Therefore, 2,3-digermabutadiene has two planar energy minimum conformations. Figure 17 shows the calculated conformational pathways of 2,3-digermabutadiene and butadiene. Energy minima of 2,3-digermabutadiene are predicted when the rotational angle Φ is either 0° (s-trans) or 180° (s-cis). The calculated energies at MP4 including ZPE corrections predict that the s-cis form of 2,3-digermabutadiene

---

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<tr>
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<th>trans-H₂EO</th>
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<th>cis-MeE₀Me</th>
<th>trans-MeE₀Me</th>
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<td>-22.6</td>
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<tr>
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</tr>
<tr>
<td>B3LYP</td>
<td>0.0</td>
<td>-49.7</td>
<td>-49.0</td>
<td>-61.7</td>
<td>-58.1</td>
<td>0.0</td>
<td>-31.0</td>
</tr>
<tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>MP4</td>
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<td>-63.7</td>
<td></td>
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<td>-46.7</td>
<td>-47.0</td>
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<tr>
<td>CCSD(T)</td>
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<td>-71.2</td>
<td>-70.1</td>
<td></td>
<td>0.0</td>
<td>-54.1</td>
<td>-54.1</td>
</tr>
<tr>
<td>B3LYP</td>
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<td>-70.7</td>
<td>-69.6</td>
<td>-46.9</td>
<td>-56.1</td>
<td>0.0</td>
<td>-55.3</td>
</tr>
</tbody>
</table>

\(^{a}\)Reference 110.  
\(^{b}\)Trimerisation energy per H₂EO molecule.  
\(^{c}\)Hydration energy.
3. Theoretical studies of organic germanium, tin and lead compounds

FIGURE 16. Optimized structures of Pb$_2$Ph$_2$ and Pb$_2$Ph$_2^*$ at B3LYP. Bond lengths in Å, angles in deg. Relative energies of Pb$_2$Ph$_2$ are given in kcal mol$^{-1}$. The number of imaginary frequencies $i$ is given in italics. Reproduced by permission of Wiley-VCH from Reference 98.
is 0.3 kcal mol\(^{-1}\) less stable than the \textit{s-trans} form. The rotational barrier relative to the global energy minimum is 1.6 kcal mol\(^{-1}\).\(^{112}\)

A combined experimental/theoretical study of germacyclopentadienes which includes species with Ge=C double bonds has been reported by Khabashesku et al.\(^{113}\). The authors photolyzed matrix-isolated 1,1-diazido-1-germacyclopent-3-ene and deuteriated analogues. They identified the reaction products by comparing the experimental IR spectra with calculated vibrational frequencies and IR intensities of molecules which might be formed during the reaction. Figure 18 shows the optimized geometries at the HF level of those compounds which could be identified as reaction products\(^{113}\). The authors observed during irradiation at selected wavelengths a photoconversion of 3 into 5 and a reversible interconversion of 4 and 6, which provide experimental evidence for a germylene-to-germene rearrangement.

Comparison of theoretical data with experimental spectra led also to the identification of compounds which have germanium–nitrogen double and triple bonds. Foucat et al. report about the results of flash vacuum thermolysis of substituted germacyclopentenes and DFT (B3LYP) calculations of model compounds of possible reaction products\(^{114}\). The authors took the experimental photoelectron (PE) spectra and compared them with
3. Theoretical studies of organic germanium, tin and lead compounds

Theoretical studies of group-14 organometallic compounds with multiply bonded tin and lead compounds are rare. Márquez et al. calculated at the HF level the structures and relative energies of vinylstannane $\text{H}_3\text{Sn}–\text{CH}–\text{CH}_2$ and its isomers $\text{H}_2\text{C}–\text{SnH}–\text{CH}_3$ and $\text{H}_2\text{Sn}–\text{CH}–\text{CH}_3$\textsuperscript{115}. The former molecule is predicted to be 16.4 and 26.5 kcal mol$^{-1}$ lower in energy than the latter two isomers, respectively. The $\text{H}_2\text{E}–\text{E’H}–\text{E}$ moieties of the three isomers are planar. The authors calculated also the neutral, cation and anion of the allyl-like species $\text{H}_2\text{SnCHCH}_2$ and $\text{H}_2\text{E}–\text{H}–\text{E}$ at the CASSCF level. The cations were found to be planar, whereas the neutral radical and the anion prefer distorted geometries\textsuperscript{115}. The cations and anions of the allylic system $\text{CH}_2\text{CHEH}_2^{+/-}$ (with $\text{E} = \text{C}$ to $\text{Pb}$) have been the subject of a theoretical study at the HF and MP2 level by Gobbi and Frenking\textsuperscript{116}. The results of the latter work will be discussed in the section about cations and anions.

Compounds with multiple bonds between a transition metal and group-14 elements as the heavier analogues of carbenes — transition metal complexes of the type (CO)$_5\text{Cr}–\text{EH}_2$ (E = C to Sn) — have been calculated at the DFT level by Jacobsen and Ziegler\textsuperscript{117}. The authors report the equilibrium geometries and the transition metal–E bond dissociation

![Figure 17. Calculated rotational profiles of butadiene and 2,3-digermabutadiene at MP4. Reprinted with permission from Reference 112. Copyright 1994 American Chemical Society](image)

the ionization energies of model compounds (Figure 19) which were calculated by taking the energy difference between the neutral molecule and the cation. They identified the compounds 7, 8 and 9 which have SiMe$_3$ groups instead of the less bulky substituents of the model compounds 7M, 8M and 9M, respectively (Figure 19). These authors have also identified 10 which has a $t$-butyl group instead of CH$_3$ as in 10M and the parent molecule GeNH (11). The calculated geometries of the molecules shown in Figure 19 are given in the paper\textsuperscript{114}.
FIGURE 18. Optimized geometries of methyl-substituted germacyclopentene and germacyclopentadiene isomers. Bond lengths in Å, angles in deg. Reprinted with permission from Reference 113. Copyright 1996 American Chemical Society

(7M) Ge=N-SiH₃

(8M) Cl

Ge

N(SiHMe₂)₂

(9M) Ge≡N—SiHMe₂

(10M) Ge=N

Ge≡N—H

FIGURE 19. Germanium–nitrogen compounds which have been investigated in Reference 114
energies. The theoretically predicted \((\text{CO})_5\text{Cr}—\text{EH}_2\) bond energies decrease for the heavier group-14 elements with the trend \(E = \text{C}(67.2 \text{ kcal mol}^{-1}) > \text{Si}(57.6 \text{ kcal mol}^{-1}) > \text{Ge}(44.5 \text{ kcal mol}^{-1}) > \text{Sn}(40.0 \text{ kcal mol}^{-1})\). The transition metal–ligand bonding interactions are analyzed with an energy decomposition scheme which shows that the intrinsic \(\pi\)-bonding of the Cr–E bonds has the trend \(E = \text{C}(48.3 \text{ kcal mol}^{-1}) > \text{Si}(19.6 \text{ kcal mol}^{-1}) > \text{Ge}(17.2 \text{ kcal mol}^{-1}) > \text{Sn}(12.2 \text{ kcal mol}^{-1})\)\(^{117}\).

ii. Compounds with single bonds of Ge, Sn, Pb. Numerous theoretical studies of methyl derivatives of \(\text{EH}_4\) (E = Ge to Pb) have been published in the past. Almlöf and Faegri investigated the relativistic effects on the molecular structure of \(\text{EH}_4\) and the tetramethyl compounds \(\text{EMe}_4\) (E = C to Pb) using the Breit-Pauli Hamiltonian and first order perturbation theory\(^{118}\). They found that relativistic effects shorten the Pb–H and Pb–C distances by 0.05 Å. The authors report also the calculated force constants for the breathing mode. The electronic structure of \(\text{EMe}_4\) molecules for all elements E was probed in a combined experimental/theoretical investigation by Aoyama et al.\(^{119}\). The authors report also the experimental ionization spectra of the molecules. The observed bands are assigned to three orbital groups, \(\sigma_{\text{EC}}, \sigma_{\text{CH}}\) and ns(E), by comparing the experimental values with MO calculations at the HF level. With increasing size of the central atom, the relative band intensity of the spectral lines for the \(\sigma_{\text{EC}}\) and ns(E) orbitals decreases. This is interpreted by diminishing contributions of the electron distribution on the methyl groups for these orbitals on going from E = C to E = Pb\(^{119}\).

The double ionization energies of \(\text{EMe}_4\) (E = Si to Pb) to triplet electronic states of the dications have been calculated by Phillips et al. using a modified MSX\(_\alpha\) method\(^{120}\). The results are used to interpret the peak positions in experimental spectra obtained by double-charge-transfer spectroscopy. The experimental spectra correlate quite well with the calculated average double-ionization energies. The geometry and vibrational spectrum of \(\text{SnMe}_4\) have been calculated by Papakondylis et al. at the HF, MP2 and MP4 levels of theory\(^{121}\). The results were found to be in good agreement with experiment. The electronic excitation spectra of \(\text{SnH}_4\) and \(\text{SnMe}_4\) was the subject of a theoretical study at the SAC-CI level by Yasuda et al.\(^{122}\). The calculated results led to new assignments of the bands in the higher energy region up to the first ionization potential. DFT studies of the force constants and electrical properties of methylsilane and methylgermane have been published in a very detailed combined experimental/theoretical work by Mathews et al. which reports also the experimental IR spectrum of \(^{13}\text{CD}_3\text{GeH}_3\)\(^{123}\).

The geometries of \(\text{Me}_2\text{EX}_2\) with E = Si, Ge and X = F, Cl have been optimized at the CISD level of theory by Vacek et al.\(^{124}\). The authors compare the theoretical values with the results of electron diffraction data. The calculated data shown in Table 27 agree with experiment in that the C–E–C angles are significantly larger than 109°28’. On the basis of the calculated data the authors question the 124° experimental C–Ge–C angle of \(\text{Me}_2\text{GeBr}_2\). The paper gives also the harmonic vibrational analysis at the HF level of the four compounds\(^{124}\).

The calculated equilibrium geometries of the molecules \(\text{Me}_2\text{ECI}_2\) for all elements E = C to Pb have been reported by Jonas et al.\(^{125}\). Table 28 shows generally good agreement between theory and experiment. The experimental values for the bond angles of the tin compound have large error bars. The theoretical values of the latter compound are probably more accurate than the experimental data. The authors analyzed the hybridization of the E–C and E–Cl bonds in order to find out if there is a correlation between the hybridization of the bond orbitals and the bond angles. Such a correlation is suggested by Bent’s rule which states that ‘Atomic s character concentrates in orbitals directed toward electropositive substituents’\(^{126}\). Because chlorine is more electronegative than carbon, it follows that the E–Cl bonds should have a lower %s character than the E–C
TABLE 27. Calculated bond lengths (Å) and angles (deg) of Me₂EX₂<sup>a</sup>

<table>
<thead>
<tr>
<th>E</th>
<th>X</th>
<th>Theory</th>
<th>r(E–C)</th>
<th>r(E–X)</th>
<th>α(C–E–C)</th>
<th>α(X–E–X)</th>
<th>α(E–C–H′)</th>
<th>α(E–C–H″)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>F</td>
<td>CISD/DZd</td>
<td>1.8474</td>
<td>1.6001</td>
<td>115.9</td>
<td>105.7</td>
<td>111.0</td>
<td>111.5</td>
</tr>
<tr>
<td>Si</td>
<td>Cl</td>
<td>CISD/DZd</td>
<td>1.8537</td>
<td>2.0545</td>
<td>114.3</td>
<td>108.4</td>
<td>111.2</td>
<td>110.9</td>
</tr>
<tr>
<td>Ge</td>
<td>F</td>
<td>CISD/DZd</td>
<td>1.9246</td>
<td>1.7344</td>
<td>120.9</td>
<td>103.7</td>
<td>109.5</td>
<td>110.6</td>
</tr>
<tr>
<td>Ge</td>
<td>Cl</td>
<td>CISD/DZd</td>
<td>1.9333</td>
<td>2.1647</td>
<td>117.6</td>
<td>106.9</td>
<td>109.8</td>
<td>110.2</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reference 124. All structures have C<sub>2v</sub> symmetry.

TABLE 28. Calculated and experimental bond lengths (Å) and angles (deg) of Me₂ECl₂<sup>a</sup>

<table>
<thead>
<tr>
<th>Structure</th>
<th>Method&lt;sup&gt;b&lt;/sup&gt;</th>
<th>X–Cl</th>
<th>X–C</th>
<th>C–X–C</th>
<th>Cl–X–Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₂CCl₂</td>
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<td>1.798</td>
<td>1.521</td>
<td>113.0</td>
<td>108.3</td>
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<td></td>
<td>MP2/II</td>
<td>1.793</td>
<td>1.516</td>
<td>113.1</td>
<td>108.7</td>
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<tr>
<td></td>
<td>expt</td>
<td>1.799</td>
<td>1.523</td>
<td>113.0(±0.4)</td>
<td>108.3(±0.3)</td>
</tr>
<tr>
<td>Me₂SiCl₂</td>
<td>HF/II</td>
<td>2.069</td>
<td>1.867</td>
<td>114.5</td>
<td>107.8</td>
</tr>
<tr>
<td></td>
<td>MP2/II</td>
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<td>1.860</td>
<td>114.2</td>
<td>108.2</td>
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<td></td>
<td>expt</td>
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<td>1.845</td>
<td>114.7(±0.3)</td>
<td>107.2(±0.3)</td>
</tr>
<tr>
<td>Me₂GeCl₂</td>
<td>HF/II</td>
<td>2.184</td>
<td>1.949</td>
<td>118.6</td>
<td>106.2</td>
</tr>
<tr>
<td></td>
<td>MP2/II</td>
<td>2.183</td>
<td>1.954</td>
<td>118.3</td>
<td>106.6</td>
</tr>
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<td></td>
<td>expt</td>
<td>2.155</td>
<td>1.926</td>
<td>121.7(±1.4)</td>
<td>106.1(±0.6)</td>
</tr>
<tr>
<td>Me₂SnCl₂</td>
<td>HF/II</td>
<td>2.379</td>
<td>2.159</td>
<td>122.1</td>
<td>105.4</td>
</tr>
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<td></td>
<td>MP2/II</td>
<td>2.380</td>
<td>2.161</td>
<td>122.0</td>
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</tr>
<tr>
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<td>expt</td>
<td>2.327</td>
<td>2.109</td>
<td>110.1(±9.1)</td>
<td>107.5(±3.9)</td>
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</tbody>
</table>

<sup>a</sup>Reference 125.
<sup>b</sup>Basis set II which is described in Reference 4 uses ECPs for the heavy atoms and valence basis sets of DZP quality.

bonds. The calculated and observed C–E–C and Cl–E–Cl angles can be explained with Bent’s rule because bond angles of sp-hybridized bonds become larger when the %s character increases. Table 29 shows that the calculated hybridization of the E–C and E–Cl bonds indeed show that the former bonds have a higher %s(E) character than the latter<sup>125</sup>.

A recent theoretical study at the MP2 level of theory by Boyd and Boyd reported about the effects of protonation and deprotonation on the bond dissociation energies of compounds of third-row elements<sup>127</sup>. The authors gave calculated energies of the homolytic Ge–C and C–Ge bond cleavage of RGeH₃ and RGeH₂⁻ where R = CH₃, C₂H₅, C₂H₃, C₂H. They also give theoretically predicted bond energies of the heterolytic bond cleavages of R–GeH₃ yielding R⁺ + GeH₃⁻ and R⁻ + GeH₃⁺ and for R–GeH₂⁻ yielding R⁺ + GeH₂⁻ and R⁻ + GeH₂, respectively<sup>127</sup>.

Several investigations have been published where the geometries of heavier group-14 molecules were determined by gas-phase electron diffraction and where the results were compared with theoretical calculations. Smart et al. report about the molecular structure of tin(II) acetate Sn(O₂CMe)₃ which is shown in Figure 20<sup>128</sup>. The calculated bond lengths
3. Theoretical studies of organic germanium, tin and lead compounds

**TABLE 29. Results of the NBO analysis of Me$_2$ECl$_2$ at MP2/II$^{a,b,c}$**

<table>
<thead>
<tr>
<th></th>
<th>E–C</th>
<th></th>
<th></th>
<th>E–Cl</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% E</td>
<td>% s(E)</td>
<td>% p(E)</td>
<td>% d(E)</td>
<td>% E</td>
<td>% s(E)</td>
</tr>
<tr>
<td>Me$_2$CCl$_2$</td>
<td>52.5</td>
<td>31.4</td>
<td>68.5</td>
<td>0.1</td>
<td>46.1</td>
<td>18.6</td>
</tr>
<tr>
<td>Me$_2$SiCl$_2$</td>
<td>26.4</td>
<td>29.3</td>
<td>69.2</td>
<td>1.5</td>
<td>22.8</td>
<td>20.7</td>
</tr>
<tr>
<td>Me$_2$GeCl$_2$</td>
<td>29.1</td>
<td>30.7</td>
<td>68.8</td>
<td>0.5</td>
<td>22.3</td>
<td>19.3</td>
</tr>
<tr>
<td>Me$_2$PbCl$_2$</td>
<td>31.2</td>
<td>31.8</td>
<td>68.2</td>
<td>0.0</td>
<td>18.6</td>
<td>18.2</td>
</tr>
</tbody>
</table>

$^a$Reference 125.

$^b$% E gives the central atom part of the E–C and E–Cl bonds; % s(E), % p(E) and % d(E) give the hybridization of the E–C and E–Cl bonds at the central atom E.

$^c$Basis set II which is described in Reference 4 uses ECPs for the heavy atoms and valence basis sets of DZP quality.

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![SnO (4) C (8) C (2) O (6)](image)

**FIGURE 20. Optimized structure of tin(II) acetate reported in Reference 128. The calculated bond lengths and angles are given in Table 30**

and angles agree very well with the experimental results (Table 30). Even the HF/3–21G* geometry optimization gives a rather accurate geometry.

The molecular structure of C(GeBr$_3$)$_4$ has also been determined by gas-phase electron diffraction and by DFT calculations by Haaland et al.$^{129}$ Table 31 shows the experimental and theoretical bond lengths and angles of the molecule which has T symmetry. The calculated values are in very good agreement with experiment. The geometries of tetragermylmethane parent compound C(GeH$_3$)$_4$ and trigermymethane HC(GeH$_3$)$_3$ have more recently been determined by gas-phase electron diffraction and by DFT calculations by Kouvetakis et al.$^{130}$ Figure 21 shows the calculated and experimental bond lengths and angles.

A paper by Dakkouri which reported about the molecular structure of (trifluorosi-l ylimethyl)cyclopropane gave also the results of HF calculations of the conformational profiles of a series of cyclopropyl-CH$_2$-EH$_3$ (E = C to Ge) and R-EX$_3$ (R = methyl, cyclopropyl, cyclopropyl-CH$_2$; E = C to Ge; X = H, F)$^{131}$. The geometry of a methyl-substituted derivative of germacyclobutane determined by gas-phase electron diffraction and HF calculations was reported by Haaland et al.$^{132}$ Figure 22 shows some relevant bond lengths and angles. The theoretical and experimental values are in very good agreement.

The compounds Me$_3$EONMe$_2$ with E = Si, Ge have been synthesized and the geometries of the molecules were determined by gas-phase electron diffraction and by MP2/6–31G(d) calculations by Mitzel et al.$^{133}$ The structures of the molecules are interesting because weak attractive interactions by the nitrogen atom of the ONMe$_2$
TABLE 30. Calculated and experimental bond distances (Å) and bond angles (deg) of tin(II) acetate shown in Figure 20

<table>
<thead>
<tr>
<th>Parameter</th>
<th>HF/3–21G&lt;sup&gt;a&lt;/sup&gt;</th>
<th>HF/DZ(P)</th>
<th>MP2/ DZ(P)</th>
<th>Expt&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn–O(4)</td>
<td>2.312</td>
<td>2.359</td>
<td>2.352</td>
<td>2.337 (12)</td>
</tr>
<tr>
<td>Sn–O(5)</td>
<td>2.119</td>
<td>2.145</td>
<td>2.184</td>
<td>2.192 (8)</td>
</tr>
<tr>
<td>C(2)–O(4)</td>
<td>1.254</td>
<td>1.236</td>
<td>1.271</td>
<td>1.245 (5)</td>
</tr>
<tr>
<td>C(2)–O(5)</td>
<td>1.296</td>
<td>1.272</td>
<td>1.301</td>
<td>1.275 (5)</td>
</tr>
<tr>
<td>C(2)–C(8)</td>
<td>1.489</td>
<td>1.500</td>
<td>1.503</td>
<td>1.510 (5)</td>
</tr>
<tr>
<td>C(8)–H (mean)</td>
<td>1.081</td>
<td>1.083</td>
<td>1.094</td>
<td>1.121 (10)</td>
</tr>
<tr>
<td>C(2)–Sn–C(3)</td>
<td>94.6</td>
<td>97.3</td>
<td>96.3</td>
<td>95.1 (13)</td>
</tr>
<tr>
<td>O(4)–Sn–O(5)</td>
<td>58.0</td>
<td>56.8</td>
<td>58.3</td>
<td>58.1 (2)</td>
</tr>
<tr>
<td>O(4)–Sn–O(6)</td>
<td>123.3</td>
<td>124.4</td>
<td>123.2</td>
<td>121.0 (4)</td>
</tr>
<tr>
<td>O(4)–Sn–O(7)</td>
<td>81.3</td>
<td>83.6</td>
<td>81.8</td>
<td>80.0 (4)</td>
</tr>
<tr>
<td>O(5)–Sn–O(7)</td>
<td>88.4</td>
<td>90.0</td>
<td>90.8</td>
<td>90.0 (3)</td>
</tr>
<tr>
<td>Sn–O(4)–C(2)</td>
<td>89.5</td>
<td>88.0</td>
<td>88.0</td>
<td>86.2 (6)</td>
</tr>
<tr>
<td>Sn–O(5)–C(2)</td>
<td>97.3</td>
<td>97.2</td>
<td>94.8</td>
<td>93.5 (4)</td>
</tr>
<tr>
<td>O(4)–C(2)–O(5)</td>
<td>115.3</td>
<td>118.0</td>
<td>118.8</td>
<td>122.0 (4)</td>
</tr>
<tr>
<td>O(4)–C(2)–C(8)</td>
<td>124.5</td>
<td>122.9</td>
<td>122.3</td>
<td>120.0 (3)</td>
</tr>
<tr>
<td>O(5)–C(2)–C(8)</td>
<td>120.3</td>
<td>119.1</td>
<td>118.9</td>
<td>117.0 (3)</td>
</tr>
<tr>
<td>C(2)–C(8)–H (mean)</td>
<td>109.4</td>
<td>109.8</td>
<td>109.3</td>
<td>111.6 (11)</td>
</tr>
<tr>
<td>τ(O&lt;sub&gt;2&lt;/sub&gt;CCH&lt;sub&gt;3&lt;/sub&gt;)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>20.2</td>
<td>20.0</td>
<td>18.5</td>
<td>16.8 (11)</td>
</tr>
<tr>
<td>O(4)–Sn–C(2)–O(5)</td>
<td>179.6</td>
<td>178.6</td>
<td>178.2</td>
<td>176.3 (16)</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reference 128.
<sup>b</sup>Gas-phase electron diffraction.
<sup>c</sup>Bending angle of the methyl group given by the angle between the midpoint of the O<sub>4</sub>–O<sub>5</sub> axis, C<sub>2</sub> and C<sub>8</sub> (see Figure 20).

TABLE 31. Calculated and experimentally interatomic distances (Å), bond and torsion angles (deg) of C(GeBr<sub>3</sub>)<sub>4</sub><sup>d</sup>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Expt&lt;sup&gt;b&lt;/sup&gt;</th>
<th>DFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–Ge</td>
<td>2.042(8)</td>
<td>2.051</td>
</tr>
<tr>
<td>Ge–Br</td>
<td>2.282(3)</td>
<td>2.297</td>
</tr>
<tr>
<td>Ge–Ge</td>
<td>3.33 (1)</td>
<td>3.348</td>
</tr>
<tr>
<td>C–Br</td>
<td>3.61 (1)</td>
<td>3.627</td>
</tr>
<tr>
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<td>3.663</td>
</tr>
<tr>
<td>Ge–Br</td>
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<tr>
<td>Ge–Br</td>
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<td>4.490</td>
</tr>
<tr>
<td>Ge–Br</td>
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<td>5.386</td>
</tr>
<tr>
<td>Br–Br&lt;sup&gt;c&lt;/sup&gt;</td>
<td>3.48 (6)</td>
<td>3.926</td>
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<tr>
<td>Br–Br</td>
<td>4.11 (4)</td>
<td>3.909</td>
</tr>
<tr>
<td>Br–Br</td>
<td>6.03 (2)</td>
<td>6.170</td>
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<tr>
<td>Br–Br&lt;sup&gt;c&lt;/sup&gt;</td>
<td>6.12 (2)</td>
<td>6.203</td>
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<tr>
<td>Br–Br&lt;sup&gt;c&lt;/sup&gt;</td>
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<tr>
<td>Br–Br</td>
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<td>τ(Ge–C–Ge–Br)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>31.4 (9)</td>
<td>39.6</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reference 129.
<sup>b</sup>Gas-phase electron diffraction.
<sup>c</sup>Within a CBr<sub>3</sub> group.
<sup>d</sup>Torsion angle.
3. Theoretical studies of organic germanium, tin and lead compounds 211

FIGURE 21. Calculated bond lengths and angles of HC(GeH₃)₃ and C(GeH₃)₄ at the DFT (B3PW91) level. Experimental values obtained from gas-phase electron diffraction are given in parentheses. Bond distances are in Å, angles in deg. Reprinted with permission from Reference 130. Copyright 1998 American Chemical Society

FIGURE 22. Calculated bond lengths and angles of 1,1,3,3-tetramethylgermacyclobutane at the HF level. Experimental values obtained from gas-phase electron diffraction are given in parentheses. Bond distances are in Å, angles in deg. Reprinted from Reference 132 with permission from Elsevier Science
substituent lead to pentacoordinated atoms E. Figure 23 shows the relevant calculated and experimental values of the bond lengths and angles. The calculated Si–N distance of the silicon compound is in good agreement with experiment, but the theoretical Ge–N distance of the Ge compound is ca. 0.1 Å too long. The authors discuss the difference between theory and experiment. They point out that earlier calculations showed that the 6-31G(d) basis set is not large enough to give good geometries of molecules which have β donor interactions as in Me₃EONMe₂¹³³. Calculations with the larger basis set 6-311G(d) were not possible because of the size of the molecules.

The insufficient size of the 6-31G(d) basis set for calculating β donor interactions came also to the fore in a paper by Feshin and Feshina who optimized the geometry of Cl₃GeCH₂CH₂C(O)NH₂ at the HF/6-31G(d) and B3LYP/6-31G(d) levels of theory¹³⁴. Figure 24 shows the relevant calculated (B3LYP/6-31G(d)) and experimental bond lengths. It becomes obvious that the calculated Ge–O distance of the pentacoordinated Ge compound is much too long. The HF/6-31G(d) calculations gave nearly the same value (2.607 Å) as B3LYP/6-31G(d).

A paper by Campbell et al. which reported about a combined experimental/theoretical study of cyclotrigallazane gave also calculated geometries of cyclotriborazane, cyclotrialumazane and 1,3,5-trigermylcyclohexane (H₂GeCH₂)₃ which is isoelectronic to cyclotrigallazane¹³⁵. The geometry optimizations were carried out for the chair and the twist-boat conformations. The calculations at the MP2 level predict that the chair conformation of (H₂GeCH₂)₃ is 1.5 kcal mol⁻¹ lower in energy than the twist-boat conformation. The theoretically predicted and experimentally observed bond distances

![Figure 23](image_url)
3. Theoretical studies of organic germanium, tin and lead compounds

![Figure 24](image1.png)

**FIGURE 24.** Calculated bond lengths of Cl₃GeCH₂CH₂C(O)NH₂ at the B3LYP/6-31G(d) level. Experimental values are given in parentheses. Bond distances are in Å. Adapted from Reference 134

![Figure 25](image2.png)

**FIGURE 25.** Calculated bond lengths of 1,3,5-trigermacyclohexane (H₂GeCH₂)₃ at the MP2 level. Experimental values obtained from X-ray structure analysis are given in parentheses. Bond distances are in Å, angles in deg. Reprinted with permission from Reference 135. Copyright 1998 American Chemical Society

and angles of the chair conformation are shown in Figure 25. The agreement between theoretical and experimental values which come from X-ray structure analysis is quite good. The larger differences of the Ge–H bond lengths are due to the experimental difficulty of locating the position of hydrogen atoms.

The influence of crystal packing forces on the molecular geometry of some diorganotin compounds has been investigated in a combined crystallographic and theoretical study by Buntine et al.136. The authors report about calculated geometries at the HF and DFT (B3LYP and BLYP) levels of theory of the model compounds MeSnCl₃ and Me₃SnCl which were taken as reference systems in order to estimate the accuracy of the theoretical
values. The newly investigated tin compounds were $\text{Ph}_2\text{Sn(S}_2\text{CNEt}_2)\text{Cl}$, $\text{t-Bu}_2\text{Sn(S}_2\text{CN(c-Hex)}_2)\text{Cl}$, $\text{Vin}_2\text{SnCl}_2\text{(bipy)}\cdot\text{0.5C}_6\text{H}_6$, $\text{MePhSnCl}_2\text{(bipy)}\cdot\text{0.25CHCl}_3$ and $\text{Me}_2\text{SnCl}_2\text{(phen)}$ (c-Hex = cyclohexyl, bipy = 2, 2'-bipyridyl and phen = phenanthroline) where the tin atom is penta- and hexacoordinated. The authors found that the geometries of the isolated molecules are more symmetric than in the solid state and that the Sn–ligand distances tend to be shorter in the solid state than in the gas phase\textsuperscript{136}. It has previously been shown that the latter conclusion is valid for other kinds of donor–acceptor bonds\textsuperscript{137}.

The electronic structures and geometries of six-coordinated $\text{SnCl}_2\text{(trop)}_2$ and $\text{SnMe}_2\text{(trop)}_2$ (trop = tropolone) have been calculated at the HF level by Bruno et al.\textsuperscript{138}. The calculations predict in agreement with X-ray structure analysis that the cis arrangement of the tropolone ligand is more stable than the trans arrangement. The gas-phase UV spectra were assigned using the calculated molecular orbitals\textsuperscript{138}. The structure of some ‘paddle-wheel’ tin and lead complexes ($\eta^5\text{-Cp}_3\text{E}/\text{NUL}$) with various counterions $\text{X}^+$ were the topic of a combined experimental and theoretical work by Armstrong et al.\textsuperscript{139}. Figure 26 shows schematically the calculated model compounds with the relevant bond lengths and angles. The analysis of the electronic structure shows that the naked species ($\eta^5\text{-Cp}_3\text{E})^{-}$ (E = Sn, Pb)\textsuperscript{13(Sn)} and \textsuperscript{13(Pb)} are best formulated as triorganometal anions, while the unsolvated ($\eta^5\text{-Cp}_2\text{E})\text{(η-Cp)}\text{Na}$ complexes\textsuperscript{12(Sn)} and \textsuperscript{12(Pb)} are loose-contact complexes of $\text{Cp}_2\text{E}$ and $\text{Cp}\text{Na}$\textsuperscript{139}. The effect of the NH\textsubscript{3} molecule in\textsuperscript{12′(Sn)} which mimics the solvent is to lengthen the Na–Cp distance and to move the bridging Cp ligand into closer contact with Sn.

Adducts of stannocene and plumbocene $\text{Cp}_2\text{E}$ (E = Sn, Pb) with the bidentate Lewis bases TMEDA (tetramethylethylenediamine) and 4,4′-Me\textsubscript{2}bipyr (4,4′-dimethyl-2,2′-bipyridyl) have also been studied theoretically and experimentally by Armstrong et al.\textsuperscript{140}. Figure 27 shows the HF optimized geometries and the most important bond lengths and atomic partial charges. The authors found that the association of the metallocenes with TMEDA is energetically more favorable than with 4,4′-Me\textsubscript{2}bipy despite the presence of longer E\textsubscript{−}/NUL bonds in the solid state of the TMEDA adducts. This finding was explained with the greater reorganization energy of the former Lewis base compared with the latter\textsuperscript{140}.

Another combined experimental/theoretical paper by Armstrong et al. reported about the observation of a Pb–Li bond in the complex $\text{Ph}_3\text{Pb}−\text{Li(pmdeta)}$ (pmdeta = (Me\textsubscript{2}NCH\textsubscript{2}CH\textsubscript{2})\textsubscript{2}NMe) and HF calculations of the model compounds $\text{Ph}_3\text{ELi}$ (E = Sn, Pb)\textsuperscript{141}. Figure 28 shows the optimized geometries and the relevant atomic partial charges of the molecules. The analysis of the $\text{E}−\text{Li}$ bonds showed that the s and p orbitals of $\text{E}$ are involved in the bonding interactions. Model calculations on solvated $\text{Ph}_3\text{SnLi(NH)}_3$ showed that the effect of the NH\textsubscript{3} ligand is a lengthening and weakening of the Sn–Li bond\textsuperscript{141}.

The heavier analogues of the Arduengo carbene imidazol-2-ylidene 14 (Figure 29) with E = Si, Ge have been the topic of several theoretical papers in the last decade. Arduengo et al. reported about photoelectron spectra and DFT (BP86) calculations of $\text{14C}$, $\text{14Si}$ and $\text{14Ge}$ with R = t-buty\textsuperscript{142}. The assignment of the PE spectra with the help of the DFT calculations showed that the first band of $\text{14C}$ arises from the in-plane lone-pair orbital of the carbene carbon atom. The first bands of the silylene and germlyene compounds $\text{14Si}$ and $\text{14Ge}$, however, come from the $\pi$ orbital of the C=C double bond. The authors analyzed the bonding situation in these compounds. They suggested that the $\pi$-bonding in the heavier homologues $\text{14Si}$ and $\text{14Ge}$ contributes little to the E–N interactions because the contour line diagrams of the $\pi$-valence electron density 0.7 Å above the molecular plane shows vanishing contributions by the p($\pi$) electrons of E\textsuperscript{142}. The authors suggested
FIGURE 26. Calculated bond lengths and bond angles of Cp_3E^- (E = Sn, Pb) and Cp_3Na(NH_3) at the HF level. Bond distances are in Å, angles in deg. Reproduced by permission of The Royal Society of Chemistry from Reference 138
a ‘chelated atom’ bonding model for 14E (E = Si, Ge) which is shown schematically in Figure 30.

The bonding model of Arduengo et al.\textsuperscript{142} was later criticized in two theoretical studies of 14E and the saturated analogues 15E (Figure 29) with R = H at the MP4 level using MP2 optimized geometries by Apeloig, Schwarz and coworkers\textsuperscript{143a} for E = C, Si and by Boehme and Frenking\textsuperscript{143b} for E = C, Si, Ge. The latter authors showed that the method of electron density mapping suggested by Arduengo et al. applied to pyridine gives no significant $\pi$-electron density distribution between nitrogen and carbon which would lead to the conclusion that there is no cyclic $\pi$-delocalization in the pyridine ring. The bonding analysis by Boehme and Frenking led them to conclude that the $\pi$-delocalization becomes smaller with the trend 14C $>$ 14Si $>$ 14Ge and 15C $>$ 15Si $>$ 15Ge and that the unsaturated series 14E has a more delocalized $\pi$-character than 15E. The same conclusion was reached for the carbon and silicon species which were analyzed in the theoretical work of Apeloig, Schwarz and coworkers\textsuperscript{143a}. Boehme and Frenking\textsuperscript{143b} found that even the saturated cyclic molecule 15Ge has a significantly populated germanium p($\pi$) orbital and thus a strong N$\rightarrow$Ge $\pi$-donation. They also optimized the geometries of numerous five-membered heterocyclic compounds, among them 14Ge, 15Ge and the Ge-hydrogenated compound 14GeH\textsubscript{2}\textsuperscript{143b}. The calculated geometries are shown in Figure 31. Note that the calculated Ge--N bond length of 14Ge is clearly longer than the experimental value. This means that the calculated p($\pi$) charge of 14Ge underestimates the degree of $\pi$-delocalization. Boehme and Frenking calculated also the heats of hydrogenation of the unsaturated compounds 14E at element E yielding the tetravalent compounds 14EH\textsubscript{2}. The calculated values are $-20.8$ kcal mol$^{-1}$ for E = C, $-9.8$ kcal mol$^{-1}$ for

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Calculated bond lengths and atomic partial charges (in parentheses) of Cp\textsubscript{2}E, Cp\textsubscript{2}E(TMEDA) and Cp\textsubscript{2}E(4,4'-Me\textsubscript{2}bipyridyl) (E = Sn, Pb) at the HF level. Bond distances are in Å. Reprinted with permission from Reference 140. Copyright 1998 American Chemical Society}
\end{figure}
FIGURE 27. (Continued)
FIGURE 27. (Continued)
3. Theoretical studies of organic germanium, tin and lead compounds

FIGURE 28. Calculated bond lengths and atomic partial charges (in parentheses) of Ph₃ELi (E = Sn, Pb) at the HF level. Bond distances are in Å, angles in deg. Reproduced by permission of The Royal Society of Chemistry from Reference 141

FIGURE 29. Arduengo-type carbenes with divalent atoms E = C, Si, Ge
FIGURE 30. Bonding model of the interactions between the nitrogen atoms and the heavier elements $E = \text{Si, Ge}$ in the imidazol-2-ylidene, suggested by Arduengo et al. Reprinted with permission from Reference 142. Copyright 1994 American Chemical Society

FIGURE 31. Calculated bond lengths and bond angles at the MP2 level of germaimidazol-2-ylidene $14\text{Ge}$ and the hydrogenated compounds $15\text{Ge}$ and $14\text{GeH}_2$. Bond distances are in Å, angles in deg. Reprinted with permission from Reference 143. Copyright 1996 American Chemical Society.

E = Si and $+23.2 \text{ kcal mol}^{-1}$ for $E = \text{Ge}^{143b}$. The geometries and bonding situations of stable carbenes $14\text{C}$, silylenes $14\text{Si}$, germynes $14\text{Ge}$ and $15\text{Ge}$ with various substituents $R$ have been calculated with MNDO and $ab$ initio methods by Heinemann et al.$^{144}$. The analysis of the bonding situation in the above molecules and some germanium model compounds with Ge—N bonds led the authors conclude that ‘Electronic stabilization via $p_\pi - p_\pi$ delocalization is an important bonding feature in amino-substituted silylenes and germynes’. 
Donor–acceptor complexes of compounds 14E (Figure 29) with CuCl, AgCl and AuCl as ligands have also been investigated by Boehme and Frenking\textsuperscript{145}. The geometries were optimized at MP2 and the metal–ligand BDEs were calculated at CCSD(T). Figure 32 shows the optimized geometries and the theoretically predicted bond energies ($D_e$) of the germanium compounds. The strongest bond is calculated for the gold complex and the weakest bond is predicted for the silver complex. The same trend was found for the analogous carbene and silylene complexes\textsuperscript{145}. The analysis of the metal–ligand bond showed that there is mainly ligand→metal $\sigma$-donation and very little metal→ligand $\pi$-back-donation. The authors investigated also the degree of aromaticity in the free ligands 14E and in the ClCu-14E complexes using the NICS (Nuclear Independent Chemical
Shift) method suggested by Schleyer et al.\textsuperscript{103}. The calculated NICS values indicate that the molecules \textbf{14E} have a significant aromatic character which becomes slightly enhanced in the CuCl complexes\textsuperscript{145}.

Divalent compounds of group-14 elements Si to Pb where the elements E are stabilized via intramolecular mono- and bidentate chelation, shown schematically in Figure 33, have been the subject of an extensive theoretical study by Schöller et al.\textsuperscript{146}. The complexes are experimentally known for $E = Si, Ge, Sn$ and $L = P$, but not yet for the other elements which were calculated. Table 32 gives relevant calculated bond lengths and angles. The analysis of the bonding situation shows that the central element $E$ is weakly coordinated by the axial $E\cdots NUL$ bonds which become somewhat stronger when

\[ (L^3) \]

\[ (L^1) \]

\[ (L^2) \]

\[ (L^4) \]

\[ E = Si, Ge, Sn, Pb \]

\[ L = N, P, As \]

\textbf{FIGURE 33.} Schematic representation of the divalent group-14 compounds studied by Schöller et al. The calculated bond lengths and angles are given in Table 32. Reproduced by permission of Wiley-VCH from Reference 146

\textbf{TABLE 32.} Optimized bond lengths (Å) and angles (deg) of divalent group-14 compounds shown in Figure 33\textsuperscript{a}

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<tr>
<th>E</th>
<th>L</th>
<th>Symmetry</th>
<th>$E\cdots L^1$</th>
<th>$E\cdots L^2$</th>
<th>$E\cdots L^3$</th>
<th>$E\cdots L^4$</th>
<th>$\angle L^1EL^2$</th>
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<td>134.1</td>
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\textsuperscript{a}Reference 146.

\textsuperscript{b}Not an energy minimum structure.
3. Theoretical studies of organic germanium, tin and lead compounds

L = N. The authors calculated also the barriers for the degenerate rearrangement of the complexes\textsuperscript{146}.

The stability of divalent group-14 diyl compounds E(PH\textsubscript{2})\textsubscript{2} with respect to isomerization to the systems with E=P double bonds (PH\textsubscript{2})HE=PH (E = Si to Pb) has been reported in a combined experimental/theoretical work about diphosphanyl and diarsanyl substituted carbene homologues by Driess et al.\textsuperscript{147}. Table 33 shows the calculated energies of the adducts, transition states and products of the rearrangement of the model compounds. It becomes obvious that the stability of the diyl form E(PH\textsubscript{2})\textsubscript{2} \textsuperscript{F} relative to \textsuperscript{G} increases with Si < Ge < Sn < Pb.

Several authors investigated also the electronic structure of group-14 organometallic compounds. Day et al. reported calculations using DFT, Hartree–Fock and semiempirical (PM3) methods of the structures and absorption spectra of metal phthalocyanine complexes of copper, tin and lead in the gas phase and in solution\textsuperscript{148}. The solvent effect was treated with the COSMO model\textsuperscript{149}. The electronic spectra were calculated with the ZINDO method. The optical spectrum of a nickel porphyrazine complex which has four bulky Sn(t-Bu)\textsubscript{2} substituents coordinated at the meso-nitrogen atoms was calculated by Liang et al. using local DFT\textsuperscript{150}. The theoretical optical spectra including oscillator strengths were found to be in good agreement with experimental absorption. The electronic structure of tin acetylenes Sn(C≡CMe)\textsubscript{4} and Sn(C≡CSiMe\textsubscript{3})\textsubscript{4} was probed in a combined theoretical/experimental work by HF calculations and gas-phase UV PE spectroscopy by Andreocci et al.\textsuperscript{151}. The calculated MO energy levels of the valence electrons were used to assign the experimentally observed bands. The same procedure was used by Aoyama et al. who calculated the compounds Me\textsubscript{3}EPh (E = C to Pb) at the HF level in order to assign the bands which were observed in ionization electron spectra measurements of the compounds\textsuperscript{152}.

The geometries and electronic structures of group-14 metalloles from silole to stannole, together with the parent cyclopentadiene, having two thienyl groups at the 2,5-positions have been investigated in a combined experimental/theoretical study by Yamaguchi et al.\textsuperscript{153}. The authors give the experimental and theoretical geometries at the DFT (B3LYP) level and the UV-Vis and fluorescence spectra of the molecules. Figure 34 shows the calculated energy levels of the HOMO and LUMO. The authors found that the central

<table>
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<tr>
<td>Pb</td>
<td>0.0</td>
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<td>32.4</td>
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\textsuperscript{4}Reference 147.
group-14 elements Si, Ge and Sn affect the LUMO energy levels of the \( \pi \)-electron system to almost the same extent through \( \sigma^* - \pi^* \) conjugation\(^{153}\). As a consequence, the systems with \( E = \text{Si to Sn} \) have comparable absorption maxima in the UV-Vis spectra, while the absorption maximum of the Cp parent system lies at much shorter wavelengths.

Theoretical studies have been undertaken in order to investigate the aromatic character of analogous compounds of organic molecules where carbon is substituted by heavier group-14 elements Si to Pb. Baldridge and Gordon published in 1988 a theoretical study at the HF level of potentially aromatic metallocycles\(^{154}\). A more recent work by Goldfuss and Schleyer at the DFT (B3LYP) level focused on the structures and the bonding situation in the neutral and positively and negatively charged group-14 metalloles which are derived from cyclopentadiene and the heavier analogues\(^{155}\). The authors used the NICS method\(^{103}\) and structural and energetic criteria for analyzing the degree of aromaticity in the cyclic compounds \( \text{C}_4\text{H}_4\text{E}_2, \text{C}_4\text{H}_4\text{E}^+, \text{C}_4\text{H}_4\text{E}^-, \text{C}_4\text{H}_4\text{ELi}, \text{C}_4\text{H}_4\text{ELi}_2 \) and the singlet and triplet state of \( \text{C}_4\text{H}_4\text{E} \) (\( E = \text{C to Pb} \)). Figure 35 shows the optimized
FIGURE 35. Calculated bond lengths and bond angles at B3LYP of the group-14 metalloles \( \text{C}_4\text{H}_3\text{EH}_2 \), \( \text{C}_4\text{H}_4\text{EH}^- \) and \( \text{C}_4\text{H}_4\text{EH}^+ \). Bond distances are in Å, angles in deg. Reprinted with permission from Reference 155. Copyright 1997 American Chemical Society
geometries of $\text{C}_4\text{H}_4\text{E}H_2$, $\text{C}_4\text{H}_4\text{E}H^-$, $\text{C}_4\text{H}_4\text{E}H^+$. The neutral parent systems and the cations have a planar $\text{C}_4\text{E}$ skeleton, but the heavier $\text{C}_4\text{H}_4\text{E}H^-$ anions have a pyramidal environment at the heteroatom $\text{E}$. The increasing pyramidality at $\text{E}$ down group-14 elements results in strongly decreased aromaticity of metallolyl anions $\text{C}_4\text{H}_4\text{E}H^-$. In contrast, calculations of the anions with enforced planar geometries are significantly more aromatic. The antiaromatic character of $\text{C}_5\text{H}_5^+$ becomes much less in the heavier analogues $\text{C}_4\text{H}_4\text{E}H^+$. The $\text{C}_4\text{H}_4\text{E}$ species in the singlet state exhibit nearly as localized geometries as the $\text{C}_4\text{H}_4\text{E}H^+$ cations, but the $\text{C}_4\text{H}_4\text{E}$ triplets are more delocalized. The geometries of the lithiated species $\text{C}_4\text{H}_4\text{EHLi}$ and $\text{C}_4\text{H}_4\text{ELi}_2$ exhibit $\text{C}_4\text{H}_4\text{E}H^-$ (in case of $\text{C}_4\text{H}_4\text{EHLi}$) or $\text{C}_4\text{H}_4\text{E}^{2-}$ (in case of $\text{C}_4\text{H}_4\text{ELi}_2$) cyclic moieties which are capped by one or two $\text{Li}^+$, respectively.

The structures and aromatic character of tria- and pentafulvenes and their exocyclic silicon, germanium and tin derivatives (Figure 36) has been the subject of a quantum chemical study at ab initio levels of theory using various correlated methods and DFT (B3LYP) by Saebø et al. The calculations predict that the triafulvenes with $\text{E} = \text{Si}$ to $\text{Sn}$ have nonplanar geometries and that the equilibrium structures have trans-bent conformations as shown in Table 34. The pentafulvenes have planar geometries. The authors take the bond alternation and the charge distribution in the compounds as criterion for assigning the molecule as more or less aromatic. They suggest that there is some contribution from 2-$\pi$-aromatic resonance forms in the heterosystems of the triafulvenes.

FIGURE 35. (Continued)
which becomes enhanced as the heteroatom becomes more pyramidal. The pentafulvene series, however, exhibits evidence for a relatively small contribution from aromatic-like resonance structures\textsuperscript{156}.

The peculiar tendency of lead to prefer the oxidation state Pb(II) in inorganic compounds while the oxidation state Pb(IV) is prevalent in organolead compounds has been the topic of a theoretical study by Kaupp and Schleyer at highly correlated MP4 and QCISD(T) levels of theory\textsuperscript{157}. The authors calculated the structures and energies of a series of halogenated lead hydrides and methyllead compounds R\textsubscript{n}PbX\textsubscript{4–n} (R = H, Me; X = F, Cl; n = 0–4) and R\textsubscript{n}PbX\textsubscript{2–n} (n = 0–2). The relative stabilities of Pb(II) and Pb(IV) compounds were estimated by calculations of model reactions. Table 35 shows one set of reactions between tetravalent and divalent lead compounds where the products have a higher number of electronegative substituents in the tetravalent species. All reactions are endothermic. The endothermicity is particularly high for the formation of PbF\textsubscript{4}. A simple bonding model is proposed to explain the thermodynamic observations. The increase of the positive metal charge upon halogen substitution results in greater contraction of the 6s orbitals than the 6p orbitals of Pb. Hence, the 6p orbitals are less effective in sp\textsuperscript{n} hybridization, and electronegatively substituted Pb(IV) compounds become destabilized. The proposed concept emphasizes the size difference between the s and p valence orbitals, in contrast to the traditional term ‘inert pair effect’ which implies that the 6s orbital is too low in energy to hybridize with the 6p orbital. Geometrical aspects and the influence of relativistic effects are also discussed\textsuperscript{157}.

The progress in calculating NMR chemical shifts of heavier nuclei made it possible to calculate \textsuperscript{73}Ge and \textsuperscript{119}Sn NMR chemical shifts. Figure 37 shows the comparison of
**TABLE 35.** Calculated energies (kcal mol\(^{-1}\)) for isodesmic reactions between divalent and tetravalent lead methyl fluorides\(^a,b\)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>HF</th>
<th>MP4(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{CH}_3)_4\text{Pb} + \text{PbF}_2 \rightarrow (\text{CH}_3)_3\text{PbF} + \text{CH}_3\text{PbF})</td>
<td>8.9</td>
<td>10.3</td>
</tr>
<tr>
<td>((\text{CH}_3)_3\text{Pb} + \text{CH}_3\text{PbF} \rightarrow (\text{CH}_3)_3\text{PbF} + (\text{CH}_3)_2\text{Pb})</td>
<td>9.8</td>
<td>10.6</td>
</tr>
<tr>
<td>((\text{CH}_3)_3\text{PbF} + \text{PbF}_2 \rightarrow (\text{CH}_3)_2\text{PbF}_2 + \text{CH}_3\text{PbF})</td>
<td>15.1</td>
<td>16.5</td>
</tr>
<tr>
<td>((\text{CH}_3)_3\text{PbF} + \text{CH}_3\text{PbF} \rightarrow (\text{CH}_3)_2\text{PbF}_2 + (\text{CH}_3)_2\text{Pb})</td>
<td>16.0</td>
<td>16.3</td>
</tr>
<tr>
<td>((\text{CH}_3)_2\text{PbF}_2 + \text{PbF}_2 \rightarrow \text{CH}_3\text{PbF}_3 + \text{CH}_3\text{PbF})</td>
<td>29.1</td>
<td>29.9</td>
</tr>
<tr>
<td>((\text{CH}_3)_2\text{PbF}_2 + \text{CH}_3\text{PbF} \rightarrow \text{CH}_3\text{PbF}_3 + (\text{CH}_3)_2\text{Pb})</td>
<td>29.9</td>
<td>30.0</td>
</tr>
<tr>
<td>(\text{CH}_3\text{PbF}_3 + \text{PbF}_2 \rightarrow \text{PbF}_4 + \text{CH}_3\text{PbF})</td>
<td>48.4</td>
<td>47.4</td>
</tr>
<tr>
<td>(\text{CH}_3\text{PbF}_3 + \text{CH}_3\text{PbF} \rightarrow \text{PbF}_4 + (\text{CH}_3)_2\text{Pb})</td>
<td>49.3</td>
<td>47.5</td>
</tr>
<tr>
<td>((\text{CH}_3)_4\text{Pb} + \text{PbF}_2 \rightarrow (\text{CH}_3)_3\text{PbF}_2 + (\text{CH}_3)_2\text{Pb})</td>
<td>24.9</td>
<td>26.4</td>
</tr>
<tr>
<td>((\text{CH}_3)_3\text{PbF} + \text{PbF}_2 \rightarrow \text{CH}_3\text{PbF}_3 + (\text{CH}_3)_2\text{Pb})</td>
<td>45.0</td>
<td>46.3</td>
</tr>
<tr>
<td>((\text{CH}_3)_2\text{PbF}_2 + \text{PbF}_2 \rightarrow \text{PbF}_4 + (\text{CH}_3)_2\text{Pb})</td>
<td>78.3</td>
<td>77.3</td>
</tr>
<tr>
<td>((\text{CH}_3)_4\text{Pb} + 2\text{PbF}_2 \rightarrow \text{PbF}_4 + 2\text{Pb}(\text{CH}_3)_2)</td>
<td>103.2</td>
<td>103.7</td>
</tr>
</tbody>
</table>

\(^a\)Reference 157b.
\(^b\)Quasi-relativistic Pb pseudopotential used.
\(^c\)Reactions involving \((\text{CH}_3)_4\text{Pb}\) have been treated at the MP4SDQ level, all others at MP4SDTQ.

**FIGURE 37.** Comparison of calculated and experimental \(^{73}\text{Ge}\) NMR chemical shifts of some simple germanium compounds. The experimental values of GeMe\(_4-n\)Cl\(_n\) \((n = 1–3)\) were not available. They have been estimated from the analogues silicon compounds using empirical correlation factors. Reproduced by permission of John Wiley & Sons, Inc. from Reference 158.
theoretically predicted (using *ab initio* finite perturbation theory) $^{73}$Ge chemical shifts of simple germanium compounds with experimental values$^{158}$. It becomes obvious that the agreement between theory and experiment is quite good. The authors investigated the diamagnetic and paramagnetic contributions to the NMR chemical shifts. Nakatsuji et al. reported also about calculated $^{119}$Sn chemical shifts of some simple Sn(IV) compounds$^{159}$. Figure 38 shows a comparison of the theoretical and experimental values. The agreement is less satisfactory than for the germanium compounds. This may be due to relativistic effects which become much more important in calculating the resonances of the heavier Sn atom. Relativistic effects were neglected in the paper by Nakatsuji et al.$^{159}$.

Finally we want to mention a recent theoretical study of a hexanuclear tin cluster (Figure 39) which has been calculated at the CIS level of theory by Arnold et al.$^{160}$. The geometry of a model compound with hydrogens instead of methyls (Figure 39) was optimized at the CIS level of theory in the lowest energy ground ($^1A_1$) and excited ($^1B_1$) state. The calculations suggest that the structural distortion which is observed for the methyl substituted system is probably caused by a first order Jahn-Teller effect and not by tin-tin bonding as previously assumed$^{160}$.

![Figure 38](image-url)  
*FIGURE 38. Comparison of calculated and experimental $^{119}$Sn NMR chemical shifts of some simple tin compounds. Reprinted with permission of Reference 159. Copyright 1992 American Chemical Society*
Inga Ganzer, Michael Hartmann and Gernot Frenking

FIGURE 39. Schematic representation of the hexanuclear tin cluster calculated in Reference 160

\[ R = \text{Me} \]
\[ R = \text{H} \]

\[ \text{Sn-O-Sn} \]

**b. Reaction mechanisms.** Organometallic compounds of germanium and tin have become important agents in many reactions and thus have been the topic of several theoretical studies. Organolead compounds play a less prominent role. This may be the reason why we could not find any theoretical work which reports about reaction mechanisms of organolead compounds.

Kudin et al. reported HF and DFT (B3LYP) calculations of the dimerization of simple germenes \( \text{H}_2\text{Ge-CH}_2 \), \( \text{MeHGe-CH}_2 \), \( \text{Me}_2\text{Ge-CH}_2 \), \( \text{FHGe-CH}_2 \) and \( \text{H}_2\text{Ge-CHF} \). The authors report about the theoretically predicted transition states of the head-to-head and head-to-tail reactions which lead to 1,2- and 1,3-digermacyclobutane, respectively. The reaction pathways which lead to cis and trans isomers of the asymmetrically substituted germenes \( \text{MeHGe-CH}_2 \), \( \text{FHGe-CH}_2 \) and \( \text{H}_2\text{Ge-CHF} \) have also been investigated. The calculations predict that the formation of the 1,3-digermacyclobutanes (head-to-tail reaction) has lower activation barriers and is more exothermic than the formation of the 1,2-digermacyclobutanes (head-to-head reaction), except for \( \text{H}_2\text{Ge-CHF} \). The calculated activation parameters (\( \Delta E^\ddagger \), and ZPE corrected activation enthalpies \( \Delta H^\ddagger \)) and the reaction energies \( \Delta E \) and enthalpies \( \Delta H \) are given in Table 36. The calculations predict that the head-to-head product of dimerization of \( \text{H}_2\text{Ge-CHF} \) is more stable than the head-to-tail product. The calculations are not very conclusive about the height of the activation barriers of the two reactions. The HF calculations give a higher barrier for the head-to-head addition, but the B3LYP optimization did not give a transition state for this reaction. Figure 40 shows three types of reaction profiles which were suggested for the head-to-tail dimerization of the germenes. The calculations predict that dimerization of \( \text{H}_2\text{Ge-CH}_2 \) and \( \text{MeHGe-CH}_2 \) toward the 1,3-isomer proceeds along the A type profile, while \( \text{FHGe-CH}_2 \) should dimerize without a barrier as shown in reaction profile C. The head-to-tail dimerization process of \( \text{Me}_2\text{Ge-CH}_2 \) and \( \text{H}_2\text{Ge-CHF} \) is predicted to proceed either along reaction path A or path B, depending on the level of theory.

The prototype Ge–H insertion reaction of \( \text{GeH}_2 \) with \( \text{GeH}_4 \) yielding \( \text{Ge}_2\text{H}_6 \) was studied in a combined experimental/theoretical work by Becerra et al. The calculations at the MP2 and G2 levels of theory predict that the reaction proceeds via initial formation of a weakly bonded donor–acceptor complex which may exist in two different conformations. The following rearrangement to digermane takes place with a very low (<3 kcal mol\(^{-1}\)) activation barrier. The authors give also the calculated heat of formation of \( \text{GeH}_2 \) (60.2 kcal mol\(^{-1}\)) which is in good agreement with the experimental value of \( \Delta H^\circ = 56.6 \pm 2.7 \) kcal mol\(^{-1}\).
### TABLE 36. Summary of transition state energies ($\Delta E^\ddagger$ and $\Delta H^\ddagger$) and dimerization energies ($\Delta E$ and $\Delta H$) (kcal mol$^{-1}$) of the dimerization of germenes$^a$

<table>
<thead>
<tr>
<th>Germene</th>
<th>Theoretical level</th>
<th>Head-to-tail</th>
<th>Head-to-head</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\Delta E^\ddagger$</td>
<td>$\Delta H^\ddagger$</td>
</tr>
<tr>
<td>H$_2$Ge=CH$_2$</td>
<td>(1)</td>
<td>4.9</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>(2)</td>
<td>5.3</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>(3)</td>
<td>2.5</td>
<td>3.6</td>
</tr>
<tr>
<td>MeHGe=CH$_2$</td>
<td>(trans)</td>
<td>0.4</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>(cis)</td>
<td>2.6</td>
<td>3.1</td>
</tr>
<tr>
<td>Me$_2$Ge=CH$_2$</td>
<td>(1)</td>
<td>0.4</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>(2)</td>
<td>0.6</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>(3)</td>
<td>-3.8</td>
<td>-3.6</td>
</tr>
<tr>
<td></td>
<td>(2)</td>
<td>0.4</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>(3)</td>
<td>-1.2</td>
<td>-1.0</td>
</tr>
<tr>
<td>FHGe=CH$_2$</td>
<td>(trans)</td>
<td>no TS</td>
<td>-123.0</td>
</tr>
<tr>
<td></td>
<td>(cis)</td>
<td>no TS</td>
<td>-94.0</td>
</tr>
<tr>
<td></td>
<td>(3)</td>
<td>no TS</td>
<td>-82.8</td>
</tr>
<tr>
<td>FHGe=CH$_2$</td>
<td>(trans)</td>
<td>no TS</td>
<td>-122.5</td>
</tr>
<tr>
<td></td>
<td>(cis)</td>
<td>no TS</td>
<td>-93.3</td>
</tr>
<tr>
<td></td>
<td>(3)</td>
<td>no TS</td>
<td>-82.2</td>
</tr>
<tr>
<td>H$_2$Ge=CHF</td>
<td>(trans)</td>
<td>-3.7</td>
<td>-3.1</td>
</tr>
<tr>
<td></td>
<td>(2)</td>
<td>11.6</td>
<td>12.2</td>
</tr>
<tr>
<td></td>
<td>(3)</td>
<td>&lt;5.8$^b$</td>
<td>&lt;6.4$^b$</td>
</tr>
<tr>
<td>H$_2$Ge=CHF</td>
<td>(cis)</td>
<td>11.7</td>
<td>12.3</td>
</tr>
<tr>
<td></td>
<td>(2)</td>
<td>11.7</td>
<td>12.3</td>
</tr>
<tr>
<td></td>
<td>(3)</td>
<td>&lt;6.2$^b$</td>
<td>&lt;6.8$^b$</td>
</tr>
</tbody>
</table>

$^a$At RHF/3-21G (1), RHF/6-311G(d,p) (2), and B3LYP/6-311G(d,p) (3). From Reference 108.

$^b$Upper limits of the activation energy and enthalpy. The optimized structure has two imaginary frequencies. V. N. Khabashesku, personal communication to G. F.

![FIGURE 40](image-url) The three types of reactions profiles suggested in Reference 108 for the head-to-tail dimerization of simple germenes
The oxygen-to-carbon migration of a germyl substituent in the free anion $\text{H}_2\text{C} = \text{O} - \text{GeH}_3^-$ was investigated in a theoretical study at the CASSCF and MP4 levels of theory by Antoniotti and Tonachini$^{162a}$. The authors calculated in a later work the same process in the presence of a lithium counterion$^{162b}$. Figure 41 shows the theoretically predicted reaction profile for rearrangement of the GeH$_3$ group in the free anion and a comparison with the analogous reaction of the SiH$_3$ migration. The strongly exothermic rearrangement of $\text{H}_2\text{C} = \text{O} - \text{GeH}_3^-$ to $\text{(GeH}_3\text{)H}_2\text{C} - \text{O}^-$ proceeds with a small activation barrier of 2.1 kcal mol$^{-1}$ which involves the rotation of the CH$_2$ group (the alternative pathway with CH$_2$ inversion has a barrier of 7.0 kcal mol$^{-1}$) via a cyclic structure which is, however, not an energy minimum structure. Thus, the overall reaction of the germyl anion has a very low activation barrier. The mechanisms of the analogous silyl migration involve the formation of a cyclic intermediate and is predicted to be significantly different from its germanium analogue. The authors calculated also the dissociative pathway which involves cleavage of the germanium-oxygen bond. The bond energy was found to be $\text{ca}$ 10 kcal mol$^{-1}$ which indicates that the dissociative pathway is not competitive with the direct 1,2-shift$^{162a}$.

The calculated reaction profile for the germyl migration in the presence of a lithium counterion is significantly different from that of the free anion. The reaction is less exothermic (−24 kcal mol$^{-1}$) than in case of the free anion (−30 kcal mol$^{-1}$) and the nondissociative pathway which proceeds without an intermediate has a barrier of 16.7 kcal mol$^{-1}$$^{162b}$. However, the dissociative pathway has still a higher activation energy of 38.1 kcal mol$^{-1}$. The authors calculated also other structures on the PES and found an electrostatically bound complex of H$_2$CO−LiGeH$_3$ which is 10.1 kcal mol$^{-1}$ lower in energy than the reactant molecule (Li)H$_2$COGeH$_3$ in the most stable form which has the lithium in a bridging position between carbon and oxygen$^{162b}$.

The reaction profiles of the [1+2] addition of EH$_2$ and EF$_2$ (E = C, Si, Ge, Sn) in the ($^1A_1$) singlet state to ethylene yielding the cyclopropanes cyclic-C$_2$H$_4$EH$_2$ and cyclic-C$_2$H$_4$EF$_2$, respectively, have been calculated by Sakai at the MP2 and MP4 levels of theory$^{87}$. Figure 42 shows stationary points which were found for the reaction EH$_2$ +
FIGURE 42. Calculated geometries at MP2 and relative energies at MP4 of the stationary points of the reaction path for the addition of \((1_A^1)\) \(\text{EH}_2\) to ethylene. Precursor complexes \textit{Comp-EH}, transition states \textit{TS-EH} and products \textit{Pro-EH}. Bond distances are in \(\text{Å}\), bond angles in deg. The energy values are \(\Delta H^\circ\) values and they are in kcal mol\(^{-1}\). The numbers in parentheses give the \(\Delta H^\circ_{298}\) values. Reproduced by permission of John Wiley & Sons, Inc. from Reference 87
C$_2$H$_4$. The addition of CH$_2$ and SiH$_2$ takes place without a barrier yielding the product molecules in strongly exothermic reactions. The reactions of the heavier analogues GeH$_2$ and SnH$_2$ lead first to side-on bonded complexes. The latter are stable at 0 K but the calculated Gibbs free energy at 298.15 K shows that they disappear at higher temperature. The [1+2] addition of GeH$_2$ at room temperature has a small barrier which becomes higher for reaction of SnH$_2$. The calculations predict that cyclic-C$_2$H$_4$GeH$_2$ should only exist at low temperatures while cyclic-C$_2$H$_4$SnH$_2$ is thermodynamically unstable at all temperatures$^{87}$.

Figure 43 shows the stationary points for the reaction of EF$_2$ with C$_2$H$_4$. Weakly bonded complexes for all reactions are predicted as minima on the PES which are unstable at

![Figure 43](image-url)

FIGURE 43. Calculated geometries at MP2 and relative energies at MP4 of the stationary points of the reaction path for the addition of (1$^A_1$) EF$_2$ to ethylene. Precursor complexes Comp-EF$_2$, transition states TS-EF$_2$ and products Pro-EF$_2$. Bond distances are in Å, bond angles in deg. The energy values are $\Delta H$ values and they are in kcal mol$^{-1}$. The numbers in parentheses give the $\Delta H^{298}$ values. Reproduced by permission of John Wiley & Sons, Inc. from Reference 87.
3. Theoretical studies of organic germanium, tin and lead compounds

298.15 K. Note that the initial complexes of EF\textsubscript{2} with ethylene have a different geometrical shape than the EH\textsubscript{2} complexes which are shown in Figure 42. The C–EF\textsubscript{2} distances of Comp-EF are the same and the fluorine atoms are located on the same side of the three-membered ring while the hydrogen atoms of Comp-EH are on opposite sides of the ring plane. The author explained the differences between Comp-EF and Comp-EH with the repulsive interactions between the \( \pi \)-electrons of ethylene and fluorine\textsuperscript{87}. The [1+2] addition of CF\textsubscript{2} has a significant barrier and is much less exothermic than the addition of CH\textsubscript{2}. The barrier for addition of SiF\textsubscript{2} is even higher than for CF\textsubscript{2}, but cyclic-C\textsubscript{2}H\textsubscript{4}SiF\textsubscript{2} is only kinetically stable at room temperature. The cyclic compounds cyclic-C\textsubscript{2}H\textsubscript{4}GeF\textsubscript{2} and
cyclic-C_2H_4SnF_2 are thermodynamically unstable, but there is an energy barrier of ca 15 kcal mol⁻¹ for EF_2 loss from the former compound and a barrier of ca 6 kcal mol⁻¹ for the latter molecule. The author reports also about IRC calculations of the EF_2 + C_2H_4 addition reaction.

The analogous [1+2] addition of EH_2 and EF_2 to acetylene yielding the metallacycloprenes cyclic-C_2H_2EH_2 and cyclic-C_2H_2EF_2 with E = C, Si, Ge, Sn has been calculated by Boatz et al. at the HF and MP2 levels and also at MP4 for the carbon and silicon systems. As for the addition to ethylene, the cycloaddition of EH_2 to acetylene is predicted at the correlated level to proceed without a barrier. Calculated transition states at the HF level disappear at higher levels of theory. The formation of the metallacyclic compounds cyclic-C_2H_2EH_2 is exothermic but the reaction energies depend strongly on the metal E. The calculated enthalpies of formation for the reaction (\(_1A_1\)) EH_2 + C_2H_2 \rightarrow cyclic-C_2H_2EH_2 at MP2/3-21G(d) corrected to 298 K (\(\Delta H_{298}^\circ\)) are -101.5 kcal mol⁻¹ for E = C, -56.8 kcal mol⁻¹ for E = Si, -20.0 kcal mol⁻¹ for E = Ge and -12.5 kcal mol⁻¹ for E = Sn. The [1+2] addition of EF_2 to C_2H_2 yielding cyclic-C_2H_2EF_2 has significant activation barriers and is much less exothermic than in case of the EH_2 addition or is even endothermic. The calculated reaction barriers \(\Delta H^\ddagger\) (reaction enthalpies \(\Delta H_{298}^\circ\) are given in parentheses) are \(\Delta H^\ddagger_{298} = 14.1\) kcal mol⁻¹, \(\Delta H^\ddagger_{298} = -47.2\) kcal mol⁻¹ for E = C, \(\Delta H^\ddagger_{298} = 14.3\) kcal mol⁻¹ (\(\Delta H_{298}^\circ = -40.9\) kcal mol⁻¹) for E = Ge, \(\Delta H^\ddagger_{298} = 38.4\) kcal mol⁻¹ (\(\Delta H_{298}^\circ = 14.4\) kcal mol⁻¹) for E = Ge and \(\Delta H^\ddagger_{298} = 27.5\) kcal mol⁻¹ (\(\Delta H_{298}^\circ = 16.5\) kcal mol⁻¹) for E = Sn.

A theoretical study of the degenerate 1,3-allyl migration of EH_3 substituents with E = C, Si, Ge, Sn was published by Takahasi and Kira. The authors found that there are two transition states TS_{ret} and TS_{inv} which yield retention (TS_{ret}) or an inversion (TS_{inv}) of the migrating EH_3 group. The geometry of TS_{inv} has a square pyramidal form while TS_{ret} is a trigonal bipyramid (Figure 44). Table 37 gives the calculated activation energies for the two transition states at the Hartree–Fock level. The most important result is that the pathway with retention of the CH_3 group has a higher energy than the reaction which proceeds with inversion of the methyl group, while the heavier EH_3 groups migrate with retention. The trend of the activation energies for the group-14 elements E is: C > Si > Ge > Sn.

The influence of carbon group substituents ER_3 (E = C to Sn; R = H, Me, t-Bu) on the energy barrier of bond shift and electrochemical reduction of substituted cyclocotetraenes (COT-ER_3) has been studied with experimental and theoretical methods by Staley et al. The ring inversion transition state (Figure 45) was taken as a model for the steric interactions in the bond shift transition state which could not be calculated.

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**FIGURE 44.** Schematic representation of the transition states of the degenerate 1,3-allyl migration of EH_3 (E = C to Sn) with inversion (TS_{inv}) and retention (TS_{ret}) of the EH_3 group. Reprinted with permission from Reference 163. Copyright 1997 American Chemical Society.
TABLE 37. Comparison of activation energies $\Delta E_a$ (kcal mol$^{-1}$) for 1,3-migration in CH$_2$=CHCH$_2$EH$_3$ (E = C, Si, Ge and Sn)$^a$

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Ge</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a$(ret)</td>
<td>133.6</td>
<td>64.0</td>
<td>79.6</td>
<td>72.9</td>
</tr>
<tr>
<td>$E_a$(inv)</td>
<td>116.9</td>
<td>75.1</td>
<td>84.6</td>
<td>77.5</td>
</tr>
<tr>
<td>$\Delta E_a^b$</td>
<td>-16.7</td>
<td>11.1</td>
<td>5.0</td>
<td>4.6</td>
</tr>
</tbody>
</table>

$^a$Reference 163.

$^b \Delta E_a = E_a$(inv) $- E_a$(ret).

FIGURE 45. Schematic representation of the ring inversion (ri) transition state of cyclooctatetraene. The calculated energies are given in Table 38. Reprinted with permission from Reference 164. Copyright 1998 American Chemical Society

directly because of the size of the molecules and the multiconfigurational character of the transition state. The validity of the model was supported by a correlation between the calculated activation energies of the ring inversion of COT-R with R = H, Me, SiMe$_3$ and $t$-Bu, with the experimental values of the free activation enthalpies of the bond shift reaction. Table 38 shows the calculated activation energies of the ring inversion of COT and COT-ER$_3$ with E = C to Sn and R = H, Me. In spite of the rather low level of theory (HF/3-21G) it turns out that the $\Delta E_{ri}$ values for the systems with EM$_3$ substituents are in fairly good agreement with the experimental results of the bond shift reaction. The latter process has $\Delta G^\ddagger$ (298 K) values of 18.1, 16.4, 16.2, and 16.2 kcal mol$^{-1}$ for CMe$_3$, SiMe$_3$, GeMe$_3$ and SnMe$_3$, respectively$^{164}$. Note that the difference in activation energy of the ER$_3$ substituent is the highest when one goes from CH$_3$ to CMe$_3$. It follows that steric effects play a crucial role in the relative activation barriers.

The influence of substituents X of 5-substituted 1,3-cyclopentadienes on the diastereoselectivity of the Diels–Alder addition with various nucleophiles has been studied at the HF/6-31G(d) level by Xidos et al.$^{165}$ The calculations with ethylene as nucleophile were also carried out with the substituents X = EH$_3$ (E = C, Si, Ge, Sn). Figure 46 shows
TABLE 38. Calculated energies of the ring inversion transition state ($\Delta E_{ri}$) shown in Figure 45 for substituted cyclooctatetraenes. $^a$

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$\Delta E_{ri}$ (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HF/3-21G</td>
</tr>
<tr>
<td>H</td>
<td>15.9</td>
</tr>
<tr>
<td>C(CH$_3$)$_3$</td>
<td>20.6</td>
</tr>
<tr>
<td>Si(CH$_3$)$_3$</td>
<td>19.1</td>
</tr>
<tr>
<td>Ge(CH$_3$)$_3$</td>
<td>18.1</td>
</tr>
<tr>
<td>Sn(CH$_3$)$_3$</td>
<td>19.6</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>17.6</td>
</tr>
<tr>
<td>SiH$_3$</td>
<td>19.1</td>
</tr>
<tr>
<td>GeH$_3$</td>
<td>18.2</td>
</tr>
<tr>
<td>SnH$_3$</td>
<td>19.8</td>
</tr>
</tbody>
</table>

$^a$Reference 164.

FIGURE 46. Schematic representation of the Diels–Alder reaction of 1,3-cyclopentadienes with ethylene yielding syn and anti products.

The authors optimized the transition states for the syn and anti attack of ethylene with respect to X. The energy differences between the transition states were compared with the experimentally observed diastereoselectivity of substituted cyclopentadienes. The calculated facial stereoselectivities are in excellent agreement with experimental data. For the EH$_3$ substituted cyclopentadienes it was found that CH$_3$ favors the anti addition by 0.83 kcal mol$^{-1}$. The calculations predict that the heavier analogues SiH$_3$, GeH$_3$ and SnH$_3$ lead to higher preferences for anti addition by 6.4, 6.7 and 9.2 kcal mol$^{-1}$, respectively$^{165}$.

The role of SnCl$_4$ as catalyst in [2+2] cycloaddition reactions of olefines which are activated by selenophenyl and silyl groups in the 1,1 position with vinyl ketones has been examined in a combined experimental/theoretical study by Yamazaki et al.$^{166}$ Calculations at the HF level showed that the formation of a chelate complex where the selenium atom of the olefin and the oxygen atom of the keto group are bonded as ligands to the
Lewis acid SnCl$_4$ is unlikely because of the large Sn—Se separation which was found in a zwitterionic intermediate. The latter structure has a Sn—O donor–acceptor bond but no Sn—Se bond. The calculations showed that a second SnCl$_4$ may perhaps bind to Se during the reaction$^{166}$.

Yamazaki et al. investigated in a combined experimental/theoretical work also the role of SnCl$_4$ in the formal [2+1] cycloaddition of 1-seleno-2-silyleneethenes to various vinylketones (Figure 47a) which give cyclopropane compounds rather than cyclobutanes that would be the result of a [2+2] cycloaddition$^{167}$. Calculations of various possible intermediates led the authors to suggest that the formation of the SnCl$_4$ stabilized intermediate $\textbf{I}_{\text{(trans)}}$ which is shown in Figure 47b is responsible for the formation of the cyclopropane. The authors give the geometries and energies calculated at the HF level of various model compounds$^{167}$.

A related study by Yamazaki et al. investigated the reaction profile of the SnCl$_4$-catalyzed [2+1] cycloaddition of 1-seleno-2-silyleneethenes to 2-phosphonoacrylates$^{168}$. Calculations at the HF level suggest that the crucial intermediate for this reaction is the chelate complex which is shown in Figure 48. The authors give the optimized geometries, energies and charge distribution of the complex and other possible intermediates of the reactions$^{168}$.

Hobson et al. investigated in a combined experimental/theoretical study the origin of 1,5-induction in Sn(IV)halide-promoted reactions of 4-alkoxyalk-2-enylstannanes with aldehydes to give product 17$^{169}$. Figure 49 shows the investigated reaction course and the postulated intermediates 18 and transition state 19. Figure 50 displays the optimized B3LYP geometry of transition state 19 for $\text{cis}$ and $\text{trans}$ addition of the aldehyde. The former structure is much lower in energy than the latter, which is in agreement with the experimentally observed formation of $\text{cis}$ alkenes$^{169}$.

\[ \text{SePh} + \text{R}_3\text{Si}^\rightarrow \xrightarrow{\text{SnCl}_4} \text{PhSe} \]

![Figure 47](image_url)

**FIGURE 47.** (a) The [2+1] cycloaddition of 1-seleno-2-silyleneethenes to various vinylketones investigated in Reference 71. (b) Schematic representation of the SnCl$_4$-stabilized intermediate $\textbf{I}_{\text{(trans)}}$. Reprinted with permission from Reference 167. Copyright 1994 American Chemical Society
FIGURE 48. Schematic drawing of the SnCl₄ chelate complex which was calculated as the crucial intermediate of the SnCl₄-catalyzed [2+1] cycloaddition of 1-seleno-2-silylthienes to 2-phosphonoacrylates. Reprinted with permission from Reference 168. Copyright 1998 American Chemical Society.

FIGURE 49. Postulated intermediates and transition state (19) of the Sn(IV)halide-promoted reactions of 4-alkoxyalk-2-enylstannanes with aldehydes.⁶⁹

FIGURE 50. B3LYP optimized transition states and activation energies of the Sn(IV)halide-catalyzed cis- and trans-addition of formaldehyde to 4-alkoxyalk-2-enylstannanes. Bond lengths are in Å, energies in kcal mol⁻¹. Reproduced by permission of The Royal Society of Chemistry from Reference 169.
The atomic charge distribution and the polarity of the LUMO of HC≡C–SnF₃ and HC≡C–SnH₃ have been calculated at the HF level by Yamaguchi et al.¹⁷⁰. The authors investigated experimentally the reaction of substituted phenols with acetylene in the presence of SnCl₄ yielding ortho-vinyl phenols as main products. They argued that the electronic nature of the tin reagent which is strongly influenced by the substituents is crucial for the reaction path. The authors speculated that a nucleophilic attack of phenoxytin at the electrophilic β-carbon atom of stannylacetylene takes place, but they could not present a transition state for the reaction¹⁷⁰.

An ab initio investigation at the HF level of the reaction pathways of organotin enolate addition to benzaldehyde and bromoethane have recently been reported by Yasuda et al.¹⁷¹. The investigated reactions are shown in Figure 51. Figure 52 gives the optimized geometries and atomic charge distribution of calculated tin compounds which are representative of triorganotin enolates, triorganotin alkoxides and triorganotin bromides. It also shows the negatively charged complexes which are formed when a Br⁻ is bonded to Sn. The calculated complexation energies are rather high. The reaction pathways of the two reactions shown in Figure 51 have been calculated with and without Br⁻ as ligand which is attached to tin. Figure 53 shows the optimized stationary points which were found for the addition of Me₃SnOC(Me)CH₂ (20) to benzaldehyde (reaction 1 in Figure 51). Figure 54 gives the theoretically predicted energy profile for this reaction. It becomes obvious that the activation barrier without the Br⁻ ligand is lower than the reaction barrier of the five-coordinated tin compound. The authors give also the calculated intermediates and the reaction profile for reaction 2 of Figure 51. The energy difference between the transition states of reaction 2 with and without the Br⁻ ligand are even higher in favor of the latter than for reaction 1¹⁷¹.

The influence of the SnCl₃ substituent on the olefin insertion reaction into the Pt–H bond of a platinum model compound has been investigated at the MP2 (for the geometries) and MP4 (for the energies) levels of theory by Rocha and De Almeida¹⁷². Figure 55 shows the calculated reaction profile of the ethylene insertion into the Pt–H bond of PtH(PH₃)₂X, where X is Cl or SnCl₃. The calculations reveal that the SnCl₃ substituent stabilizes the pentacoordinated intermediates much more than Cl. The reaction proceeds through a rate-determining four-center transition state where the hydrogen atom migrates to the β-carbon atom of ethylene. The activation barrier for X = SnCl₃ is much lower than for X = Cl. The authors give the geometries and energies of the intermediates and the transition states. They also discuss the nature of the metal–ligand bonding in the relevant intermediates¹⁷².

\[
\text{Me₃SnO} + \text{HPh} \rightarrow \text{Me₃SnOPh}
\]

(1)

\[
\text{Me₃SnO} + \text{BrSnMe₃} \rightarrow \text{Me₃SnBr} + \text{O}
\]

(2)

FIGURE 51. Reactions which have been calculated in Reference 171
FIGURE 52. Optimized geometries and energies at the HF level for Br\(^-\) addition to tin compounds 20–22 taken from Reference 171. Bond distances are in Å. The atomic partial charges are given in parentheses. Reprinted with permission from Reference 171. Copyright 2000 American Chemical Society.
3. Theoretical studies of organic germanium, tin and lead compounds

FIGURE 53. Calculated stationary points at the HF level for the addition of Me$_3$SnO-C(Me)=CH$_2$ to benzaldehyde with and without Br$^-$. Precursor complexes 23 and 23(Br$^-$), transition states 24 and 24(Br$^-$) and products 25 and 25(Br$^-$). Bond distances are in Å. See Figure 54 for the corresponding energy profiles. Reprinted with permission from Reference 171. Copyright 2000 American Chemical Society
A theoretical study at the HF level on the reaction mechanisms of the regioselective silastannation of acetylenes with a model palladium catalyst has been published by Hada et al.\textsuperscript{173}. Figure 56 shows the calculated reaction profile for the addition of H\textsubscript{3}SiSnH\textsubscript{3} to RC\textsubscript{1}CH (R = Me) in the presence of the model catalyst Pd(PH\textsubscript{3})\textsubscript{2}. The transition states TS\textsubscript{3} and TS\textsubscript{4} could not be localized on the PES. The given energies are upper limits of the ligand exchange reactions. The authors give also the energy profiles for the insertion step of RC\equiv CH with R = H, CN and OCH\textsubscript{3} and they analyze the electronic structure of the intermediates\textsuperscript{173}.

2. Cations and anions

Theoretical studies have been published which investigated the changes in the geometries and bonding situations in carbocations when carbon is substituted by a heavier group-14 atom Si to Pb. Gobbi and Frenking calculated the structures and analyzed the bonding situation in the allyl cations and anions CH\textsubscript{2}C\textsubscript{2}H\textsubscript{2}\textsuperscript{+/-} for E = C to Pb at the HF and MP2 levels\textsuperscript{116}. The allyl cations are predicted to have a planar geometry. All allyl cations are stabilized by $\pi$-conjugative interactions. The strength of the resonance interactions as measured by the rotational barrier decreases from 37.8 kcal mol\textsuperscript{-1} (E = C) to 14.1 kcal mol\textsuperscript{-1} (E = Si), 12.0 kcal mol\textsuperscript{-1} (E = Ge), 7.2 kcal mol\textsuperscript{-1} (E = Sn) and 6.1 kcal mol\textsuperscript{-1} (E = Pb). The allyl cations are additionally stabilized by $\sigma$-bonding and through-space charge interactions, which have the same magnitude as the resonance stabilization. The equilibrium geometries of the heavy-atom allyl anions have strongly pyramidal EH\textsubscript{2} groups. The planar forms are much higher in energy. The calculations suggest that there is no resonance stabilization in the allyl anions, except in the parent anion CH\textsubscript{2}CHCH\textsubscript{2}\textsuperscript{-}. The electronic structure of the molecules was investigated using the Laplacian of the electron density distribution\textsuperscript{116}.

The trend of the $\pi$-donor ability of the halogens X = F to I in the cations EX\textsubscript{3}\textsuperscript{+} and EH\textsubscript{2}X\textsuperscript{+} (E = C to Pb) and in the isoelectronic neutral compounds AX\textsubscript{3} and AH\textsubscript{2}X
FIGURE 55. Calculated reaction profile at the MP4//MP2 level of ethylene insertion into the Pt–H bond of PtH(PH₃)₂X. The calculated energies (kcal mol⁻¹) refer to X = SnCl₃; the numbers in parentheses refer to X = Cl. Reprinted with permission from Reference 172. Copyright 1998 American Chemical Society
(A = B, Al, Ga, In, Tl) was the focus of a theoretical study at the MP2 level by Frenking and coworkers\textsuperscript{174}. The strength of the $\pi$-donation was probed by the population of the $p(\pi)$ AO of the central atoms E and A, by calculating the reaction energy of isodesmic reactions and by calculation of the complexation energies with H\textsubscript{2}O. All three criteria suggest that the $\pi$-donor strength has the trend F $<$ Cl $<$ Br $<$ I. Figure 57 shows a diagram of the theoretically predicted BDEs of the complexes X\textsubscript{3}E$^+$–OH\textsubscript{2}. It becomes obvious that carbon plays a special role among the group-14 elements. However, all EX\textsubscript{3}$^+$–OH\textsubscript{2} species exhibit a trend of the BDEs X = F $>$ Cl $>$ Br $>$ I which indicates that iodine stabilizes the cation EX\textsubscript{3}$^+$ the most and fluorine the least\textsuperscript{174}.

The potential energy surface of C\textsubscript{2}GeH\textsubscript{5}$^+$ was investigated by Antoniotti et al. at correlated levels up to QCISD(T) using HF optimized geometries\textsuperscript{175}. Figure 58 shows the
3. Theoretical studies of organic germanium, tin and lead compounds

FIGURE 57. Calculated complexation energies at the MP2 level of \( X_3E^+ - OH_2 \) with \( E = C \) to \( Pb \) and \( X = H, F \) to \( I \). Bond energies are in kcal mol\(^{-1}\). Reprinted with permission from Reference 174. Copyright 1997 American Chemical Society

FIGURE 58. Calculated energy minima on the \( GeC_2H_5^+ \) singlet potential energy surface. Relative energies have been calculated at QCISD(T) using HF optimized geometries. Bond distances are in Å, angles in deg. Reprinted with permission from Reference 175. Copyright 1993 American Chemical Society
optimized structures and the relative energies of the energy minima 33–41 which have been found. The global energy minimum structure is the hydrogen-bridged nonclassical cation 33, which is 11.8 kcal mol$^{-1}$ more stable than the 1-germaallyl cation 34, the second most stable isomer on the PES. There are seven other energy minima which were found on the PES. The authors give also the structures and energies of some C$_2$GeH$_5^+$ transition states. The same group investigated also the C$_2$GeH$_7^+$ PES. The geometries were optimized at the MP2 level and the energies were calculated at QCISD(T) using MP2 optimized structures. Figure 59 gives the geometries and the relative energies of four structures which were found to be energy minima on the C$_2$GeH$_7^+$ PES. The global energy minimum structure is the classical 2-germapropyl-2 cation 42 which has C$_{2v}$ symmetry. The energetically nearly degenerate two rotamers 43 and 44 of the 1-germapropyl-1 cation are predicted to be ca 20 kcal mol$^{-1}$ less stable than 42. The nonclassical form 45 is much higher in energy. The authors give also the structures and
FIGURE 59. Calculated energy minima on the GeC₂H₇⁺ singlet potential energy surface. Relative energies (kcal mol⁻¹) have been calculated at QCISD(T) using MP2 optimized geometries. Bond distances are in Å, angles in deg. Reprinted with permission from Reference 176. Copyright 1995 American Chemical Society.

energies of some transition states and higher-order saddle points on the C₂GeH₇⁺ PES¹⁷⁶.

Some of the C₂GeH₇⁺ isomers were previously calculated at the HF level by Nguyen et al.¹⁷⁷.

The relative energies of classical and nonclassical isomers of tropylium, silatropylium and germatropylium cations were calculated by Nicolaides and Radom at the G2 level of theory using MP2 optimized geometries¹⁷⁸. Figure 60 shows the structures 46–53 which were found as energy minima on the C₆H₇E⁺ (E = C, Si, Ge) PES. Table 39 gives the relative energies. It becomes obvious that the classical isomers 46 and 47 (which is identical to 48 when E = C) are the most stable C₇H₇⁺ carbocations, while for E = Si and Ge the nonclassical form 50Si and 50Ge becomes the global minimum on the respective PES.

The substituent effect of group-14 substituents on the stability of the bicyclic carbocations J⁺ and K⁺ (Figure 61) has been the subject of a theoretical study at the MP2 level by Hrovat and Borden¹⁷⁹ and a combined experimental/theoretical work by Adcock et al.¹⁸⁰. The former workers calculated J⁺ and the parent system JH with X = H, SiH₃, SnH₃. They found that the cations are stabilized by SiH₃ and even more by SnH₃ via hyperconjugation¹⁷⁹. Adcock et al. calculated the 4X-1-norbonyl cation K⁺ and the parent compound KH with X = H, SiH₃, Me, SiMe₃ and SnMe₃¹⁸⁰. Table 40 shows the theoretically predicted relative hydride affinities of the cations. It becomes obvious that SiMe₃ and particularly SnMe₃ have a large stabilizing effect on the 1-norbonyl cation. The calculated energies also show that the hyperconjugative stabilization of the SiMe₃
FIGURE 60. Schematic representation of the energy minima which were found on the EC₆H₇⁺ singlet potential energy surface. Relative energies are given in Table 39. Reprinted with permission from Reference 178. Copyright 1997 American Chemical Society

TABLE 39. Relative G2(MP2, SVP)⁴ isomer energies (kcal mol⁻¹) at 298 K of the cations shown in Figure 60⁵

<table>
<thead>
<tr>
<th>E</th>
<th>46E</th>
<th>47E</th>
<th>48E</th>
<th>49E</th>
<th>50E</th>
<th>51E</th>
<th>52E</th>
<th>53E</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0</td>
<td>6.9</td>
<td>6.9</td>
<td>50.2</td>
<td>66.2</td>
<td>97.0</td>
<td>—</td>
<td>36.8</td>
</tr>
<tr>
<td>Si</td>
<td>34.2</td>
<td>25.1</td>
<td>31.8</td>
<td>67.9</td>
<td>0</td>
<td>30.4</td>
<td>34.9</td>
<td>36.8</td>
</tr>
<tr>
<td>Ge</td>
<td>55.9</td>
<td>39.9</td>
<td>52.8</td>
<td>78.9</td>
<td>0</td>
<td>28.0</td>
<td>32.3</td>
<td>—</td>
</tr>
</tbody>
</table>

⁴G2(MP2, SVP) is an approximation scheme for obtaining correct total energies using QCISD(T) and MP2 calculations. For details see Reference 178.

⁵Reference 178.

³No energy minimum found.
3. Theoretical studies of organic germanium, tin and lead compounds

Theoretical studies of organic germanium, tin and lead compounds [251]

**FIGURE 61.** Bridged carbocations with group-14 substituents X which have been calculated in References 179 and 180. For the calculated energies see Table 40

**TABLE 40.** MP2/6-31G(d) calculated energies (kcal mol$^{-1}$) of substituted norbornyl cation $K^+$ (Figure 61) and $KH^a$

<table>
<thead>
<tr>
<th>Structure</th>
<th>$E(K^+) - E(KH)$ $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K^+ (X = H)$</td>
<td>0</td>
</tr>
<tr>
<td>$KH (X = H)$</td>
<td>0</td>
</tr>
<tr>
<td>$K^+ (X = SiH_3)$</td>
<td>$-3.0$</td>
</tr>
<tr>
<td>$KH (X = SiH_3)$</td>
<td>$-3.5$</td>
</tr>
<tr>
<td>$K^+ (X = Me)$</td>
<td>$-11.1$</td>
</tr>
<tr>
<td>$KH (X = SiMe_3)$</td>
<td>$-15.5$</td>
</tr>
<tr>
<td>$K^+ (X = SnMe_3)$</td>
<td>$-15.5$</td>
</tr>
</tbody>
</table>

$^a$Reference 180.  
$^b$Energies relative to $E(K^+, X = H) - E(KH, X = H)$, i.e. relative hydride affinities with respect to the parent ion.

The group is not well reproduced by the SiH$_3$ substituent. This is an important result because SiR$_3$ groups are often modeled in theoretical studies by SiH$_3$. The authors also discuss the different geometries and the electronic structure of the $K^+$ and $KH$ systems [180].

The geometries and relative energies of isomers of the (3-oxopropyl) trimethylstannane radical cation $Me_3Sn-CH_2CH_2CHO^+$ have been calculated at *ab initio* and DFT (B3LYP) levels of theory by Yoshida and Izawa [181]. The calculations were part of a combined experimental and theoretical study of the intramolecular assistance by carbonyl groups in electron transfer driven cleavage of C—Sn bonds. Figure 62 shows the structures of three energy minima on the PES. The cyclic isomers 54 and 55 are clearly lower in energy than structure 56.

The $\beta$- and $\gamma$-effects of group-14 elements were probed by Sugawara and Yoshida using intramolecular competition between $\gamma$-elimination of tin and $\beta$-elimination of Si, Ge and Sn in reactions of $\alpha$-acetoxy(arylmethyl)stannanes with allylmetals where the metal is Si, Ge or Sn [182]. In order to gain information about the stability of carbocations substituted by group-14 elements the authors carried out *ab initio* calculations at the MP2 level of theory. Figure 63 shows the optimized structures and relative energies of the cations $H_3SnCH_2CH_2CHCH_2EH_3^+$ ($E = Si, Ge, Sn$) which have been calculated. Two structures 57(E) and 58(E) were found for E = Sn, while three energy minima 57(E), 58(E) and 59(E) were found for E = Si, Ge. The energetically lowest lying form in all cases is structure 57(E). The three-membered cyclic structure 59(E) is a low-lying energy minimum for E = Si and an energetically rather high-lying isomer for E = Ge, while it is not an energy minimum for E = Sn [182].
Relativistic effects on the metal–carbon bond strengths of Me$_2$M, where M = Au$^-$, Hg, Tl$^+$ and Pb$^{2+}$, were studied by Schwerdtfeger$^{183}$. The author found that in Me$_2$Pb$^{2+}$ the BDEs of the Pb$^{2+}$–Me bonds increase by ca 15% and the force constant of the symmetric Me–Pb$^{2+}$–Me stretching mode by ca 20% when relativistic effects are included in the calculations.

The structures and stabilization energies of methyl anions X-CH$_2^-$ with main group substituents X from the first five periods have been investigated at correlated ab initio levels by El-Nahas and Schleyer$^{184}$. The work includes calculations of the anions H$_3$Ge–CH$_2^-$ and H$_3$Sn–CH$_2^-$ and the neutral parent compounds. The optimized geometries of the energy minima are shown in Figure 64. The structures have a pyramidal XCH$_2^-$ geometry. The inversion barrier of the CH$_2$ group is predicted to be 3.2 kcal mol$^{-1}$ for X = GeH$_3$ and 3.0 kcal mol$^{-1}$ for X = SnH$_3$. The EH$_3$ substituents stabilize the methyl anion relative to CH$_3^-$ by 19.7 kcal mol$^{-1}$ (E = Ge) and by 23.7 kcal mol$^{-1}$ (E = Sn)$^{184}$.

Negatively charged species of group-14 compounds have also been calculated by Anane et al. at the G2 level$^{185}$. The authors optimized the donor–acceptor complexes of the
FIGURE 63. Calculated energy minimum structures and relative energies at MP2 of the cations H₃SnCH₂CH₂CHCH₂EH₃⁺ (E = Si, Ge, Sn). Bond distances are in Å, angles in deg. Reprinted with permission from Reference 182. Copyright 2000 American Chemical Society.
FIGURE 63. (Continued)

FIGURE 64. Calculated energy minimum structures of H₃ECH₃ and H₃ECH₂⁻ at MP2. Bond distances are in Å, angles in deg. Reproduced by permission of John Wiley & Sons, Inc. from Reference 184
Lewis acids AlH₃ with the anionic Lewis bases EH₃⁻ (E = C, Si, Ge) and with neutral species AH₃ (A = N, P, As). The H₃Al–EH₃⁻ BDEs (Dₓ) at the G2 level are predicted to be 84.7 kcal mol⁻¹ (E = C), 54.4 kcal mol⁻¹ (E = Si) and 49.9 kcal mol⁻¹ (E = Ge).¹⁸⁵

The geometries of the cyclopentadienyl anions C₄H₄ESiH₃⁻ with E = C, Si, Ge, Sn have been optimized at the HF level by Freeman et al.¹⁸⁶. The calculated molecules were used as models for the methyl-substituted systems C₄Me₄ESiMe₃⁻. The X-ray structure analysis of the latter compound with E = Si was also reported. Table 41 gives the theoretically predicted relevant bond lengths and angles of C₄H₄ESiH₃⁻ and the experimental data for C₄Me₄GeSiMe₃⁻. The authors conclude that the heavier analogues of the Cp⁻ ring with E = Si, Ge, Sn are clearly not aromatic. This becomes obvious by the large alteration of the C–C bond lengths and the pyramidal arrangement of the substituents at the atom E.¹⁸⁶

3. Radicals

It is well known that molecules of the heavier main-group elements with unpaired electrons are usually more stable than the respective radicals of the first-row elements. Theoretical studies have been carried out which investigate the structures and energies of neutral molecules of germanium, tin and lead which have unpaired electrons. The group of Schiesser has been particularly active in the field. They published several papers which report about quantum chemical investigations of reactions of free radicals containing the heavier group-14 elements.¹⁸⁷–¹⁹⁴

The homolytic substitution reaction at sulfur, selenium and tellurium carrying EH₃ groups (E = C to Sn) was calculated by Schiesser and Smart at the QCISD//MP2 level.¹⁸⁷ Figure 65 shows the reactions which were studied. Figure 66 gives the optimized transition states for substitution of EH₃ by a methyl group and the calculated activation energies. The ΔE₁‡ values are the activation barriers with respect to CH₃YH + EH₃ (Y = S, Se, Te) and the ΔE₂‡ values are the barriers with respect to EH₃YH + CH₃. The trend of the activation energies with respect to atom E is Si > Ge > Sn and the trend with respect to

<table>
<thead>
<tr>
<th>E</th>
<th>C</th>
<th>Si</th>
<th>Ge</th>
<th>Sn</th>
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<td>104.5</td>
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<td>(100.1)</td>
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<td>1.358</td>
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<tr>
<td>d(C₂-C₃)</td>
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<td>1.477</td>
<td>1.484(1.46)</td>
<td>1.493</td>
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</table>

aAt the RHF level. From Reference 186.
bExperimental values are given in parentheses.
cOut-of-plane bonding angle of SiH₃.
Y is S > Se > Te; i.e. the activation barrier becomes lower when atom \( E \) or \( Y \) becomes heavier\(^{187} \).

Schiesser et al. also calculated at the HF and correlated (MP2 and QCISD) levels the reaction profiles of some free-radical homolytic substitution reactions at silicon, germanium and tin centers\(^{188} \). The reactions which were studied are the methyl and hydrogen substitution of \( EH_3 \) and \( EM_3 \) by hydrogen and methyl radicals, respectively. Figure 67 gives the optimized structures of the transition states and the calculated activation energies \( \Delta E_1^\ddagger \). The authors found shallow energy minima \( Me-EH_3-Me \) at correlated levels with pentacoordinated atoms \( E \) which are slightly \((<1 \text{ kcal mol}^{-1}) \) lower in energy than the transition states \( Me-EH_3-Me^\ddagger \). The pentacoordinated structures become higher in energy than the transition states when ZPE corrections are included\(^{188} \). The calculated barriers for substituting hydrogen by methyl show the trend \( Ge > Si > Sn \); i.e. they do not follow the size of the atoms. The activation barrier for breaking the \( E- Me \) bonds shows the regular trend \( Si > Ge > Sn \). The differences between the values for \( Si \) and \( Ge \) are, however, much less than between \( Ge \) and \( Sn \).

Schiesser and Skidmore reported a combined experimental/theoretical study of free-radical substitution reactions of aryltellurides with stannyl, germyl and silyl radicals\(^{189} \). The authors calculated at the QCISD/MP2 level the adducts, products and transition states of the reactions which are shown in Figure 68. The optimized geometries of the transition states and the activation barriers for the forward \((\Delta E_1^\ddagger)\) and reverse \((\Delta E_2^\ddagger)\) reactions are shown in Figure 69. The related substitution reactions with methyl radical were studied before (see Figure 66). The calculated activation barriers for the forward and reverse reactions show that the trend for the group-14 groups \( EH_3 \) is \( Si > Ge > Sn \). The trend for the alkyl groups is \( Me < Et < i-Pr \) for the forward reactions while the opposite trend \( Me < Et < i-Pr \) is predicted for the reverse reaction\(^{189} \).

Schiesser and Styles investigated in another theoretical study at the QCISD//MP2 level the reaction course of the 1,2-migration of silyl, germyl and stannyl substituents of radicals \( H_3E-CH_2X^* \) to \( H_3EX-CH_2^* \) \((X=CH_2, NH, O; E=Si, Ge, Sn)\)^{190}. Figure 70 gives the optimized geometries of the transition states and the calculated reaction barriers. The degenerate rearrangement of \( H_3ECH_2CH_2^* \) has nearly the same activation energy for \( E=Si \) and \( E=Ge \) while the reaction barrier for the stannyl group is lower. The forward reactions of the aminyl and oxyl radicals \( H_3E-CH_2NH^* \) and \( H_3E-CH_2O^* \) yielding \( H_3ENH-CH_2^* \) and \( H_3EO-CH_2^* \), respectively, have lower barriers for rearrangements than the methylene analogues. Thus, the activation barrier of the forward reactions for rearrangement of \( H_3EX-CH_2^* \) show the trend \( E=Ge > Si > Sn \) and \( X=CH_2 > NH > O\)^{190}. Note that the geometry and the energy of the transition structure of the stannyloxo...
FIGURE 66. Optimized transition states at MP2 for the homolytic substitution reaction of the CH$_3$ substituent in HYCH$_3$ (Y = S, Se, Te) by H$_3$E$^*$ (E = Si, Ge, Sn). Bond distances are in Å, angles in deg. The calculated activation energies (kcal mol$^{-1}$) at QCISD//MP2 refer to the forward reaction ($\Delta E_1^{\dagger}$) and the reverse reaction ($\Delta E_2^{\dagger}$), respectively (see Figure 65). Reprinted from Reference 187 with permission from Elsevier Science.
\( \theta \) (SiTeH) = 88.1  
\( \theta \) (CTeH) = 85.4  
\( \omega \) (CTeHSi) = 152.3  
\( \Delta E_1^{\dagger} = 2.3 \)  
\( \Delta E_2^{\dagger} = 9.3 \)  

\( \theta \) (GeTeH) = 88.5  
\( \theta \) (CTeH) = 85.5  
\( \omega \) (CTeHGe) = 157.2  
\( \Delta E_1^{\dagger} = 4.8 \)  
\( \Delta E_2^{\dagger} = 7.2 \)  

\( \theta \) (SnTeH) = 88.5  
\( \theta \) (CTeH) = 85.9  
\( \omega \) (CTeHSn) = 161.7  
\( \Delta E_1^{\dagger} = 7.2 \)  
\( \Delta E_2^{\dagger} = 6.7 \)  

FIGURE 66. (Continued)
3. Theoretical studies of organic germanium, tin and lead compounds

![Figure 67](image)

**FIGURE 67.** Optimized transition states at MP2 for the homolytic methyl and hydrogen substitution reaction of EH$_4$ and EH$_3$Me by H$^*$ and Me$^*$ (E = Si, Ge, Sn). Bond distances are in Å. The calculated activation energies (kcal mol$^{-1}$) at QCISD//MP2 refer in the case of (b) to the forward reaction ($\Delta E_1^{\dagger}$) and the reverse reaction ($\Delta E_2^{\dagger}$), respectively. Reproduced by permission of The Royal Society of Chemistry from Reference 188

![Figure 68](image)

**FIGURE 68.** Free-radical substitution reactions of hydridotellurides HTeEH$_3$ (E = Si, Ge, Sn) and HTeSi(SiH$_3$)$_3$ with alkyl groups R$^*$. The optimized transition states and calculated activation energies are given in Figure 69
FIGURE 69. Optimized transition states at MP2 for the homolytic free-radical substitution reactions shown in Figure 68 of hydridotellurides HTeEH₃ (E = Si, Ge, Sn) and HTeSi(SiH₃)₃ with alkyl groups. Bond distances are in Å. The calculated activation energies (kcal mol⁻¹) at QCISD//MP2 refer to the forward reaction (ΔE₁‡) and the reverse reaction (ΔE₂‡), respectively. Reprinted from Reference 189 with permission from Elsevier Science.
species H$_3$SnCH$_2$O$^•$ is given only at the HF level. The results of the other species show that the inclusion of correlation effects at QCISD lowers the barriers of the stannyl radicals by 5–8 kcal mol$^{-1}$.

Another paper from the Schiesser group by Dakternieks et al. reported about ab initio and semiempirical calculations of the hydrogen abstraction from R$_3$SnH by alkyl radicals R$^•$\textsuperscript{191}. Figure 71 shows the investigated reactions. Figure 72 gives the optimized transition states and the activation barriers for the forward and reverse reactions at the QCISD//MP2 level of theory. It becomes obvious that larger alkyl groups R decrease the activation barrier for hydrogen abstraction from R$_3$SnH with the order R = Me > Et > i-Pr > t-Bu\textsuperscript{191}.

Hydrogen abstraction reactions from trialkylsilanes and trialkylgermanes by hydrogen atom or alkyl radicals are the topic of another lengthy theoretical study at ab initio and semiempirical levels by Dakternieks et al.\textsuperscript{192}. The alkyl groups which were considered are methyl, ethyl, isopropyl and tert-butyl. The calculated activation barriers for hydrogen abstraction from silicon were found to be higher than from germanium. Table 42 gives the theoretically predicted activation energies for the forward and reverse hydrogen abstraction reactions of R$_3$GeH with R$^•$. The forward reactions are strongly exothermic and have lower barriers than the reverse reactions because the R$^•$–H bonds are stronger than the Ge–H bonds. Methyl substituents at germanium have little influence on the activation barriers of the forward reaction, and their effect on the reverse reaction is also rather small. The trend of the activation barriers for the forward reaction with different radicals is Me > Et > H > i-Pr > t-Bu\textsuperscript{192}.

A third theoretical paper by Dakternieks et al. about hydrogen abstraction reactions calculated the equilibrium structures and transition states for hydrogen transfer between silyl, germyl and stannyl radicals and their hydrides\textsuperscript{193}. Figure 73 shows the transition states for the homonuclear and heteronuclear hydrogen transfer from EH$_4$ to EH$_3^•$ (E = Si, Ge, Sn). The energy barrier of the homonuclear hydrogen exchange shows the expected trend: Si > Ge > Sn. The barriers of the heteronuclear reactions between EH$_4$ and E'H$_3^•$
FIGURE 70. Calculated transition states at MP2 of the 1,2-migration of silyl, germyl and stannyl substituents of radicals H\textsubscript{3}E-CH\textsubscript{2}X to H\textsubscript{3}EX-CH\textsubscript{2} (X = CH\textsubscript{2}, NH, O; E = Si, Ge, Sn). Bond distances are in Å, angles in deg. The calculated activation energies (kcal mol\textsuperscript{-1}) at QCISD/MP2 refer to the forward reaction (\(\Delta E\textsuperscript{‡}\)) and the reverse reaction (\(\Delta E\textsuperscript{‡}\)), respectively. Reproduced by permission of The Royal Society of Chemistry from Reference 190.
are higher than those of the homonuclear reactions of elements E and E′ if the reaction is endothermic (ΔE₁‡ in Figure 73) and they are lower if the reaction is exothermic (ΔE₂‡ in Figure 73). Figure 74 shows the transition state structures for the homonuclear and heteronuclear hydrogen transfer between Me₂EH and H₃E′ (forward reaction) and between EH₄ and Me₂E′ (reverse reaction). The calculated activation barriers for the forward reaction ΔE₁‡ and for the reverse reaction ΔE₂‡ are also given. Note that the energies of the methyl-substituted systems are only given at MP2 while the parent systems were also calculated at QCISD. The trend of the theoretically predicted activation barriers is Si > Ge > Sn. The authors discuss also the geometries of the transition states.

The latest paper about radical reactions of group-14 compounds by the Schiesser group reports *ab initio* and DFT calculations of the frontside and backside radical substitution reactions of H₃EE′H₃ with E′H₃*: (E, E′, E″ = Si, Ge, Sn)¹⁹⁴. Figure 75 shows schematically the structures of the transition states for the backside attack (transition state L) and for the frontside attack (transition state M) which have been calculated at different levels of theory. Table 43 gives the theoretically predicted activation energies. The first three entries give the calculated values for the degenerate substitution reaction of the systems with E = E′ = E″. At the highest level of theory (CCSD(T)/DZP/MP2/DZP) it is found that the silicon and germanium compounds favor the backside attack by 2–3 kcal mol⁻¹ over the frontside attack, while the frontside and backside attack of the stannyl compounds are nearly degenerate. Calculations of the silicon systems at CCSD(T) with larger basis sets up to cc-pVDZ do not change the results significantly¹⁹⁴. Note that the B3LYP data for the activation energies in Table 43 are always too low.

The next six entries in Table 43 give the activation barriers of the degenerate substitution reactions where E = E″ with different central atoms E′. It is found that the backside attack is more favored than the frontside attack by 3–4 kcal mol⁻¹ (CCSD(T)/MP2) except when E = E″ = Sn. The remaining 9 entries give the barriers for the frontside and backside nondegenerate substitution of EH₃ groups by E″H₃. Table 43 gives for L and M the activation barriers for the forward reaction (ΔE₁‡ with respect to H₃EE′H₃ + E″H₃*) and for the reverse reaction (ΔE₂‡ with respect to H₃E″E′H₃ + EH₃*). The backside attack is in most cases favored over the frontside attack. In a few cases involving stannyl

![Figure 71. Schematic representation of the reaction profile for some hydrogen abstraction reactions of trialkylstannane with hydrogen and alkyl radicals](image-url)
FIGURE 72. Calculated transition states at MP2 of the hydrogen abstraction reactions of trialkyl-
stannane with hydrogen and alkyl radicals which are shown in Figure 71. Bond distances are in Å, angles in deg. The calculated activation energies (kcal mol⁻¹) at QCISD//MP2 (MP2 values in parentheses) refer to the forward reaction (ΔE₁‡) and the reverse reaction (ΔE₂‡), respectively. Reproduced by permission of The Royal Society of Chemistry from Reference 191.
TABLE 42. Calculated energy barriers (kcal mol\(^{-1}\)) at QCISD//MP2 for the forward ($\Delta E_1^\ddagger$) and reverse ($\Delta E_2^\ddagger$) hydrogen atom abstraction reactions of germanes by hydrogen atoms and various alkyl radicals R\(^a\)

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<tr>
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\(^a\)Reference 192.

groups, however, the frontside attack becomes competitive and is even predicted to be slightly more favorable than the backside attack. The authors tried also to locate transition states for the frontside attack of the systems involving the methyl radical. However, except for reactions of methylstannane they were unable to locate transition states for frontside attack at correlated levels of theory\(^{194}\).

Small germyl radicals in the ground state and first excited state have been calculated using DFT (B3PW91) and \textit{ab initio} methods by BelBruno\(^{195}\). The author reports the optimized geometries of the doublet ground states and quartet excited states of GeH, GeCH\(_3\) and GeC\(_2\)H\(_5\). An experimental and theoretical study of gaseous products in the radiolysis of GeH\(_4\)/C\(_2\)H\(_4\) mixtures was reported by Antoniotti et al.\(^{196}\). The authors carried out \textit{ab initio} calculations at the QCISD(T)/6-311G(3df,2p) level using MP2/DZP.
FIGURE 73. Calculated transition states at MP2 of the hydrogen abstraction reactions of \( \text{EH}_4 \) by \( \text{EH}_3^* \) radicals \( (E = \text{Si}, \text{Ge}, \text{Sn}) \). Bond distances are in \( \text{Å} \), angles in \( \text{deg} \). The calculated activation energies (kcal mol\(^{-1}\)) at QCISD/MP2 (MP2 values in parentheses) refer to the forward reaction \( (\Delta E_1^{\dagger}) \) and the reverse reaction \( (\Delta E_2^{\dagger}) \), respectively. Reprinted with permission from Reference 193. Copyright 1998 American Chemical Society

optimized geometries of \( \text{GeC}_2\text{H}_n \) \( (n = 4–7) \) molecules. Figures 76–79 show the geometries and relative energies of the stationary points on the PES. Three energy minima were found for \( \text{GeC}_2\text{H}_4 \) (Figure 76). The singlet state of germylidenecyclopropane 60 is predicted to be the global energy minimum followed by the triplet state 61 which is 17.6 kcal mol\(^{-1}\) higher in energy. Structure 62 in Figure 76 is the side-on bonded complex of germylene with acetylene and is 38.4 kcal mol\(^{-1}\) less stable than 60. The authors do not report about germacyclopropene.\(^{196}\) The earlier work by Boatz et al. which was discussed above gave at the MP2 level only the \( C_{2v} \) symmetric structure of germacyclopropane...
as an energy minimum while the complex 62 was not found as an energy minimum structure88.

Five energy minima and one transition state which are shown in Figure 77 were found on the GeC₂H₅ doublet PES¹⁹⁵. Structures 63 and 64 are rotational isomers with the
connectivity H₂Ge—CH—CH₂ which are energetically nearly degenerate. Structure 65 is the transition state for the interconversion of 63 and 64. The other energy minima 66, 67 and 68 are 21–27 kcal mol⁻¹ higher in energy than 63.

Five singlets and four triplets have been found as stationary points on the GeC₂H₆ PES (Figure 78). All singlets are lower in energy than the triplets. Germylethene 69 is the global energy minimum. Structure 70 is the transition state for rotation about the Ge–C bond. Germylethane 71 is only 4.3 kcal mol⁻¹ higher in energy than 69. Germacyclopropane 72 and 1-germapropene 73 are 10.0 and 14.7 kcal mol⁻¹ less stable than 69. The triplet states 74, 75 and 77 are high-lying energy minima on the GeC₂H₆ PES. The triplet structure 76 is a transition state.
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$^\dagger$Reference 194.

$^\ddagger$Values for L refer to backside attack, values for M refer to frontside attack (see Figure 75).
Three energy minima and one transition state were located on the GeC$_2$H$_7$ doublet PES (Figure 79). The germyleneethane radical 78 is clearly the lowest lying form while 79 and 80 are 16–17 kcal mol$^{-1}$ higher in energy. Structure 81 is a transition state. The authors calculated also the reaction energies of possible reactions of GeH$_n$ ($n = 0–3$) with ethylene. The results are shown in Table 44.

V. CLOSING REMARKS

This review of the theoretical literature published since 1990 about organic germanium, tin and lead compounds demonstrates how important quantum chemical methods have become in modern chemical research. Prior to 1990, molecules containing heavier atoms than third-row elements were only rarely treated with the goal of obtaining accurate data about the geometry and energy of the compounds. The general acceptance of pseudopotentials and DFT as reliable quantum chemical methods, together with
FIGURE 77. Optimized energy minima \((i = 0)\) and transition states \((i = 1)\) at MP2 on the doublet PES of GeC\(_2\)H\(_5\). Calculated relative energies at QCISD(T). Bond distances are in Å, angles in deg. Reproduced by permission of The Royal Society of Chemistry from Reference 195.
3. Theoretical studies of organic germanium, tin and lead compounds

![Diagrams of optimized energy minima and transition states at MP2 on the singlet and triplet PES of GeC<sub>2</sub>H<sub>6</sub>. Calculated relative energies at QCISD(T). Bond distances are in Å, angles in deg. Reproduced by permission of The Royal Society of Chemistry from Reference 195](image_url)
ongoing developments of faster algorithms and computers, made it possible that information about heavier group-14 compounds produced by quantum chemical calculations is almost routinely used as complementary to experimental research. This is particularly evident in those numerous studies where both experimental and theoretical methods are used for the investigations. Relativistic effects and the large number of core electrons no longer present an insuperable obstacle when calculating molecular structures or reactions pathways of heavy-atom molecules. It is to be expected that the number of theoretical studies of organometallic compounds of Ge, Sn and Pb will further increase in the next decade.

**VI. ACKNOWLEDGMENTS**

This work was financially supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.
FIGURE 79. Optimized energy minima \((i = 0)\) and transition states \((i = 1)\) at MP2 on the doublet PES of GeC₂H₇. Calculated relative energies at QCISD(T). Bond distances are in Å, angles in deg. Reproduced by permission of The Royal Society of Chemistry from Reference 195.
TABLE 44. Calculated enthalpies of reactions of GeHₙ with C₂H₄ leading to the most stable products shown in Figures 76–79

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<td>GeH₃ + C₂H₄ → GeC₂H₇</td>
<td>-25.2</td>
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*Reference 196.

VII. REFERENCES


3. Theoretical studies of organic germanium, tin and lead compounds


13. Selective examples are:


3. Theoretical studies of organic germanium, tin and lead compounds

3. Theoretical studies of organic germanium, tin and lead compounds 281


164. (b) P. Antoniotti and G. Tonachini, Organometallics, 18, 4539 (1998).


CHAPTER 2

Similarities and differences of organic compounds of germanium, tin and lead

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I. INTRODUCTION

The problem of the similarity and difference of organic compounds of the heavy silicon subgroup elements—germanium, tin and lead—has many aspects. The four aspects listed below seem to us to be especially important and interesting.

1. Similarities and differences between Ge, Sn, Pb (M) atoms and their M—Y bonds (Y = inorganic, organic or organometallic substituents). In some cases the specific character of the M atom and the M—Y bonds is more clearly seen when compared with properties and bonds of carbon and especially silicon atoms—the lighter elements of the group 14 column of the periodic table. The peculiarities of M atoms and M—Y bonds determine to a considerable extent the similarity and difference of the physical properties and chemical behaviour of organic compounds of the elements in question.

2. Classical and recent quantum-chemical concepts about the electronic structure of M element compounds. The dependence of intramolecular electronic, steric and stereoelectronic interactions on the nature of the M atom and the M—Y bonds.

3. Similarities and differences of electronic effects of the R₃M groups (R = organic substituent) in compounds of the R₃MX (X = an atom with at least one unshared electron pair—halogen, O=, S=, N< etc.) and R₃MRπ (Rπ = an aromatic or α,β-unsaturated group) type. The intramolecular electronic interactions in these compounds are determined by the magnitude and sign of charge which is induced on the reaction centre Rπ or X by physical or chemical influence. Such dependencies allow one to verify the existing theoretical concepts about the mechanism of these intramolecular electronic interactions. Therefore, the physical properties of R₃MRπ and R₃MX substances as well as of their molecular complexes allow one to model heterolytic reactions of these compounds.

4. Similarities and differences of chemical reactions of organic M element derivatives. The specific character of these processes becomes apparent in comparison with the analogous reactions of compounds of the lighter elements of group 14—carbon and silicon. Unfortunately, so far there are no systematic investigations of the reactivity of R₃MRπ and R₃MX type compounds as a function of M (C, Si, Ge, Sn, Pb) based on a representative sample of R, Rπ and X groups. Only such an approach will enable one to establish the validity of existing theoretical concepts of the electronic structure of silicon subgroup element compounds for a detailed description of their reactivity and comparison of chemical and physical properties. Until now only isolated fragments of this complete idealized picture have been published, some of which we consider in this chapter.

We shall take a brief look at some characteristics of M (Ge, Sn and Pb) atoms in comparison with Si and C. In the ground state the electron configurations of C, Si, Ge, Sn and Pb atoms are [He] 2s²2p², [Ne] 3s²3p², [Ar]3d¹⁰4s²4p², [Kr]4d¹⁰5s²5p² and [Xe]5d¹⁰6s²⁶p², respectively.

The atomic covalent radius (one half of the M—M distance) has been used for a long time for estimates of the nature of chemical bonds. Its magnitude correlates with the M—M bond energy. The notion of the van der Waals radius of an atom is ambiguous.

The sum of van der Waals radii of two atoms is defined in crystallography as the minimum distance at which they can approach each other.

The covalent and van der Waals radii of M atoms increase as their atomic number rises (Table 1). When going from C to Si the covalent atomic radius increases sharply, and it increases gradually from Si to Pb. The value of the van der Waals radius of lead (2.02 Å)
stands out in the general trend. Owing to their large radii, the atoms of Ge, Sn and Pb are sterically accessible for nucleophilic interaction and it favours their transition to the hypervalent state.

The first ionization potential \( I_p \) (the energy required for removal of one electron from the neutral atom) of the \( M \) (Ge, Sn, Pb) atoms is less than that of Si and, the more so, of C. Therefore, the \( M \) element compounds are characterized by greater electrophilicity in comparison with isostructural derivatives of C and Si.

According to Pauling, the electronegativity of an atom in the molecule is defined by its capacity to pull electrons from substituents bonded to it \(^1\). It was established later that the electronegativity depends also on the valence state (the hybridization) of the atom\(^4\), \(^6\), \(^8\). Carbon is the most electronegative among the group 14 elements (Table 1). As the atomic number increases, the electronegativity of the group 14 elements changes non-monotonically (see, however, Reference 1). The electronegativity values and series listed in Table 1 can change sharply under the influence of intramolecular resonance interactions, e.g. by varying the substituents bonded to C, Si and M atoms\(^10\).

The refraction \( R \) and polarizability \( \alpha \) \((\frac{3}{4\pi N_A})R\), where \( N_A \) is the Avogadro number, characterize the deformability of the atom’s electron shell under external influence (charge, electric field). The atomic and covalent refraction relate to isolated atoms and to atoms involved in a covalent bond, respectively. The \( R \) and \( \alpha \) values grow as the atomic number of \( M \) increases. The high polarizability of \( M \) atoms and of \( M/X \) bonds is an important property of compounds of heavier group 14 elements. The sensitivity of conjugation in the molecule to changes in the charge on the reaction centre grows as the polarizability of the central \( M \) atom increases; see, for example, Reference 11.

We shall now consider some properties of \( M/X \) bonds (\( M = \text{Ge, Sn, Pb} \)) in comparison with \( Si/X \) and \( C/X \). As the atomic number of \( M \) increases, these bond distances \( d \) (Table 2) become longer. It is caused by the increase in the covalent radius of the group 14 element as its atomic number rises. The \( d \) values of the \( Me_3M/Me \) and \( Me_3M/MMe_3 \) bonds coincide to within 0.05 Å with the sum of covalent radii of the atoms forming this bond. The \( Si/Cl \) bond distances in \( SiCl_4 \) are 0.15 Å shorter than the sum of covalent radii of \( Si \) and \( Cl \) atoms. As the atomic number of \( M \) increases, the difference between the experimental \( d \) values in \( MCl_4 \) molecules and the expected ones (based on the sum of the

---

**Table 1. Selected properties of C, Si, Ge, Sn and Pb atoms**

<table>
<thead>
<tr>
<th>Property</th>
<th>C</th>
<th>Si</th>
<th>Ge</th>
<th>Sn</th>
<th>Pb</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>6</td>
<td>14</td>
<td>32</td>
<td>50</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>Atomic weight</td>
<td>12.011</td>
<td>28.0855</td>
<td>72.59</td>
<td>118.69</td>
<td>207.2</td>
<td>2</td>
</tr>
<tr>
<td>Covalent radius (Å)</td>
<td>0.77</td>
<td>1.17</td>
<td>1.22</td>
<td>1.42</td>
<td>1.48</td>
<td>4</td>
</tr>
<tr>
<td>van der Waals radius (Å)</td>
<td>1.70</td>
<td>2.10</td>
<td>2.15</td>
<td>2.17</td>
<td>2.02</td>
<td>5</td>
</tr>
<tr>
<td>Ionization potential (eV)</td>
<td>11.26</td>
<td>8.15</td>
<td>7.88</td>
<td>7.34</td>
<td>7.42</td>
<td>2</td>
</tr>
<tr>
<td>Electronegativity</td>
<td>2.60</td>
<td>1.90</td>
<td>2.00</td>
<td>1.93</td>
<td>2.45</td>
<td>6</td>
</tr>
<tr>
<td>Atomic refraction (cm³ mol⁻¹)</td>
<td>2.5</td>
<td>7.5</td>
<td>9.7</td>
<td>13.3</td>
<td>34.3</td>
<td>9</td>
</tr>
<tr>
<td>Covalent refraction (cm³ mol⁻¹)</td>
<td>2.1</td>
<td>9</td>
<td>11</td>
<td>16.5</td>
<td>19</td>
<td>8</td>
</tr>
<tr>
<td>Polarizability ((10⁻²⁴ cm³ mol⁻¹))</td>
<td>0.82</td>
<td>3.59</td>
<td>4.39</td>
<td>6.34</td>
<td>7.10</td>
<td>2</td>
</tr>
</tbody>
</table>
TABLE 2. Selected bond distance (Å) data

<table>
<thead>
<tr>
<th>Bond</th>
<th>C</th>
<th>Si</th>
<th>Ge</th>
<th>Sn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>D₃M−H⁹</td>
<td>1.092</td>
<td>1.480</td>
<td>1.532</td>
<td>1.701</td>
<td>—</td>
</tr>
<tr>
<td>Me₃M−CH₃       b</td>
<td>1.539</td>
<td>1.875</td>
<td>1.980</td>
<td>2.143</td>
<td>2.238</td>
</tr>
<tr>
<td>Me₃M−(C≡CH) b</td>
<td>1.498</td>
<td>1.826</td>
<td>1.896</td>
<td>2.082</td>
<td>—</td>
</tr>
<tr>
<td>M−N d</td>
<td>1.451</td>
<td>1.734</td>
<td>1.836</td>
<td>2.038</td>
<td>2.082</td>
</tr>
<tr>
<td>M−O g</td>
<td>1.416</td>
<td>1.631</td>
<td>1.766</td>
<td>1.940</td>
<td>1.940</td>
</tr>
<tr>
<td>Me₃M−Cl b</td>
<td>1.803</td>
<td>2.022</td>
<td>2.170</td>
<td>2.37</td>
<td>2.706</td>
</tr>
<tr>
<td>Me₃M−Br b</td>
<td>1.94</td>
<td>2.235</td>
<td>2.323</td>
<td>2.49</td>
<td>2.852</td>
</tr>
<tr>
<td>I₃M−I a</td>
<td>2.15</td>
<td>2.43</td>
<td>2.50</td>
<td>2.64</td>
<td>—</td>
</tr>
<tr>
<td>Me₃M−MMe₃</td>
<td>1.582</td>
<td>2.340</td>
<td>2.403</td>
<td>2.776</td>
<td>2.88</td>
</tr>
</tbody>
</table>

aReference 12.
bReference 13.
cMeasured for H₃Ge−(C≡CH).
dMeasured for (H₃M)₃N (M = C, Si, Ge) and (Me₃Sn)₃N compounds.
eReference 14.
fReference 15.
gMeasured for (H₃M)₂O (M = C, Si, Ge) and (Me₃Sn)₂O compounds.
hMeasured for H₃GeGeH₃ (Reference 16).
iReference 17.
jReference 18.

covalent radii) diminishes (0.12, 0.09 and ca 0.04 Å for M = Ge, Sn and Pb, respectively). The shortened interatomic distances in silicon halogenides led to the hypothesis of d–n conjugation between the 3d-orbitals of Si and the unshared electron pairs of the halogen atom. Modern ideas of conjugation in compounds of the silicon subgroup elements are discussed in Section II.

The electric dipole moment, $\bar{\mu}$, of an electroneutral molecule, $\bar{\mu} = q\bar{I}$ (where $\bar{I}$ is the radius vector directed from the centre of gravity of negative charges to the centre of gravity of positive charges and $q$ is the absolute value of each charge), reflects its polarity. The quantity $\bar{\mu}$ may be represented as a vector sum of dipole moments of separate bonds: $\bar{\mu} = \sum_{i=1}^{n} \mu_i$. The $\mu_i$ values consist of several components. Therefore, the calculation of atom charges on the basis of $\bar{\mu}$ and $\mu_i$ values is a complicated problem. The $\mu_i$ values also depend on the electronic effects of the substituents attached to the bond in question. The dipole moments of five series of isostructural compounds of group 14 elements are listed in Table 3. These compounds may be divided into two types.

For the compounds of the first type (Me₃MSPh and Me₃MSMMe₃) the $\mu$ value increases as the atomic number of M increases. It correlates well with one of the electronegativity scales of the M atoms. For the compounds of the second type (Me₃MOMMe₃, Me₃MCl, Me₃MBr) the $\mu$ value decreases or does not virtually vary as M changes from C to Si. It is contradictory to the electronegativity values of the C and Si atoms. Based on the minimum electronegativity of Si among all of the group 14 elements, the Si compounds should have the highest $\mu$ values. However, the dipole moments of Si compounds are in fact the smallest. When M changes further from Si to Ge, Sn, Pb, the $\mu$ value grows. This does not correlate with some of the electronegativity scales. The traditional explanation of these anomalies in the $\mu$ values is based on the hypothesis of d–n conjugation.
2. Similarities and differences of organic compounds of germanium, tin and lead

### TABLE 3. Dipole moments ($D$) of some compounds

<table>
<thead>
<tr>
<th>Series</th>
<th>C</th>
<th>Si</th>
<th>Ge</th>
<th>Sn</th>
<th>Pb</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me$_3$MOMMe$_3$</td>
<td>1.20</td>
<td>0.78</td>
<td>1.41</td>
<td>1.60</td>
<td>—</td>
<td>20</td>
</tr>
<tr>
<td>Me$_3$MSPh</td>
<td>1.49</td>
<td>1.76</td>
<td>2.18</td>
<td>2.58</td>
<td>3.20</td>
<td>21</td>
</tr>
<tr>
<td>Me$_3$MSMMMe$_3$</td>
<td>1.52</td>
<td>1.75</td>
<td>2.18</td>
<td>2.62</td>
<td>3.08</td>
<td>21</td>
</tr>
<tr>
<td>Me$_3$MCl</td>
<td>2.18</td>
<td>2.13</td>
<td>2.91</td>
<td>3.57</td>
<td>4.82</td>
<td>22</td>
</tr>
<tr>
<td>Me$_3$MBr</td>
<td>2.24</td>
<td>2.28</td>
<td>2.98</td>
<td>3.61</td>
<td>4.46$^a$</td>
<td>22</td>
</tr>
</tbody>
</table>

$^a$Measured for Et$_3$PbBr (Reference 23).

### TABLE 4. Polarity of M−X bonds in MX$_4$ molecules$^a$

<table>
<thead>
<tr>
<th>X</th>
<th>C</th>
<th>Si</th>
<th>Ge</th>
<th>Sn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>27</td>
<td>44</td>
<td>42</td>
<td>42</td>
<td>39</td>
</tr>
<tr>
<td>Cl</td>
<td>6</td>
<td>22</td>
<td>19</td>
<td>19</td>
<td>17</td>
</tr>
<tr>
<td>Br</td>
<td>3</td>
<td>17</td>
<td>14</td>
<td>14</td>
<td>12</td>
</tr>
<tr>
<td>I</td>
<td>0</td>
<td>10</td>
<td>9</td>
<td>9</td>
<td>6</td>
</tr>
</tbody>
</table>

$^a$In percent, relative to a hypothetical pure ionic bond. From Reference 8.

According to Pauling$^1$, the polarity $p$ of a chemical bond is the measure of its ionicity. It is related to the dipole moment $\mu_i$ by the equation: $p = \mu_i/d$, where $d$ is the interatomic distance. The polarity of M−X bonds in MX$_4$ molecules$^8$ is illustrated in Table 4. The polarity of a specific M−X bond increases significantly as M changes from C to Si, and it diminishes slightly on going from Si to Ge, Sn and Pb. At the same time, the polarity of a specific M−X bond decreases sharply as the atomic number of the halogen X increases.

The refraction ($R_D$) and polarizability ($\alpha$) are important properties of M−X bonds. The $R_D$ values are not universal, because the refraction magnitude depends on the type of substituents attached to a given bond. As a rule, $R_D$ and $\alpha$ values of M−X bonds rise as the atomic number of the M element increases. Thus, $R_D$ values of M−C$_{Alk}$ bonds for M = C, Si, Ge, Sn and Pb are 1.30, 2.47, 3.05, 4.17 and 5.25 cm$^3$ mol$^{-1}$, respectively$^8$. The $R_D$ values of M−F bonds (M = C, Si, Ge) change non-monotonically as the atomic number of M atom increases. This may be due to the polarizability anisotropy of these bonds$^{24}$. The polarizability anisotropy ($\gamma$) of a $\sigma$-bond is the difference of polarizabilities along and perpendicular to the bond axis. $\gamma$ values, except for M−F bonds, increase as the atomic number of M increases. For example, the $\gamma$ values of M−Cl bonds in MCl$_4$ for M = C, Si, Ge, Sn and Pb are 2.40, 3.05, 4.24, 4.96 and 6.22 Å$^3$, respectively$^{25}$. Thus, M−X bonds of heavy elements of group 14 are characterized by higher polarizability and polarizability anisotropy in comparison with the corresponding Si−X and C−X bonds.

It appears from the above that attempts to consider the nature of M−X bonds (M = Si, Ge, Sn, Pb) in analogy to C−X bonds on the basis of simple electronegativity usually fail. A deeper understanding of the observed trends is possible only on the basis of modern concepts on the electronic structure of compounds of the silicon subgroup elements.
II. ELECTRONIC STRUCTURE

In the second half of the 20th century, numerous physical and chemical investigations were conducted. They suggest that the electronic structure of isostructural compounds of carbon on the one hand and of silicon subgroup elements on the other differ fundamentally (see, for example, References 26–29). This difference is more clearly manifested in various conjugation effects which are discussed below. R₃M substituents in compounds of the type R₃MR₇ and R₃MX (M = Si, Ge, Sn, Pb; for the R, R₇ and X symbols, see Section I), unlike in R₃MCH₂R₇, have two resonance effects with respect to reaction centres R₇ and X — both as donor and as acceptor. Depending on the atomic number of the M element, these effects change in the following way¹⁰, 25, 30–34.

1. Resonance acceptor effect of R₃M substituents towards R₇ (d–π conjugation) and X (d–n conjugation) decreases as M changes in the order: Si > Ge > Sn > Pb. The question whether the R = Pb group still has resonance acceptor properties is under debate.

2. The resonance donor effect of R₃M substituents towards R₇ (σ–π conjugation), shown schematically in 1, increases as M changes in the order: C < Si < Ge < Sn < Pb. One can observe a weak σ–π conjugation effect even in organic compounds.

\[
\begin{align*}
R & \quad \text{M} \quad \text{CH} = \text{CH}_2 \\
R & \quad \text{R} \\
\end{align*}
\]

(1)

3. The resonance donor effect of R₃M substituents towards X (σ–n conjugation), shown schematically in 2, increases as M changes in the order: Si < Ge < Sn < Pb. The σ–n conjugation effect (unlike σ–π conjugation) was disregarded for a long time, though there were indications of its existence³⁰. The importance of this effect was demonstrated recently³¹.

\[
\begin{align*}
R & \quad \text{M} \quad \hat{S} \\
R & \quad \text{R} \\
\end{align*}
\]

(2)

4. The R₃MCH₂ substituent has only a donor effect in R₃MCH₂R₇ molecules towards R₇ (σ–π conjugation), shown schematically in 3. It is enhanced as M changes in the series: C < Si < Ge < Sn < Pb³².

\[
\begin{align*}
\text{R₃M} & \quad \text{CH}_2 \quad \text{CH} = \text{CH}_2 \\
\end{align*}
\]

(3)

5. The σ–π conjugation effect in R₃MR₇ molecules is enhanced when there is a positive charge on the reaction centre R₇. The higher the atomic number of the M element, the stronger the conjugation effect. The resonance acceptor properties of the R₃M substituents towards R₇ are almost the same for M = Ge and Sn, if there is no partial positive charge on R₇. Therefore, the change of sign of the overall resonance effect under the influence of the positive charge on R₇ is more typical for R₃GeR₇ and R₃SnR₇ compounds³², 3³.

Thus, the dominance of d–π or d–n conjugation acceptor effects in R₃MR₇ and R₃MX compounds is more typical for M = Si and probably Ge, and the σ–π or σ–n conjugation donor effect dominates for M = Pb.
2. Similarities and differences of organic compounds of germanium, tin and lead

The overall resonance effect of the $R_3M$ substituents depends on the nature of $R_\pi$ and $X$ and also on the value of the effective positive charge on the M atom and reaction centre $R_\pi$.

The existence of $\sigma-\pi$ or $\sigma-n$ conjugation effects is by now widely accepted. However, opinions on the mechanisms of $d-\pi$ or $d-n$ conjugation differ. We shall consider briefly the evolution of theoretical views on the acceptor resonance effects mentioned above.

The first stage was based on the hypothesis that unoccupied nd-orbitals of silicon subgroup elements in $R_3MR_\pi$ and $R_3MX$ participate in conjugation with $\pi$- or $n$-orbitals of the reaction centre bound to them. It was established that the $\pi$-acceptor properties of the M atom weaken with increase of its atomic number and that there is a close analogy between $d-\pi$ or $d-n$ interaction and the conjugation effects in organic molecules. This hypothesis agrees qualitatively with general quantum-chemical ideas. But quantitative information concerning the participation of nd-orbitals of M, which was obtained by semi-empirical quantum-chemical methods, proved to be ambiguous and often led to opposing conclusions.

In the second stage an erroneous interpretation of hyperconjugation as an alternative to the $d-\pi$ conjugation appeared (for more details see Reference 33). However, it led to the realization of the important role of hyperconjugation in organic molecules.

In the third stage of the evolution of views on conjugation effects, the acceptor properties of M atoms of the silicon subgroup towards $R_\pi$ and $X$ were explained not by the presence of unoccupied nd-orbitals, but by the participation of antibonding $\sigma^*$ orbitals of the M$-Y$ bonds in molecules of the $Y_3MR_\pi$ and $Y_3MX$ type ($Y =$ inorganic or organic substituent). The important role of $\sigma^*$ orbitals in the hyperconjugation was first pointed out as long ago as 1973 by Pitt.

The consideration of the participation of antibonding $\sigma^*$ orbitals of M$-Y$ bonds (the $n-\sigma^*$ conjugation effect) as an alternative to the nd-orbital hypothesis was shown afterwards by non-empirical quantum-chemical methods to be wrong. This effect takes place, for example, in compounds of nitrogen and carbon (M = N, C), for which the nd-orbital contributions are known to be absent.

The fourth stage of evolution was the unifying concept, which is considered in detail elsewhere. It was based on two fundamental principles of physical organic chemistry: linear free-energy relationships as well as independence and additivity of the influence of inductive, resonance and steric effects on free-energy change. According to Pitt, the energy of frontier $\pi$ and $\pi^*$ orbitals of hydrocarbons $HR_\pi$ ($R_\pi =$ Ph, HC=CH$_2$ etc.) changes in the following way when $Me_3M$ (M = a silicon subgroup element) is substituted for the H atom (Figure 1). The substituents $Me_3M$ have a positive inductive $+I$ effect, so that their influence leads to an increase in the energy (destabilization) of the $\pi$ and $\pi^*$ orbitals. Further destabilization occurs owing to hyperconjugation, i.e. mixing of the $\sigma(M-C)$ orbitals of $Me_3M$ with the $\pi$ and $\pi^*$ orbitals. The degree of mixing of $\sigma, \pi$ is higher than that of $\sigma, \pi^*$. Therefore, the HOMO of $Me_3MR_n$ is more destabilized than the LUMO.

We shall now consider the acceptor component of the overall resonance effect in $Me_3MR_\pi$ molecules. The most important factor here is the proximity of the energies of the nd-orbitals of M and of the antibonding $\sigma^*$-orbitals of the M$-C$ fragment of $Me_3M$. Thus, the energy of nd-orbitals of Si, Ge, Sn and Pb atoms is $-1.97, -1.8, -1.93$ and $-1.78$ eV, respectively, and the energy of the $\sigma^*(M-C)$ orbitals in $Me_3M$ (M = Si, Ge and Sn) is 3.8, 3.4 and 2.89 eV, respectively. The mixing of nd and $\sigma^*(M-C)$ results in the formation of two new orbitals. One of them (designated as $d, \sigma^*$) has a lower energy than the initial d-orbitals.
FIGURE 1. The influence of the substituents Me₃M on the energies of the frontier orbitals $\pi$ and $\pi^*$ of Me₃MR₃ compounds: (A) inductive +I effect of Me₃M; (B) $\sigma-\pi$ and $\sigma-\pi^*$ conjugation; (C) mixing of $\sigma^*(M-C)$ orbitals of the Me₃M substituent with the nd-orbitals of the M atoms (a mixed d, $\sigma^*$-orbital with a lower energy is illustrated); (D) mixing of d, $\sigma^*$-orbitals with $\sigma$, $\pi^*$ and $\sigma$, $\pi$; the formation of the HOMO (d, $\pi$) and LUMO (d, $\pi^*$) of the molecule.

The $\sigma,\pi$- and $\sigma,\pi^*$-orbitals also interact with the d, $\sigma^*$-orbital. This results in the stabilization (decrease in energy) of the $\sigma,\pi$- and $\sigma,\pi^*$-orbitals, involving the formation of two new orbitals with lower energy, namely d, $\pi$ and d, $\pi^*$. The designations d, $\pi$ and d, $\pi^*$ represent resonance acceptor properties of Me₃M substituents towards the frontier $\pi$- and $\pi^*$-orbitals of Me₃MR₃ (see also References 30 and 33).

Thus, in the fourth stage of evolution of views on conjugation the fundamental idea that the acceptor resonance effect is a joint influence of unoccupied nd- and antibonding $\sigma^*$-orbitals was formed.

More recently, another explanation of the acceptor effect of M (Si) towards X (F, O, N) in M–X bonds (M = Si) was proposed. The high bond energy of Si–X bonds was attributed to an increase in the contribution of ionic structures of the type H₃Si⁺X⁻. However, the polarities of all M–X bonds (M = Si, Ge, Sn, Pb) are quite similar (Table 4), whereas according to all available data the d–n conjugation weakens when the atomic number of M increases. Therefore, these ideas cannot be considered as an alternative to d–n conjugation.
2. Similarities and differences of organic compounds of germanium, tin and lead

Later on the intramolecular interactions in $R_3MR_\pi$ and $R_3MX$ were studied by non-empirical quantum-chemical calculations. This provided important information on the existence of two effects of opposite direction—a donor effect (hyperconjugation of $\sigma–\pi$ or $\sigma–n$ type) and an acceptor effect (d–$\pi$ or d–n conjugation). We discuss below several of the important studies on this question.

First we shall consider the allylalkylchlorostannanes $R_3-nCl nSnCH_2CH=CH_2$ ($R = Me, n-Bu; \ n = 0–2$), in which the $\sigma–\pi$ conjugation is the only operative resonance effect. It weakens when $n$ increases. This seems to be connected with a decrease in the number of bonding $\sigma(Sn–C)$ orbitals. According to Cauletti and coworkers, the steric effect of the butyl group, which hinders the optimal mutual orientation of the interacting $\sigma(Sn–C)$ and $\pi(C=C)$ orbitals for $\sigma–\pi$ conjugation, plays a certain role when $R$ is changed from Me to Bu.

The acceptor properties of the central M atom are well studied by quantum-chemical methods for $M = Si^{36}$. These properties weaken if $M = Ge$, for example, changing from $c$-PrSiH$_3$ to $c$-PrGeH$_3$. Starting with $M = Sn$, the donor component of the overall resonance effect of the $R_3M$ groups becomes more dominant. Thus strong mixing of the $\sigma(Sn–C)$ and $\pi(C=C)$ orbitals has been established for Me$_3SnC≡CX$ ($X = H, Me, SnMe_3$)\(^{46}\). The strength of the $\sigma–\pi$ conjugation effect depends on the energy of the initial orbitals. Therefore, this effect is enhanced in compounds $R_3SnC≡CH$ when $R$ is changed from Me to Et\(^{46}\). The HOMO energy of molecules Sn(C=CX)$_4$ depends on the type of $X$. As $X$ changes from Me to SiMe$_3$, stabilization (energy decrease) of the HOMO occurs. This is caused by the acceptor properties (d–$\pi$ conjugation) of the silicon atom\(^{47}\).

The metallamines (H$_3M$)$_3N$ ($M = Si, Ge$) have planar structures due to the rehybridization of the central nitrogen atom, which results from electrostatic repulsion of the $M\cdots M$ and $H\cdots H$ atoms as well as from the resonance acceptor effect of the $M$ atoms\(^{48,49}\). The calculated values of the HOMO energy, which are 9.11, 9.61 and 8.91 eV for $M = C, Si, Ge$, respectively, agree satisfactorily with the experimental values (8.44, 9.7 and 9.2 eV\(^{48,49}\), respectively). These data confirm that d–n conjugation is more important for $M = Si$ than for $M = Ge$. In comparison with the d–n conjugation, the $\sigma–n$ conjugation effect (the interaction of the 2p$_\pi$ orbital of the nitrogen atom with the $\sigma(M–H)$ orbitals) exerts less influence on the HOMO and decreases as $M$ changes in the series: C $>$ Si $>$ Ge\(^{48}\). In $Me_nSn(NCS)$_4$–n$ ($n = 2, 3$), the HOMO is localized mainly on sulphur atom and the influence of the electron-accepting NCS groups on the tin atom is very small\(^{50}\).

Quantum-chemical calculations of MH$_4$ and MCl$_4$ ($M = C, Si, Ge, Sn, Pb$) demonstrated that it is necessary to take into account the relativistic effects, which are proportional to the square of the atomic number of $M$ and therefore essential when $M = Ge, Sn, Pb$\(^{51}\). This was considered in calculations of the $Me_{4–n}SnCl_n$ ($n = 0–4$) series\(^{50}\). The mixing of orbitals of the unshared electron pairs of the chlorine atoms with the $\sigma(Sn–C)$ orbitals ($\sigma–n$ conjugation) intensifies with the rise of the number of methyl groups. On the contrary, increase in the number of chlorine atoms is accompanied by an increase in the population of the 5d-orbitals of the tin atom due to the d–n conjugation\(^ {50}\). The calculated HOMO energies\(^{50}\) and NMR chemical shifts of $Me_{4–n}SnCl_n$\(^{52}\) conform satisfactorily with experimental values.

The HOMO of $(Me_3Sn)_2S$ and $(Me_2SnS)_3$ is localized mainly on the unshared electron pairs of the sulphur atoms\(^ {53}\), but the orbitals of methyl groups also contribute to $\sigma–n$ conjugation. This contribution exceeds 20% for $(Me_3Sn)_2S$.

Among derivatives of group 14 elements, the lead compounds are characterized by the highest degree of hyperconjugation. Some important features of the $\sigma–n$ conjugation in the halo lead compounds $R_{4–n}PbX_n$ ($R = H, Me; X = F, Cl; n = 0–4$) were established.
by quantum-chemical methods\textsuperscript{54}. The $\sigma$–n conjugation effect is enhanced on going from H$_{4-n}$PbCl$_n$ to H$_{4-n}$PbF$_n$ and further to Me$_{4-n}$PbF$_n$. The aptitude for $\sigma$–n conjugation of $\sigma$(Pb–C) bonds is stronger, and that of the $\sigma$(Pb–F) bonds is weaker, than that of $\sigma$(Pb–H) bonds. Therefore, the $\sigma$–n conjugation effect changes non-additively when $n$ in H$_{4-n}$PbF$_n$ decreases\textsuperscript{54}.

The interaction of $\sigma$-orbitals of M–C and M′–C bonds ($\sigma$–$\sigma$ conjugation) in the dimetalla compounds, R$_3$MM′R$_3$, was evaluated by quantum-chemical calculations. Thus, the HOMO of Me$_3$SnSnMe$_3$ is localized mainly on the Sn atoms but it also includes contributions of C and H atoms, whose magnitude exceeds 30\%\textsuperscript{55}. Calculations of H$_3$MM′H$_3$ (M and M′ = C, Si, Ge, Sn, Pb) show the necessity to take into account both the bonding and antibonding orbitals of M–H, M′–H and M–M\textsuperscript{16}. Orbital interactions are enhanced as the atomic numbers of M and M′ increase\textsuperscript{55}.

It is usual to consider the inductive interaction as a universal electron effect\textsuperscript{56}. This means that the inductive influence of the R$_3$M substituent on the reaction (indicator) centre R$_\pi$ and X does not depend on the reaction centre type. This seems to be true for M = C, but for M = Si, Ge, Sn, Pb some comments, given below, are required.

The inductive effect of an inorganic, organic or organometallic substituent, Y, is characterized quantitatively by several widespread constants, such as $\sigma_I$ and others ($\sigma^*$, $\sigma^/'$, F etc.)\textsuperscript{34,57}. The relationship $\sigma_I(Y) = \sigma^*(Y) = F(Y) = 0.45 \sigma^*(CH_2Y)$ is well known. The inductive constant $\sigma_I$ of a certain Y substituent (Table 5) reflects several electronic interactions. The most important independent mechanisms of polarization of bonds between the substituent Y and the reaction centre are the field and the inductive interactions. The contribution of each mechanism depends on the type of substituent Y\textsuperscript{29}.

We shall consider the most reliable\textsuperscript{34,57} values of $\sigma_I$ for three series of isostructural substituents containing M (Table 5). In the Me$_3$M series the highest $\sigma_I$ value is observed for M = C. This corresponds to the highest electronegativity of the carbon atom among all group 14 elements (Table 1). As mentioned above, the existing electronegativity series of M (M = Si, Ge, Sn, Pb) are inadequate. It is caused not only by differences in the methods for determining electronegativity, but also by features of the electron structure of investigated objects\textsuperscript{34}. The most important is the presence of hyperconjugation contributions (the $\sigma$–$\sigma$, $\sigma$–$\pi$ and $\sigma$–n conjugation effects) which complicate the determination of electronegativity and inductive constants $\sigma_I$.

Unfortunately, the methods for determining the electronegativity of M and the $\sigma_I$ constants of R$_3$M substituents (in particular, Me$_3$M) do not yet provide a rigorous separation of the inductive and hyperconjugation effects.

Negative $\sigma_I$ values of substituents Me$_3$M and Me$_3$MCH$_2$ for M = Si, Ge, Sn, Pb are higher in absolute magnitude than those for M = C (Table 5). This is in accord with the higher electronegativity of C.

<table>
<thead>
<tr>
<th>Y</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Me$_3$M</td>
<td>$-0.07$</td>
</tr>
<tr>
<td>Me$_3$MCH$_2$</td>
<td>$-0.03$</td>
</tr>
<tr>
<td>Cl$_3$M</td>
<td>$+0.37$</td>
</tr>
</tbody>
</table>

\textsuperscript{a}From Reference 34 unless otherwise specified. 
\textsuperscript{b}Reference 57.
2. Similarities and differences of organic compounds of germanium, tin and lead

The donor inductive effect of the Me₃M groups (M = Ge, Sn, Pb) is approximately equal (\(\sigma_1 = -0.12 \pm 0.01\)), and somewhat higher in the case of Me₃Si (\(\sigma_1 = -0.15\)), pointing to the anomalous position of Si among the group 14 elements. The positive \(\sigma_1\) values of Cl₃M groups rise with increasing atomic number of M (Table 5) and this points to their electron-accepting character. It is caused by the presence of three high electronegative chlorine atoms at M and probably by the field effect\(^{29}\). The \(-\mu\) effect of the Cl₃M groups increases in direct proportion to the magnitude of the dipole moment \(\mu\) of the M–Cl bond\(^{56}\). For M = C, Si and Ge the \(\mu\) values are ca 1.3, 2.1 and 3 D, respectively\(^{29}\), i.e. they change in parallel to the \(\sigma_1\) values of Cl₃M substituents.

III. SPATIAL STRUCTURE

In the discussion of the spatial structure of organic compounds of the heavy silicon subgroup elements it is necessary to dwell on their molecular structure, structure of condensed state and complexes of donor–acceptor type.

When studying the molecular structure of group 14 elements, such as R₄M, it is important to take into account the presence of the non-bonded interactions R···R between substituents caused by repulsion of their electron shells, along with the valence bonds in the MR fragments. Non-bonded interactions can decrease when the interatomic distances M–R increase or when the R₄M molecule is arranged in a conformation with minimum R···R interactions. Several examples will illustrate these points.

The M–O–M fragments in (PhCH₃)₃MOM(CH₂Ph)₃ (M = Si, Ge, Sn) have a linear structure\(^{58}\). In contrast, the M–O–M angles in Ph₃MOMPh₃ are 127.9, 180, 135.2 and 137.3° for M = C, Si, Ge and Sn, respectively\(^{59}\). For M = C, the C–O–C angle is the smallest in the series, in spite of the possibility of non-bonded interactions between the phenyl groups which are located at the opposite carbon atoms. The Ge–O–Ge and Sn–O–Sn angles in Ph₃MOMPh₃ are somewhat larger, while the Si–O–Si fragment has a linear structure. All this indicates that the magnitude of M–O–M angles is determined mainly by electronic effects.

Steric hindrance for free rotation around the M–C bonds in n-Pr₃MCl decreases along the series: Si > Ge > Sn due to successive decrease of the non-bonded interactions between the propyl groups\(^{60}\).

The interatomic distances \(d(M–M)\) in R₃MMR₃ (M = Ge, Sn) depend not only on the electronic effects, but also on the bulk of the R substituents. Thus the Ge–Ge bond distances in the series: H₃GeGeH₃, Ph₃GeGePh₃ and (Me₃C)₃GeGe(CMe₃)₃ are 2.403, 2.437 and 2.710 \(\text{Å}\), respectively\(^{16,61,62}\).

For R = Me₃C, the \(d(\text{Ge–Ge})\) value exceeds noticeably the double atomic radius of germanium (2.44 \(\text{Å}\)) clearly demonstrating the influence of non-bonded interactions between the substituents.

Non-bonded interactions in distannane derivatives R₃SnSnR₃ are weaker owing to larger covalent radius of tin relative to germanium. Thus, the \(d(\text{Sn–Sn})\) distances in Ph₃SnSnPh₃, (Me₃C)₃SnSn(CMe₃)₃, (Me₃C)₃SnSn(CMe₃)₂Sn(CMe₃)₃ and (2,6-Et₂C₆H₃)₃SnSn(2,6-Et₂C₆H₃)₃ are 2.77, 2.894, 2.966 and 3.052\(\text{Å}\), respectively\(^{63–65}\). The \(d(\text{Sn–Sn})\) distances in the last three molecules exceed the double covalent radius of the tin atom (2.82 \(\text{Å}\)). However, the observed lengthening of the Sn–Sn bond is less than that of the Ge–Ge bond in similar digermane derivatives. There is no evidence of significant non-bonded interactions in hexaphenyldiplumbane Ph₃PbPbPh₃ and its heteroanalouges Ph₃PbMPh₃ (M = Ge, Sn). The experimental values of \(d(\text{Pb–M})\) values, 2.623, 2.829 and 2.844 \(\text{Å}\) for \(M = \text{Ge}, \text{Sn}\) and \(\text{Pb}\), respectively\(^{66,67}\), are all less than the sums of the covalent radii of Pb and M atoms (2.69, 2.88 and 2.94 \(\text{Å}\), respectively). The non-bonded interactions of substituents in hexasubstituted benzene derivatives C₆(MMe₃)₆
cause deformation of the planar benzene ring which distorts into a chair form, i.e. such substitution causes dearomatization of the central benzene ring\textsuperscript{68}. It is noteworthy that the distortion of the ring is more significant for M = Si than for M = Ge. This indicates that d–π conjugation of M with the aromatic ring might be important.

In some cases the molecular structure of organic compounds of heavy group 14 elements is determined by a stereoelectronic effect. According to quantum-chemical calculations, the neutral C\(_6\)H\(_5\)CH\(_2\)MH\(_3\) and their protonated forms (carbocations) 4-HC\(_6\)\(_\text{H}_{2}\)CH\(_2\)MH\(_3\) (M = Si, Ge, Sn, Pb) adopt a gauche conformation (the C–C–M angle is 90°)\textsuperscript{69}. The σ–π conjugation effect attains a maximum in these conformers. The σ–π conjugation is enhanced when changing from the neutral molecules to the carbocations (i.e. substituted phenonium ions) and when M becomes heavier.

The structure of organic compounds of heavy group 14 elements in the condensed state, for example R\(_4\)M, depends not only on intramolecular R · · · R (R = Alk, Ar, H or other nucleophilic substituent) non-bonded interactions, but also on intermolecular R · · · R and R · · · M interactions. If the M atom is greatly shielded by bulky R substituents, the intra- and inter-molecular R · · · R interactions prevail. If the M atom is weakly shielded by R substituents, the possibility of intermolecular R · · · M non-bonded interactions as well as M · · · M (if R = H) interactions become more important. This favours the association of R\(_4\)M molecules\textsuperscript{70}. As the atomic number of M increases, the shielding of the central M atom in isostructural molecules R\(_4\)M diminishes. This is the reason why intra-molecular non-bonded interactions are more typical for M = Ge, and inter-molecular interactions are more typical for M = Sn and Pb.

Non-tetrahedral structures of organic derivatives of the silicon subgroup elements are often caused by inter- or intra-molecular coordination interaction X → M. This takes place in compounds where there is a nucleophilic substituent at the central M atom. An electronegative X atom, which has at least one unshared electron pair (X = N, P, O, S, halogen) and is directly bonded to M, can be such a substituent. Compounds of this kind tend to be involved in inter-molecular coordination. There can be also a heteroatom X as part of the organic substituent at M; in this case an intra-molecular coordination usually occurs\textsuperscript{71–73}. Such compounds, which contain five- or six-membered coordination rings, include, for example, draconoides (4)\textsuperscript{74,75}, their analogues (5)\textsuperscript{76,77}, metalloatranes (6)\textsuperscript{78} and others. The stability of a coordination bond X → M increases with the atomic number of M: Si < Ge < Sn < Pb.

\[
\begin{align*}
\text{(4)} & \quad \text{(5)} & \quad \text{(6)} \\
(R & = \text{O, S, NCH}_3, \text{CH}_2) \\
n & = 1, 2
\end{align*}
\]

The donor–acceptor interaction X → M results in a rise of the coordination number of the M atom. For M = Si, Ge it amounts to a coordination number of 5, 6 and 7 (very seldom). For M = Sn, Pb, the coordination number can be as high as 8. The higher coordination number reflects mainly the increase in the atomic number of M and therefore its steric accessibility.
The M atom is tetravalent in many of its organic compounds and the substituents are placed at the vertices of a tetrahedron. If the coordination number of M atom is 5, 6, 7 and 8, then the central M atom has a configuration of a trigonal bipyramid, octahedron, pentagonal bipyramid and distorted cube, respectively.

Steric factors play a marked role in inter- and intra-molecular coordination of compounds of heavy elements of group 14. The complexation requires an approach of the donor and acceptor centres to an optimal distance. If these centres are shielded by bulky substituents, the complexation becomes difficult or impossible. Thus, for example, the tributylalkoxystannanes Bu₃SnOR are monomeric for any R. At the same time the dibutyl-dialkoxystannanes Bu₂Sn(OR)₂ are monomeric only when containing bulky R substituents such as CH₂CHMe₂ or CMe₃. The butylalkoxystannanes BuSn(OR)₃ are monomeric only when the alkyl substituents R are not smaller alkyl radicals (Me, Et, Pr)⁷⁹.

Lead compounds with very large bulky groups such as Ph₃PbSiPh₃⁸⁰ and [2,4,6-(Me₃Si)₂CH₆H₂]₂PbBr₂⁸¹ are monomeric due to steric shielding of the Pb atom by the bulky aryl substituents.

Unlike many associated compounds of tin and lead, the germanium compounds of type R₄-MXₙ (n = 1–3) are usually monomeric⁸²,⁸³.

The inter-molecular complexes of compounds of the type PhₙMR₄₋ₙ (M = Si, Ge, Sn) with molecular O₂, which have been studied by the method of low-temperature luminescence quenching⁸⁴ᵃ, are of special interest. Towards O₂ these compounds can possess both π-donor (owing to the phenyl groups) and ν-acceptor⁸⁴ᵇ (owing to the M atom) properties. The ν-acceptor properties of the M atom increase along the series: Si < Ge < Sn. When M = Si, the ν-acceptor properties are not revealed and only the π-donor ability of the aromatic rings is realized, on which the steric effects of the SiR₄₋ₙ substituents have no influence. For M = Ge, these compounds exhibit both π-donor and ν-acceptor properties. On going from PhGeH₃ to Ph₄Ge, the equilibrium constant for complexation with oxygen (Kₐ) diminishes by a factor of about 20 due to a sharp increase in the steric shielding of the Ge atom (the π-donor properties of these two compounds are almost equal). The Kₐ values of the complexation reactions of SnR₄ with O₂ decrease as the steric bulk of the alkyl radicals R increases in the series: Me < Bu < pentyl⁸⁴ᵃ.

The complexes of tetraalkylstannanes SnR₄ with tetracyanoethylene (TCNE)⁸⁵ are more stable than those with oxygen. The Sn—C bond serves as a σ-donor in this case. The Kₐ values of such complexes are also defined predominantly by the degree of shielding of the donor centre. With change of R these constants diminish in the series: Me >> Et >> i-Pr > i-Bu > t-Bu. The steric hindrance to the complexation with Me₄₋ₙPbEtₙ with TCNE is smaller in comparison with the isostructural tin compounds as expected on the basis of the larger Pb interatomic Pb–C distance⁸⁵.

In complexes of R₃SnC≡CSnR₃ with iodine, the C≡C bond is the donor centre. If R = Me, the interaction with I₂ occurs at a very high rate, and if R = Me₃C, complex formation with I₂ is not observed⁸⁶.

Finally, we shall briefly discuss the compounds of the silicon subgroup elements in their divalent state (germylenes, stannylenes and plumbylenes) R₂M: (R = alkyl, aryl). The chemical bonds in R₂M: are formed by the px and py orbitals of M. The pz orbital is unoccupied and there is an unshared electron pair in an s-orbital of M. Therefore, the R₂M: compounds have both electrophilic and nucleophilic properties. The valence angle R—M—R diminishes as the atomic number of M increases. The distances of M—R bonds in R₂M: are less than in the corresponding tetracoordinate R₄M derivatives⁸⁷. The spatial structure of R₂M: compounds, the shielding of the reaction centre (M:) as well as the possibility for R₂M: molecules to transit from a singlet state into a triplet state depend on the steric bulk of the R substituents. If the R substituents are bulky, some R₂M:
compounds can form the $R_2M=MR_2$ dimers. The stability of the $M=M$ bond decreases as the atomic number of $M$ becomes larger. Thus, for $R = 2$-t-Bu-4, 5,6-Me$_3$C$_6$H, the $M=M$-type dimers are formed only for $M = \text{Ge}$ and $\text{Sn}$, while the corresponding plumbelyne exists as a monomer $R_2\text{Pb}$.

IV. PHYSICAL PROPERTIES

A great number of investigations was dedicated to studying the physical properties of organic compounds of germanium, tin and lead. We discuss here only those that include a comparative study of these compounds as well as studies which verify or develop theoretical concepts of their electronic structure.

A. Vibrational Spectra

Table 6 presents a list of the force constants $k$ of some $M-X$ bonds which are calculated by means of normal coordinate analysis, for example$^{89,90}$. The $k$ values characterize the curvature of the potential well close to the equilibrium internuclear distance. It is widely believed that the higher the value of $k$, the stronger the corresponding chemical bond. Such a relation is found in narrow series of isostructural compounds. It follows particularly from the $k$ values of $\text{H}_4-\text{MX}_n$, where $M = \text{C}, \text{Si}, \text{Ge} ; X = \text{F}, \text{Cl}, \text{Br}, \text{I} ; n = 1–3$.$^{90}$

It follows from Table 6 that the values of force constants of $M-X$ bonds diminish for all given series of isostructural compounds as the atomic number of $M$ increases. The decrease in the strength of these bonds on going from $M = \text{Si}$ to $M = \text{Ge}, \text{Sn}$ and $\text{Pb}$ is confirmed by the parallel behaviour of the values of $k$ and of the bond dissociation energy ($D$). Thus the $D$ values in the series $\text{Me}_3M-\text{H}$ for $M = \text{Si}, \text{Ge}, \text{Sn}$ and $\text{Pb}$ are respectively 378, 343, 309 and 259 kJ mol$^{-1}$.88,99, and in series $\text{Me}_3M-\text{MMe}_3$ 354, 259, 234 and 228 kJ mol$^{-1}$.100. When the number of $X$ atoms ($n$) is increased, the $k$ values of the $M-X$ ($X = \text{Cl}, \text{Br}, \text{I}$) bonds increase for a fixed $M$ atom in all series $\text{Me}_4-n\text{MX}_n$ ($n = 1–4$). A similar dependence between the values of $k(M-C)$ and $n$ in the same series $\text{Me}_4-n\text{MX}_n$ exists as a general trend only. In the same series for fixed $M$ and $n$ values the $k(M-X)$ values diminish as the atomic number of the halogen ($X$) increases. So the $D$ values of $\text{Cl}_3\text{Ge}-\text{Cl}, \text{Br}_3\text{Ge}-\text{Br}$ and $\text{I}_3\text{Ge}-\text{I}$ bonds are 338, 270 and 213 kJ mol$^{-1}$, respectively. The change from $\text{Me}_4M$ to $\text{Me}_3\text{MMMe}_3$ (i.e. substitution of one methyl group by a more electron-donating substituent $\text{MMMe}_3$) for a fixed $M$ atom leads to a decrease in $k(M-C)$. If methyl groups in $\text{Me}_4M$ are replaced by hydrogen atoms (change to $\text{Me}_3MH$ and $\text{MeMH}_3$), the $k(M-C)$ as well as $k(M-H)$ values increase. Unfortunately, the interrelation of the force constants and donor–acceptor properties of the substituents at $M$ are poorly explored as yet.

The influence of the $R$ and $X$ substituents on the stretching modes of the $M-H$ bond in IR spectra of the series $R_3-n\text{X}_n\text{MH}$ ($M = \text{Si}, \text{Ge}, \text{Sn}$) has been investigated in some detail. The form of these vibrations is highly characteristic. Therefore, their frequency $\nu(M-H)$ and intensity $A(M-H)$, which characterize the $M-H$ bond strength and polarity respectively, depend only on the electronic effects of the $R$ and $X$ substituents. If the $R$ substituents at the $M$ have only inductive influence upon $\nu$ and $A$, the correlations given in equations 1 and 2 are observed$^{35}$ (for $M = \text{Si}$ and Ge).

$$
\nu_{\text{ind}}(M-H) = a + 23 \sum \sigma^*
$$

$$
A^{1/2}_{\text{ind}}(M-H) = b - 20 \sum \sigma^*
$$

If one, two or three $X$ substituents form $d,n$ or $d,\pi$ bonds with the $M$, the experimental values of $\nu_{\text{exp}}$ and $A^{1/2}_{\text{exp}}$ differ from those calculated according to equations 1 and 2.
### TABLE 6. Force constant data (mdyn Å⁻¹) for M–X, M–C and M–M stretching modes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k$ (M–H)</th>
<th>$k$ (M–C)</th>
<th>$k$ (M–X)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeMH₃</td>
<td>3.14</td>
<td>3.08</td>
<td>2.97</td>
</tr>
<tr>
<td>Me₃MH</td>
<td>2.77</td>
<td>2.94</td>
<td>2.44[^b]</td>
</tr>
<tr>
<td>Me₄M</td>
<td>2.94</td>
<td>2.73[^d]</td>
<td>2.19[^e]</td>
</tr>
<tr>
<td>Me₃MCl</td>
<td>2.54</td>
<td>3.23</td>
<td>2.22[^c]</td>
</tr>
<tr>
<td>Me₂MCl₂</td>
<td>2.70</td>
<td>3.34</td>
<td>2.27[^d]</td>
</tr>
<tr>
<td>MeMCl₃</td>
<td>2.88</td>
<td>3.36</td>
<td>2.50[^d]</td>
</tr>
<tr>
<td>MCl₄</td>
<td>3.47</td>
<td>3.47</td>
<td>3.11</td>
</tr>
<tr>
<td>Me₃MBr</td>
<td>2.44</td>
<td>3.24</td>
<td>1.78</td>
</tr>
<tr>
<td>Me₂MBr₂</td>
<td>2.54</td>
<td>3.39</td>
<td>2.07</td>
</tr>
<tr>
<td>MeMBr₃</td>
<td>2.64</td>
<td>3.37</td>
<td>2.28</td>
</tr>
<tr>
<td>MBr₄</td>
<td>2.61</td>
<td>3.37</td>
<td>2.39</td>
</tr>
<tr>
<td>Me₃MI</td>
<td>—</td>
<td>—</td>
<td>1.13[^e]</td>
</tr>
<tr>
<td>MI₄</td>
<td>—</td>
<td>—</td>
<td>2.87[^e]</td>
</tr>
<tr>
<td>Me₃MMMe₃[^h]</td>
<td>1.70</td>
<td>2.49</td>
<td>1.54</td>
</tr>
</tbody>
</table>

[^a] From Reference 89, unless otherwise specified.
[^b] Reference 91.
[^c] Reference 92.
[^d] Reference 93.
[^e] Reference 94.
[^f] Reference 95.
[^g] Reference 96.
[^h] Reference 97.

The differences from the theoretical values, $\Delta v = v_{\text{ind}} - v_{\text{exp}}$ and $\Delta A^{1/2} = A^{1/2}_{\text{exp}} - A^{1/2}_{\text{ind}}$, constitute a quantitative characteristic of the d–n or d–π conjugation. The correlations given in equations 3.103 and 4.104

\[
\Delta v_{\text{Si}} = 1.77 \Delta v_{\text{Ge}} - 4 \\
\Delta A^{1/2}_{\text{Si}} = 1.11 \Delta A^{1/2}_{\text{Ge}} + 0.07
\]

are valid for isostructural compounds of silicon and germanium. These correlations suggest that the d–n and d–π conjugation is weaker for M = Ge than for M = Si. As the effective positive charge on M increases (it may be characterized by the sum of the $\sigma_p$ constants of R and X), the d–n and d–π conjugation is enhanced, more so for M = Si than for...
M = Ge. This follows from the correlations in equations 5\textsuperscript{104} and 6\textsuperscript{105}.

\[
\Delta A^{1/2}_{\text{Si}} = 1.21 \sum \sigma_p + 0.47
\]

(5)

\[
\Delta A^{1/2}_{\text{Ge}} = 1.09 \sum \sigma_p + 0.36
\]

(6)

The correlations 1 and 2 fail for alkylstannanes \(R_4^n\text{SnH}_n(n = 1–3)\textsuperscript{106}.\) This is caused by the enhancement of \(\sigma–\sigma\) conjugation between the C–H and M–H bonds (shown in 7) with increase in the atomic number of M. According to this and other data\textsuperscript{54}, the validity of correlations 1 and 2 for organic lead compounds containing the Pb–H bond is even less probable.

\[
\text{H} \quad \text{H} \quad \text{C} \quad \text{M} \quad \text{H}
\]

(7)

The valence vibrations of the C≡C bond in IR spectra of \(\text{Me}_3\text{MC≡CR}\) (M = Si, Ge, Sn) are characteristic. The intensity \(A\) of the \(\nu(C≡C)\) bands is found to be related linearly (equation 7) to the resonance constants \(\sigma_R^0\) of the R substituent.

\[
A^{1/2} = a + b\sigma_R^0
\]

(7)

The coefficient \(a\) depends on the atomic number of M while \(b\) is almost independent of M\textsuperscript{107}. The \(A^{1/2}\) values are also linearly correlated with the \(\Delta q_\pi\) values (calculated by the \textit{ab initio} method), which denote the \(\pi\)-electron exchange between R and the triple bond in HC≡CR\textsuperscript{108}. According to these correlations the \(\sigma_R^0\) and \(\Delta q_\pi\) (the magnitude of the \(\pi\)-electron transfer from the \(\pi\)-system to Me\textsubscript{3}M, and the d–\(\pi\) conjugation effect), which weakens in the series Si > Ge > Sn\textsuperscript{107}.

The electronic effects of the Me\textsubscript{3}M substituents (M = C to Pb), bonded to n- or \(\pi\)-donor centres, were studied by the method of hydrogen bond IR spectroscopy. This method is demonstrated in equation 8.

\[
Y_iA-H + BX_i \xleftrightarrow{\text{H-bond}} Y_iA^{5-} - H \cdots B^{5+} X_i
\]

(8)

If three of the four variables (acceptor A–H, donor centre B, substituents \(X_i\) and \(Y_i\)) are fixed (\(Y_i\), A and B), a series of H-bonded complexes are formed, such as the phenol complexes shown in equation 9.

\[
\text{PhO-H} + O(X_i)_2 \xleftrightarrow{\text{H-bond}} \text{PhO-H} \cdots O(X_i)_2
\]

(9)

The frequency shift \(\Delta \nu = \nu(\text{OH}) - \nu(\text{OH} \cdots \text{O})\), where \(\nu(\text{OH})\) is the frequency of the stretching mode of the O–H bond of the isolated phenol and \(\nu(\text{OH} \cdots \text{O})\) in the presence of the electron donor \(O(X_i)_2\), is very informative for this series. The quantity \(\Delta \nu\) is linearly correlated with the change of enthalpy (energy of donor–acceptor bond in the H-complex) and free energy (stability of the H-complex)\textsuperscript{109}, as well as with the value of effective charge \(q\) on the donor centre B, which was calculated by quantum-chemical
2. Similarities and differences of organic compounds of germanium, tin and lead methods. The second correlation shows the dominant role of electrostatic interactions in the formation of the hydrogen bond. The correlations given in equations 10 and 11 are also valid for the H-complexes.

\[
\Delta \nu = a \sum \sigma_p + b \\
\Delta \nu = c \sum \sigma_I + d \sum \sigma_R + k
\]

They allow one to calculate the resonance constants \( \sigma_R \) of the Me\(_3\)M substituents and to estimate the effective charge component of the donor centre, resulting from conjugation.

The \( \Delta \nu \) values for H-complexes formed by the electron donors of \( \pi \)-type (Table 7) and \( n \)-type (Table 8) obey a general rule. The \( \Delta \nu \) values decrease in all 8 series of Me\(_3\)M(CH\(_2\))\(_n\)R\(_\pi\) and Me\(_3\)MX molecules when changing from M = C to Si and then increase in the order Si < Ge < Sn < Pb. Such dependence of \( \Delta \nu \) on the atomic number of M cannot be explained by a simple correlation with the electronegativity of M. According to the minimum electronegativity of the Si atom (Table 1) the \( \Delta \nu \) values of its compounds should have been the highest.

In contrast, the experimental values of \( \Delta \nu \) for M = Si are the lowest. This strongly supports the maximum acceptor ability of silicon towards donor centres R\(_\pi\) and X as a

<table>
<thead>
<tr>
<th>M</th>
<th>n</th>
<th>Ph(^a)</th>
<th>H(_2)C=CH(^b)</th>
<th>2-Fu(^c)</th>
<th>Me(_3)CC≡C(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \Delta \nu )</td>
<td>( \sigma_R )</td>
<td>( q_{\pi} )</td>
<td>( \Delta \nu )</td>
<td>( \sigma_R )</td>
</tr>
<tr>
<td>C</td>
<td>0</td>
<td>61</td>
<td>-0.13</td>
<td>-0.13</td>
<td>72</td>
</tr>
<tr>
<td>Si</td>
<td>0</td>
<td>0.05</td>
<td>0.05</td>
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<td>0.00</td>
</tr>
<tr>
<td>Ge</td>
<td>0</td>
<td>0.01</td>
<td>-0.05</td>
<td>-0.09</td>
<td>-0.18</td>
</tr>
<tr>
<td>Sn</td>
<td>0</td>
<td>0.01</td>
<td>-0.06</td>
<td>-0.18</td>
<td>-0.24</td>
</tr>
<tr>
<td>Si</td>
<td>1</td>
<td>-0.20</td>
<td>-0.24</td>
<td>-0.29</td>
<td>-0.30</td>
</tr>
<tr>
<td>Ge</td>
<td>1</td>
<td>-0.23</td>
<td>-0.29</td>
<td>-0.42</td>
<td>-0.32</td>
</tr>
<tr>
<td>Sn</td>
<td>1</td>
<td>-0.24</td>
<td>-0.29</td>
<td>-0.42</td>
<td>-0.32</td>
</tr>
</tbody>
</table>

\(^a\)Reference 111.  
\(^b\)Reference 112.  
\(^c\)Reference 113.  
\(^d\)Reference 114.
result of the d–π and d–n conjugation effect. As the atomic number of M increases, its resonance acceptor effect diminishes. The σ_R parameters, which characterize the overall resonance effect (both acceptor and donor) of the Me_3M substituents towards the π-system and reflect its magnitude and sign, diminish as well (Table 7). However, these parameters are not universal. For example, the σ_R values of SnMe_3 for R_π = Ph and for R = Me_3CC≡C are respectively +0.01 and −0.24. The first value points to a balance between acceptor and donor effects of SnMe_3 while the second value indicates that in Me_3CC≡CSnMe_3, the Me_3Sn substituent is a donor (σ–π conjugation). The σ–π conjugation effect in Me_3MR_π and Me_3MCH_2R_π increases as M becomes heavier (i.e. Sn > Ge > Si).

The q_π parameter characterizes the resonance effects of substituents in isolated neutral molecules, and the σ_R^0 parameter in molecules having formed a hydrogen bond (at the same time a partial positive charge δ^+ appears on the donor centre B (equation 8)). Therefore the correlation between the q_π and σ_R^0 parameters is rigorous while between the q_π and σ_R parameters it is only approximate. The q_π values (Table 7) calculated from Δν are approximate as well. The δ^+ charge on R_π is higher, the stronger the σ–π conjugation in Me_3MR_π and Me_3MCH_2R_π and the higher the atomic number of M. This becomes apparent in the differences between the σ_R^0 and σ_R (in parentheses) values in Me_3MC≡CCMe_3 are +0.12 (0.00), +0.06 (−0.18) and +0.04 (−0.24) for M = Si, Ge and Sn, respectively. Thus, even relatively weak perturbations of the electronic structure of the donor molecules Me_3MR_π due to hydrogen bonding can cause reversal of the sign of the resonance effect of GeMe_3 and SnMe_3 substituents.

The Δν^R = Δν^ind − Δν parameters are given in Table 8. The Δν^ind values characterize the inductive effect of a substituent only approximately. Hence, also the Δν^R values may be used only for rough estimates of the inductive effect. The Δν^R values are positive in the series Me_3MMe_2 for M = Si, Ge, Sn. Lower experimental values of Δν in comparison with the expected ones based only on the inductive effect of the Me_3M substituents (Δν^ind) can be taken as evidence of the reduced n-donor properties of Me_3M substituents.

<table>
<thead>
<tr>
<th>M</th>
<th>NMe_2</th>
<th>OMMe_3</th>
<th>SMMe_3</th>
<th>Cl^d</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>96</td>
<td>33</td>
<td>40</td>
<td>74</td>
</tr>
<tr>
<td>ΔνR</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Si</td>
<td>61</td>
<td>13</td>
<td>29</td>
<td>55</td>
</tr>
<tr>
<td>ΔνR</td>
<td>58</td>
<td>263</td>
<td>62</td>
<td>29</td>
</tr>
<tr>
<td>Ge</td>
<td>76</td>
<td>55</td>
<td>38</td>
<td>90</td>
</tr>
<tr>
<td>ΔνR</td>
<td>36</td>
<td>−126</td>
<td>−37</td>
<td>−14</td>
</tr>
<tr>
<td>Sn</td>
<td>108</td>
<td>84</td>
<td>43</td>
<td>113</td>
</tr>
<tr>
<td>ΔνR</td>
<td>8</td>
<td>−324</td>
<td>−57</td>
<td>−34</td>
</tr>
<tr>
<td>Pb</td>
<td>—</td>
<td>—</td>
<td>51</td>
<td>—</td>
</tr>
<tr>
<td>ΔνR</td>
<td>—</td>
<td>—</td>
<td>−127</td>
<td>—</td>
</tr>
</tbody>
</table>

aFrom References 110 and 116.
bFrom Reference 117.
cΔν^R values from Reference 31 (acceptor = PhOH).
dFrom Reference 115 (acceptor = PhOH).
2. Similarities and differences of organic compounds of germanium, tin and lead

The nitrogen atom due to the d–n conjugation. This effect weakens as the atomic number of the M element increases. The d–n conjugation dominates also in the series Me₃MX (X = OMe₃, SMMe₃, Cl) for M = Si. However, starting with M = Ge the resonance donor effect of the σ–n conjugation of the Me₃M group prevails, and it increases along the series Ge < Sn < Pb. This is clearly indicated by the negative Δνᵣ values.

### B. Nuclear Magnetic Resonance (NMR) Spectra

The main parameters of NMR spectroscopy are the chemical shift δₐ (the difference of the magnetic shielding of a reference (σᵣ) and studied (σₐ) nucleus) and the spin–spin coupling constant J between nuclei. The shielding constant of a nucleus A (σₐ) includes diamagnetic σₐ^d and paramagnetic σₐ^p components, as well as a ΣσᵣÂ term (magnetic anisotropy) characterizing the shielding of the nucleus A by the electrons of the other nuclei (B); see equation 12

\[
σₐ = σₐ^d + σₐ^p + ΣσᵣÂ
\]  

(12)

The σₐ^d component prevails for ^1H nuclei. According to some data, the σₐ^p component prevails for the ^13C, ^19F, ^29Si, ^73Ge, ^117Sn, ^119Sn and ^207Pb nuclei, but according to others both components (σₐ^d and σₐ^p) are significant. When estimating the ΣσᵣÂ term in equation 12, appreciable difficulties arise. Calculations of ΣσᵣÂ taking the inductive effect of X into account have been carried out for simple systems R₂MX (R = Me, Et; X = F, Cl, Br, OMe)\(^{121}\). According to these studies the d–n conjugation has been established to decrease along the series Si > Ge > F > Cl > Br and F > OMe.

The main efforts were aimed, however, at searching systems where the chemical shifts δ and coupling constants J are connected with the electronic effects of the substituents by simple dependencies. The primary idea was to move the variable substituents R₃M as far as possible from the indicator centre A (i.e. minimizing the ΣσᵣÂ term in equation 12). At the same time, the sensitivity of δₐ to the effect of R₃M must not be lost\(^{122,123}\).

Table 9 presents 5 examples of such systems. The ^13C chemical shifts depend on the inductive and resonance effects of the Me₃M and Me₃MCH₂ groups. The series 1–3 illustrate the effect of Me₃M substituents in Me₃MR₇ on the ^13C chemical shifts in position 4 of benzene and naphthalene rings, as well as of the β-carbon atom of the vinyl group. Depending on M the δ values change in the following sequence: C < Si > Ge >

<table>
<thead>
<tr>
<th>No.</th>
<th>Series</th>
<th>Position</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>^13C</td>
</tr>
<tr>
<td>1</td>
<td>Me₃MPh⁵</td>
<td>δ (C-4)</td>
<td>122.5</td>
</tr>
<tr>
<td>2</td>
<td>Me₃MNaph-1⁵</td>
<td>δ (C-4)</td>
<td>127.4</td>
</tr>
<tr>
<td>3</td>
<td>p-Me₃M–C₆H₄–CH=CH₂⁶</td>
<td>δ(C₂)</td>
<td>111.84</td>
</tr>
<tr>
<td>4</td>
<td>Me₃MCH₂Ph⁷</td>
<td>δ (C-4)</td>
<td>125.8</td>
</tr>
<tr>
<td>5</td>
<td>p-Me₃MCH₂–C₆H₄–CH=CH₂⁸</td>
<td>δ(C₂)</td>
<td>112.43</td>
</tr>
</tbody>
</table>

\(^{a}\)In ppm vs Me₄Si.

\(^{b}\)Reference 122.

\(^{c}\)Reference 123.

\(^{d}\)Reference 124. The \(^1J(^{13}C₉–^{13}C₁)\) values for M = C, Si, Ge and Sn are 36.0, 40.9, 42.5 and 42.8 Hz, respectively.
Sn > Pb. This trend agrees with a maximal resonance acceptor effect (d–π conjugation) for M = Si mentioned above repeatedly, which weakens as the atomic number of M increases.

In series 4 and 5, Me₃MCH₂R, the δ values decrease as M changes along the series C > Si > Ge > Sn > Pb. This is yet another confirmation that σ–π conjugation becomes stronger when M becomes heavier.

The values of coupling constants $^1J(^{13}C–^{13}C)$ in organic compounds are proportional to the C–C bond order.$^{125}$ In series 4 this constant characterizes the interaction of nuclei of aliphatic (C$_\alpha$) and aromatic (C$_1$) carbon atoms. The $^1J(^{13}C_{\alpha}–^{13}C_1)$ value increases when M changes from M = C to M = Sn, corresponding to an increase of the C$_{ar}$–CH$_2$ bond order, i.e. to the enhancement of the σ–π conjugation as the atomic number of M increases.

$^{13}$C and $^{19}$F NMR spectroscopy are classical methods for determining the resonance σ$_R^0$ and inductive σ$_I$ constants of X substituents bonded to an aromatic ring$^{34,57}$. This method is based on correlations of the type shown in equation 13 for chemical shifts δ of $^{13}$C and $^{19}$F atoms in the para- and meta-positions to X in the spectra of C$_6$H$_5$X, as well as of $p$-FC$_6$H$_4$X and $m$-FC$_6$H$_4$X.

$$\delta = a\sigma_I + b\sigma_R^0 + c \quad (13)$$

The σ$_R^0$ values characterize in addition (see above) the similarities and differences of the resonance interactions of Ge-, Sn- and Pb-containing substituents with a benzene ring. The principal similarity between the R$_3$M groups lies in a smaller d–π conjugation and a larger σ–π conjugation in R$_3$MPh and R$_3$MCH$_2$Ph for M = Ge, Sn, Pb than for M = Si. The main difference between the R$_3$M groups results from the fact that as the atomic number of M increases from Ge to Pb, the d–π conjugation weakens and the σ–π conjugation becomes stronger.

The chemical shifts of heavy group 14 nuclei are interconnected by the correlations$^{126,127}$ shown in equations 14–17, where $n$ is the number of data points and $r$ is the correlation coefficient.

$$\delta(^{29}\text{Si}) = 0.787\delta(^{13}\text{C}) - 61.7 \quad r = 0.825 \quad n = 13 \quad (14)$$
$$\delta(^{119}\text{Sn}) = 5.119\delta(^{29}\text{Si}) - 18.5 \quad r = 0.990 \quad n = 48 \quad (15)$$
$$\delta(^{119}\text{Sn}) = 2.2\delta(^{73}\text{Ge}) - 11.3 \quad r = 0.984 \quad n = 14 \quad (16)$$
$$\delta(^{207}\text{Pb}) = 2.424\delta(^{119}\text{Sn}) + 74.8 \quad r = 0.975 \quad n = 35 \quad (17)$$

The high sensitivity of the chemical shifts of $^{73}$Ge,$^{119}$Sn and $^{207}$Pb to substituent effects calls for a detailed study of the resonance interactions in these organometallic compounds.

**C. Photoelectron Spectra and UV Spectra of Charge Transfer (CT) Complexes**

Important information on the similarities and differences of germanium, tin and lead compounds was obtained using two mutually complementary types of spectroscopy. Photoelectron spectroscopy is widely used to determine the first (Ip) and subsequent ionization potentials of molecules. According to Koopmans’ theorem, the Ip is equated with the HOMO energy (equation 18)$^{128}$.

$$Ip = -E_{\text{HOMO}}. \quad (18)$$
2. Similarities and differences of organic compounds of germanium, tin and lead

The electronic absorption spectroscopy of charge transfer (CT) complexes of donor molecules of π-, n- and σ-type (DX) with π- and σ-acceptors (A = TCNE, I2 etc.) allows one to study the influence of the X substituents bonded to a donor centre, D, on the energies of charge transfer bands, \( h\nu_{CT} \). The \( h\nu_{CT} \) and Ip parameters are connected by a linear dependence given in equation 19.

\[
h\nu_{CT} = aI_p + b
\]  

If steric effects of substituents do not affect the formation of the complex and A (e.g. TCNE) is constant, coefficients \( a \) and \( b \) in equation 19 depend on \( D \) only. In approximation 18, \( h\nu_{CT} \) and Ip depend on the inductive and resonance effects of the X substituents for constant \( D \). As the donor properties of X become stronger, the HOMO energy increases and the \( h\nu_{CT} \) and Ip values decrease.

In Table 10 we bring data for 9 series of group 14 compounds. As M changes from C to Si, the Ip and \( h\nu_{CT} \) values (in the UV spectra of the CT complexes with TCNE) of compounds with the Me₃M group (series 1, 2 and 4–9) increase. However, these values decrease along the series: Si > Ge > Sn > Pb. The Ip values in series 1 for M = Si and Ge, as well as in series 8 for M = C and Si, are close. The given sequence of the Ip and \( h\nu_{CT} \) change does not agree with the electronegativity scales of group 14 elements (Table 1). This is additional evidence that the maximal d–π and d–n conjugations are reached for M = Si, which weakens gradually as the atomic number of M increases. On the contrary, the σ–π conjugation effect increases when changing consecutively from M = C to M = Pb. Therefore, the Ip and \( h\nu_{CT} \) values decrease smoothly in series 3 as the atomic number of M increases.

### Table 10. First vertical ionization potentials Ip (eV) and energies of charge transfer bands \( h\nu_{CT} \) (eV) in spectra of organic compounds of group 14 elements (M)

<table>
<thead>
<tr>
<th>No.</th>
<th>Series</th>
<th>Ip/(( h\nu_{CT} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me₃MPh(^a,b)</td>
<td>8.74 (2.80) 8.94 (2.93) 8.95 (2.90) 8.75 (2.78) 8.54 (2.60)</td>
</tr>
<tr>
<td>2</td>
<td>p-Me₃MC₆H₄MMe(^c)</td>
<td>8.40 (2.44) 8.98 (2.73) 8.60 (2.68) 8.50 (2.59) 8.25 (2.48)</td>
</tr>
<tr>
<td>3</td>
<td>Me₃MCH₂Ph(^b,d)</td>
<td>8.77 (2.83) 8.42 (2.50) 8.40 (2.40) 8.21 (2.19) —</td>
</tr>
<tr>
<td>4</td>
<td>Me₃MFu-3(^e)</td>
<td>8.32 (2.46) 8.64 (2.54) 8.52 (2.50) 8.49 (2.48) 8.46 (2.47)</td>
</tr>
<tr>
<td>5</td>
<td>Me₃MThi-2(^a,e)</td>
<td>8.18 (2.53) 8.74 (2.63) 8.40 (2.58) 8.22 (2.53) 7.78 (2.48)</td>
</tr>
<tr>
<td>6</td>
<td>Me₃MSMMe(^f)</td>
<td>8.38 (2.46) 8.69 (2.54) 8.50 (2.50) 8.37 (2.48) 8.13 (2.47)</td>
</tr>
<tr>
<td>7</td>
<td>Me₃MSMe(^f)</td>
<td>10.76 (10.76) 10.35 (10.76) 10.16 (10.76) 9.70 (10.76)</td>
</tr>
<tr>
<td>8</td>
<td>Me₃MCl(^g)</td>
<td>10.05 (10.23) 9.78 (10.23) 9.60 (10.23) 9.30 (10.23)</td>
</tr>
<tr>
<td>9</td>
<td>Me₃MBr(^g)</td>
<td>— — — — —</td>
</tr>
</tbody>
</table>

\(^{a}\)Reference 130.

\(^{b}\)References 131 and 132.

\(^{c}\)References 128 and 133.

\(^{d}\)Reference 134.

\(^{e}\)References 135 and 136.

\(^{f}\)Reference 137.

\(^{g}\)Reference 138.
The above views regarding the dependence of the Ip and \( h\nu_{\text{CT}} \) values on the atomic number of M were recently shown to be rather simplified and the approximation in equation 18 to be rough\(^{130} \). The donor component \( D^{\ddagger \ast}X \) of the compact radical ion-pair which is formed in the excited state of a CT complex in solution according to equation 20

\[
A + DX \leftrightarrow [A, DX] \xrightarrow{h\nu_{\text{CT}}} [A^{\ast}, D^{\ddagger \ast}X] \tag{20}
\]

and the radical cation generated by photoionization of individual DX molecules in the gas phase (equation 21)

\[
DX \xrightarrow{h\nu} D^{\ast}X + e^- \tag{21}
\]

are very similar in their electronic structure.

Therefore, the Ip and \( h\nu_{\text{CT}} \) values obey, to a high degree of accuracy, equations of the type given in equation 22:

\[
\text{Ip (or } h\nu_{\text{CT}}\text{)} = k + l\sigma_1 + m\sigma_{R^+} + n\sigma_\alpha. \tag{22}
\]

The quantity \( \sigma_1 \) in equation 22 is an inductive X substituent constant and \( \sigma_{R^+} \) is an electrophilic resonance constant. The constant \( \sigma_{R^+} \) accounts for the influence of X on the reaction centre \( D^{\ddagger \ast} \), which has large positive charge arising in the processes shown in equations 20 and 21. The constant \( \sigma_\alpha \) denotes an electrostatic attraction between the positive charge of the radical-cation and the dipole moment induced by this charge in the X substituent. The coefficients \( k, l, m \) and \( n \) depend on the type of donor centre D. When correlating the Ip and \( h\nu_{\text{CT}} \) values according to equation 22, these coefficients are equal for \( D = \text{const} \).\(^{130} \)

Equation 22 allows one to calculate parameters \( \sigma_{R^+} \) on the basis of the Ip or \( h\nu_{\text{CT}} \), \( \sigma_1 \) and \( \sigma_\alpha \) values. Characteristic examples of the \( \sigma_{R^+} \) values of the \( \text{Me}_3M \) and \( \text{Me}_3\text{MCH}_2 \) groups in 6 series of organic compounds of the silicon subgroup elements calculated in such a way are given in Table 11.

The \( \sigma_{R^+} \) values of the \( \text{Me}_3M \) (series 1–4) and \( \text{Me}_3\text{MCH}_2 \) (series 5 and 6) groups depend essentially on the nature of the radical-cation centre. It was already pointed out in Section IV.A that the \( \sigma-\pi \) conjugation increases under the influence of a partial positive

<table>
<thead>
<tr>
<th>No.</th>
<th>Series</th>
<th>( \sigma_{R^+} )</th>
<th>( \sigma_1 )</th>
<th>( \sigma_\alpha )</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( \text{Si} )</td>
<td>( \text{Ge} )</td>
<td>( \text{Sn} )</td>
<td>( \text{Pb} )</td>
</tr>
<tr>
<td>1</td>
<td>( \text{Me}_3\text{MPh} )</td>
<td>0.02</td>
<td>-0.10</td>
<td>-0.21</td>
<td>-0.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.05)</td>
<td>(0.01)</td>
<td>(0.01)</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>( \text{Me}_3\text{MThi-2} )</td>
<td>0.25</td>
<td>0.01</td>
<td>-0.01</td>
<td>-0.05</td>
</tr>
<tr>
<td>3</td>
<td>( \text{Me}_3\text{MC} = \text{CH} )</td>
<td>0.00</td>
<td>-0.22</td>
<td>-0.36</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.00)</td>
<td>(-0.18)</td>
<td>(-0.24)</td>
<td>—</td>
</tr>
<tr>
<td>4</td>
<td>( \text{Me}_3\text{MSMMe}_3 )</td>
<td>0.15</td>
<td>-0.10</td>
<td>-0.15</td>
<td>-0.31</td>
</tr>
<tr>
<td>5</td>
<td>( \text{Me}_3\text{MCH}_2\text{Ph} )</td>
<td>-0.49</td>
<td>-0.59</td>
<td>-0.76</td>
<td>-0.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-0.20)</td>
<td>(-0.23)</td>
<td>(-0.24)</td>
<td>—</td>
</tr>
<tr>
<td>6</td>
<td>( \text{Me}_3\text{MCH}_2\text{CH} = \text{CH}_2 )</td>
<td>-0.65</td>
<td>-0.83</td>
<td>-1.00</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-0.24)</td>
<td>(-0.29)</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

\(^a\text{Values of } \sigma_R \text{ (in parentheses) from Table 6.}\)
charge developing on the donor centre when an H-complex is formed. This is illustrated in equation 8. With CT complex formation and photoionization taking place according to equations 20 and 21, the positive charge on the donor centre rises sharply (in comparison with that in H-complexes). Therefore, the $\sigma - \pi$ conjugation increase is even greater than upon formation of a hydrogen bond. This shows up in smaller $\sigma_R^+$ values in comparison with the $\sigma_R$ values. The absolute value of the difference $|\sigma_R^+ - \sigma_R|$ increases as the atomic number of $M$ increases (Table 11).

The $\sigma_R^+ - \sigma_R$ differences allow one to support the presence of both d–$\pi$ and $\sigma – \pi$ conjugation in phenyl derivatives of the silicon subgroup elements\(^\text{11}\). It doing so it was taken into consideration that $\sigma_R^+ - \sigma_R = \sigma_p^+ - \sigma_p$, because $\sigma_p^+ = \sigma_R^+ + \sigma_1$ and $\sigma_p = \sigma_R + \sigma_1$. For compounds of the general formula $(\text{Me}_3M)_{m+n}X_nR_{3-m,n}$CPh ($M = Si, Ge, Sn, Pb; X = \text{inorganic or organic substituent}; R = H, alk; m, n = 0–3$), the correlation given in equation 23 (where $\Sigma R_D$ is the sum of the refractions of its bonds) is valid.

$$\sigma_p^+ - \sigma_p = -0.117\Sigma R_D + 0.53 \quad r = 0.968 \quad n = 19 \quad (23)$$

For all benzene substituents which are resonance donors, $\sigma_p > \sigma_p^+$. It follows from equation 23 that the differences $\sigma_p^+ - \sigma_p$ characterizing the strengthening of the $\sigma – \pi$ conjugation increase with the enhancement of the polarizability of all the bonds within the substituent bonded to the aromatic ring. The quantitative characteristic of the overall substituent polarizability is the sum of the refractions of its bonds, $\Sigma R_D$ (see Section I). The values of $\sigma_p^+$ and $\sigma_p$ are approximately equal for organic substituents which are resonance acceptors. If the $R_{3-n}X_nM$ substituents had only a resonance acceptor effect (the d–$\pi$ conjugation), the correlation in equation 23 would fail for compounds $R_{3-n}X_n$MPH. In fact, equation 24

$$\sigma_p^+ - \sigma_p = -0.025\Sigma R_D + 0.23 \quad r = 0.985 \quad n = 30 \quad (24)$$

similar to equation 23, is valid for these compounds. Hence the $R_{3-n}X_nM$ substituents possess two resonance effects towards a phenyl group—they act both as a donor (the $\sigma – \pi$ conjugation) and an acceptor (the d–$\pi$ conjugation). If the two effects operate in opposite directions, the sensitivity of the value of $\sigma_p^+ - \sigma_p$ to the parameter $\Sigma R_D$ is reduced. The smaller slope of equation 24 in comparison with that of equation 23 points it out\(^\text{11}\).

It also follows from these equations that the polarizability of $M$ and of the $M–R$ bonds is the most important factor determining the enhancement of the $\sigma – \pi$ conjugation in $R_3MCH_2R_\pi$ and $R_3MR_\pi$ molecules when a positive charge develops on the reaction (indicator) centre $R_\pi$. As the atomic number of $M$ increases, the polarizability of $M$ and of the $M–R$ bonds increases (see Section I). Therefore, the $\sigma – \pi$ conjugation in an isostructural series increases under the influence of a positive charge on $R_\pi$ both when going from $M = C, Si$ to $M = Ge, Sn, Pb$ and when $M$ changes along the series $Ge < Sn < Pb$.

The electronic structure and physical properties of organic compounds of germanium, tin and lead (in comparison with isostructural derivatives of silicon and carbon) discussed in the previous sections lead to the following main conclusions regarding their similarities and differences.

Points of similarity as a function of $M$ in compounds of the types $R_3MR_\pi, R_3MX$ and $R_3MCH_2R_\pi$ ($R$ = organic substituent; $M = Ge, Sn, Pb; R_\pi$ = aromatic or $\alpha,\beta$-unsaturated group; $X$ = halogen, $N<-, O–, S–$ or other atoms having at least one unshared electron pair) are:

1. Large atomic radius of $M$ and accessibility of $M$ atoms to nucleophilic attack.
2. High polarizability of the electron shell of $M$ atoms as well as of $M–C$ and $M–X$ bonds.
3. Relatively low ionization potentials of M atoms and their compounds.
4. Lower electronegativity of M in comparison with carbon.
5. Virtually equal negative $\sigma_I$ values ($-0.12 \pm 0.01$) of all the Me$_3$M groups (M = Ge, Sn, Pb).
6. The presence of two components, acceptor and donor, in the total resonance effect of R$_3$M substituents towards a reaction (indicator) centre R$_\pi$ or towards X.
7. A complex mechanism of the resonance acceptor effect (the d–$\pi$ conjugation in R$_3$MR$_\pi$ and the d–n conjugation in R$_3$MX, for M = Ge, Sn, Pb). This effect is absent when M = C. The acceptor effect includes the participation of unoccupied nd-orbitals of M and of antibonding $\sigma^*$-orbitals of the M–R bonds of the R$_3$M fragments (R = alkyl).
8. The important role of the resonance donor effect (hyperconjugation) in R$_3$MR$_\pi$ [the $\sigma$–$\pi$ conjugation; mixing of $\sigma$(M–R) orbitals with the $\pi$-orbitals of the R$_\pi$ group] and R$_3$MX molecules [the $\sigma$–n conjugation; mixing of $\sigma$(M–R) orbitals with the n-orbitals of an X fragment].
9. The presence of a strong resonance donor $\sigma$–$\pi$ conjugation effect in R$_3$MCH$_2$R$_\pi$ molecules.
10. Enhancement of the d–$\pi$ and d–n conjugation when the effective positive charge on M increases.
11. Enhancement of the $\sigma$–$\pi$ conjugation when increasing the effective positive charge on the reaction (indicator) centre R$_\pi$. In some cases there is a reversal of the donor–acceptor properties of R$_3$M substituents towards R$_\pi$ when the charge of R$_\pi$ is changed.
12. The tendency to expansion of the coordination sphere of M, which increases when going from Ge to Sn, Pb.
13. Change of interatomic distances and valence angles under the influence of non-bonded interactions (steric effect).
   Points of difference of R$_3$MR$_\pi$, R$_3$MX and R$_3$MCH$_2$R$_\pi$ compounds (M = Ge, Sn, Pb) as a function of M are:
   1. Increase of the atomic radius of M and of its accessibility to a nucleophilic attack when increasing the atomic number of M.
   2. Enhancement of the polarizability of the M atom as well as of M–C and M–X bonds when increasing the atomic number of M.
   3. Decrease of the ionization potentials of organic compounds of Ge, Sn, Pb when increasing the atomic number of M.
   4. Absence of the commonly accepted united scale of electronegativity for M.
   5. Complicated mechanism of the inductive effect of R$_3$M groups involving increase in the field effect contribution with increase in the atomic number of M.
   6. Different ratio of the acceptor and donor resonance effects of R$_3$M for M = Ge, Sn, Pb.
   7. Weakening of the d–$\pi$ and d–n conjugation effects with increase in the atomic number of M.
   8. Enhancement of the $\sigma$–$\pi$ and $\sigma$–n conjugation effects with increase in the atomic number of M.
   9. An increased role of $\sigma$–$\pi$ conjugation in R$_3$MCH$_2$R$_\pi$ molecules in comparison with R$_3$MR$_\pi$, where this effect competes with the d–$\pi$ conjugation. There is an enhancement of the $\sigma$–$\pi$ conjugation in R$_3$M(CH$_2$)$_n$R$_\pi$ ($n = 0, 1$) when going consecutively from M = Ge to Pb.
   10. The enhancement of the d–$\pi$ and d–n conjugation effects when increasing the positive charge on M differs for M = Ge, Sn, Pb and becomes smaller as the atomic number of M increases.
   11. The sensitivity of the $\sigma$–$\pi$ conjugation in R$_3$MR$_\pi$ molecules to the influence of the effective positive charge of R$_\pi$ rises as the atomic number of M increases. Therefore,
the reversal in the donor–acceptor properties of $R_3M$ substituents (i.e. transformation of resonance acceptors to donors) is most probable for $M = \text{Pb}$.

12. The enhancement of the tendency to increase the coordination number of $M$ when going consecutively from $M = \text{Ge}$ to Pb.

13. Weakening of the importance of the steric effects of substituents on the spatial structure around the $M$ atom with increase in the atomic number of $M$.

In general, it seems that, on the basis of physical, chemical and biological properties, one should divide the compounds of the silicon subgroup elements into two groups, one with $M = \text{Si}, \text{Ge}$ and the other with $M = \text{Sn}, \text{Pb}$.

V. CHEMICAL PROPERTIES

Differences in the chemical behaviour of organic compounds of the silicon subgroup elements are caused mainly by the increase in the covalent atomic radius as well as in bond distances and polarity (and therefore in steric accessibility of $M$ atom) and the decrease in the bond dissociation energy when the atomic number of $M$ increases. In the same order, i.e. $\text{Pb} > \text{Sn} > \text{Ge} > \text{Si}$, the electrophilicity of $M$ and its tendency for complexation increases and its electronegativity (according to the spectroscopic hydride scale which is based on the $M$–$H$ bond stretching modes in $X_3MH$ and $MH_4$), which excludes the influence of conjugation and association effects, gradually diminishes. The stability of compounds having a low-valent $M$ atom (e.g. metalenes $R_2M$ and free radicals $R_3M^*$) also rises as the atomic number of $M$ increases. The chemical properties of organic compounds of the silicon subgroup elements were first compared in 1934 and next in 1947 by Kocheshkov, and 20 years later almost simultaneously and independently by Schmidt and Glockling. They were the first to have taken note of the fact that Mendeleyev’s assertion, that properties of isostructural compounds of silicon, germanium and tin must change regularly in accordance with the position of these elements in the periodic table, is not always valid. The Allred and Rochow’s electronegativity scale of $C, Si, Ge, Sn, Pb$ is a clear verification of this point. According to this scale the electronegativity of lead is close to that of carbon, and the electronegativity of silicon is less than that of germanium.

Numerous literature data mentioned in the previous chapter, including the data in References 144–146 and 150, allow one to conclude that the chemical properties of organic compounds of germanium, tin and lead have much in common, though there are essential differences in some cases. In general, organic compounds of germanium are closer in their properties to isostructural derivatives of silicon than to those of tin and lead. This is reflected in particular by a higher thermal and chemical stability of $C$–$Si$, $Si$–$O$, $C$–$Ge$ and $Ge$–$O$ bonds in comparison with corresponding bonds of Sn and Pb. At the same time, $Sn$–$S$ and $Pb$–$S$ bonds are much more stable than $Si$–$S$ and $Ge$–$S$ bonds. All in all the reactivity of bonds of organic derivatives of the silicon subgroup elements ($M$) as well as of compounds containing non-quadrivalent $M$ atoms increases in the series $Si < Ge < Sn < Pb$.

A. C$–M$ Bonds

The thermal and chemical stability of $C$–$M$ bonds ($M = Si, Ge, Sn, Pb$), and therefore of all organic compounds of the silicon subgroup elements, decreases, both in homolytic and in heterolytic processes, when the atomic number of the $M$ element increases. For example, the thermal stability of tetraalkyl derivatives $R_4M$ diminishes essentially when $M$ is changed consecutively from $Si$ to Pb. The ease of oxidation of $R_4M$ compounds and the ease of cleavage of $C$–$M$ bonds by halogens, protons and aprotic acids, etc.,
increases in the same order. When halogens and hydrohalogens react with R₄M (M = Ge) only one R—Ge bond is cleaved, and only in the presence of AlCl₃ are two M—R bonds cleaved. At the same time, if M = Sn and Pb, two or all four R—M bonds decompose easily under mild conditions (for M = Pb even at temperatures below 0°C). R—M bonds (R = alkyl, aryl) are not cleaved by nucleophilic reagents unless reacted under severe conditions. An acid cleavage rate of the M—Ph bond in R₃MPh (R = alkyl), which occurs as an electrophilic aromatic substitution process, increases in the following order: Si < Ge << Sn << Pb. The sharp distinction between the reactivity of the isostructural compounds with M = Si, Ge on the one hand and Sn, Pb on the other is explained by a change in the reaction mechanism by which they react. The (sp²)—M bond in vinyl derivatives is cleaved by electrophilic reagents faster, the heavier is M.

B. M—H Bonds

In accordance with the dissociation energy of M—H bonds, the reactivity of organometallic hydrides R₄−nMHₙ increases sharply as the atomic number of M and the number of hydrogen atoms (n) increase. The thermal stability of compounds of this series decreases in the same direction (especially for M = Pb). Trialkylplumbanes R₃PbH (especially with short-chain R) begin to decompose even below −78°C. Unlike the Si—H bond, which is easily decomposed by water solutions of inorganic bases, the M—H bonds for M = Ge, Sn, Pb fail to react with them and their hydrolysis is more difficult. When R₃SiH reacts with organolithium reagents, the hydrogen atom is substituted by an organic function. In contrast, the reaction of R₃MH, where M = Ge, Sn, Pb leads to R₃MLi (in the case of M = Sn, both reactions, alkylation and lithiation, can occur). Hydrosilylation of unsaturated compounds in the absence of catalysts or free radical initiators occurs only at a temperature above 250°C. In contrast, hydrogermylation occurs often under mild temperature conditions. Hydrostannylation occurs without the need for a catalyst and it occurs at temperatures below 100°C (usually 20–80°C, in some cases below 0°C). It is noteworthy that the hydrosilylation catalysts do not affect the rate of this reaction. Hydroplumbylation, a poorly studied reaction, is carried out in the absence of both catalysts and initiators.

As the atomic number of M increases, the possibility of reducing R₃MH rises sharply as well. For example, the reduction of organohalides by trialkylsilanes (M = Si) requires the use of catalysts (AlCl₃, Ni, Pt and others), but the heavier R₃MH (M = Ge, Sn, Pb) react in the absence of catalysts. The reactivity of the M—H bond in R₃MH towards elemental chalcogens increases as the atomic number of M increases.

Catalytic reactions of triorganylsilanes with ammonia and amines lead to the formation of the Si—N bond. In contrast, reaction of triphenylstannane with primary amines gives an Sn—N bond, i.e. Ph₃SnSnPh₃.

It is remarkable that triorganylgermanes R₃GeH can be synthesized by the reduction of germyl halides R₃GeX by zinc amalgam in hydrochloric acid. An analogous reaction of R₃MH for M = Si, Sn fails.

C. M—M Bonds

As the atomic number of M increases, the thermal stability of the M—M bond decreases. The ease of cleavage of the M—M bond by halogens, trifluoriodomethane, phenyllithium, potassium and sodium alkoxides, alkali metals, sulphur etc. increases in the same order.
D. M–X bonds (X = halogen)

M–X bond ionicity rises as the atomic number of M increases. Organylfluorosilanes and organylfluorogermanes $\text{R}_4\text{M} = \text{MF}_n$ ($\text{M} = \text{Si}, \text{Ge}$) are monomeric, but organylfluorostannanes ($\text{M} = \text{Sn}$) are polymeric due to an intermolecular $F \rightarrow \text{Sn}$ coordination. The lead compounds of the $\text{RMX}_3$ series ($X =$ halogen) are extremely unstable (as well as $\text{PbX}_4$) and virtually unknown.

The $\text{M}–\text{X}$ bonds of $\text{M} = \text{Ge}, \text{Sn}, \text{Pb}$ are hydrolysed by basic water solutions (for $\text{M} = \text{Si}$ and $\text{Ge}$, just by water), forming $\equiv\text{M}–\text{OH}$ or $\equiv\text{M}–\text{O}–\text{M}≡$ groups.

Halides $\text{R}_2\text{MX}$ ($\text{M} = \text{Si}, \text{Ge}$) react easily with water to produce first $\text{R}_3\text{MOH}$. If $\text{M} = \text{Sn}$ or $\text{Pb}$, the ethers $\text{R}_3\text{MOMR}_3$ are formed instantaneous. Hydrolysis of $\text{R}_2\text{MX}_2$ results usually in the formation of oligomeric or polymeric metalloxanes, while for $\text{M} = \text{Pb}$, monomeric dialkyllead dihydrooxides $\text{R}_2\text{Pb(OH)}_2$ are formed.

Depending on the hydrolysis conditions, $\text{R}_2\text{SiX}_2$ can lead to the formation of both $\text{R}_2\text{Si(OH)}_2$ and $(\text{R}_2\text{SiO})_n$. Hydrolysis of $\text{R}_2\text{MX}_2$ for $\text{M} = \text{Si}$, $\text{Ge}$ leads as a result to polymers $(\text{R}_3\text{MO}_{1.5})_n$, and for $\text{M} = \text{Sn}$, $\text{Pb}$ to $[\text{RM(OH)}\text{O}]_n$ and $\text{HO}[\text{RM(OH)}\text{O}]_n\text{H}$. Thus, the hydrolysis of $\text{R}_4–\text{MX}_n$ is facilitated when the atomic number of $\text{M}$ decreases and that of the $\text{X}$ halogen increases.

E. M–O Bonds

As the atomic number of $\text{M}$ increases, the strength of the $\text{M}–\text{O}$ bonds decreases and the ease of cleavage of the $\equiv\text{M}–\text{O}–\text{M}≡$ group by water, alcohols and acids rises. The stability towards protolysis of oligomers and polymers $\text{R}_n\text{MO}_{2–0.5n}$ is enhanced as the number of organic substituents at $\text{M}$ ($n$) decreases. Polyorganylsilsesquioxanes ($\text{RSiO}_{1.5})_m$ are stable towards protic acids. In contrast, even $(\text{RGeO}_{1.5})_m$ and $[\text{RSn(OH)}\text{O}]_m$ react easily with organic and mineral acids; the substitution of oxygen atoms by the anion of the acid. $\text{Sn}–\text{O}–\text{Sn}$ and $\text{Sn}–\text{O}–\text{C}$ groups are decomposed easily by $–\text{SH}, –\text{NH}$ and even $\text{CH}$ acids. Unlike this, $\text{Si}–\text{O}–\text{Si}$ groups are not cleaved by $–\text{SH}, –\text{NH}$ and $\text{CH}$ acids and they react with weak $\text{OH}$ acids only in the presence of catalysts. While linear polydiorganylsiloxanes, such as $\text{X(R}_2\text{MO})_n\text{MR}_2\text{X}$ ($\text{M} = \text{Si}$), are easily formed and are stable, their structural analogues for $\text{M} = \text{Ge}$ are poorly studied. At the same time, the analogous polymers for $\text{M} = \text{Sn}$ and $\text{Pb}$ are well known, but the metalloxane chains in these polymers are associated.

$\text{R}_3\text{MOH}$ ($\text{R} = \text{alkyl}; \text{M} = \text{Si}$) are weak acids, and for $\text{M} = \text{Ge}, \text{Sn}, \text{Pb}$ they are quite strong bases. While $\text{R}_3\text{MOH}$ ($\text{M} = \text{Si}, \text{Ge}$) condense easily to give $\text{R}_3\text{MOMR}_3$, $\text{R}_3\text{SnOH}$ and $\text{R}_3\text{PbOH}$ only under the action of dehydrating agents. $\text{R}_3\text{MOH}$, $\text{M} = \text{Sn}$ and $\text{Pb}$, also do not form metal derivatives $\text{R}_3\text{MONa}$ when interacting with metal sodium, in contrast to $\text{R}_3\text{MOH}$ ($\text{R} = \text{Si, Ge}$).
The stability of nitrates $\text{Me}_3\text{MONO}_2$ and the ionicity of the $\text{M}–\text{O}$ bond in these molecules rises sharply as the atomic number of $\text{M}$ increases. The compounds of this type with $\text{M} = \text{Sn}, \text{Pb}$ are salt-like.

**F. $\text{M}–\text{S}$ Bonds**

The $\text{M}–\text{S}$ bonds with $\text{M} = \text{Si}, \text{Ge}$ on the one hand and with $\text{M} = \text{Sn}, \text{Pb}$ on the other are very different in their stability and reactivity. With $\text{M} = \text{Si}, \text{Ge}$ these compounds are decomposed easily by water, alcohols and protic acids. In the case of $\text{M} = \text{Sn}, \text{Pb}$, they are converted into $\text{Sn}–\text{O}$ and $\text{Pb}–\text{O}$ bonds under the action of water solutions of strong bases. The reaction of $\text{R}_3\text{MCl}$ with $\text{H}_2\text{S}$ for $\text{M} = \text{Sn}, \text{Pb}$ leads smoothly to $\text{R}_3\text{MSMR}_3$. If $\text{M} = \text{Si}, \text{Ge}$, the reaction occurs only in the presence of nitrogen bases.

Affinity of the silicon subgroup elements towards a thiocarbonyl group ($\text{C}–\text{S}$) decreases in the order $\text{Sn} > \text{Pb} > \text{Ge} >> \text{Si}$, but even silicon forms coordination bonds of the type $\text{C}=\text{S} \rightarrow \text{Si}$ (see, for instance, Reference 167).

**G. $\text{M}–\text{N}$ Bonds**

Ammonolysis and aminolysis of $\text{M}–\text{X}$ bonds ($\text{X} = \text{Cl, Br, I}$) for $\text{M} = \text{Si}, \text{Ge}$ leads to the formation of $\text{M}–\text{NR}_2$ ($\text{R} = \text{H, alkyl}$) or $\text{M}–\text{N}($($\text{R}$)$–\text{M}$) groups, respectively, and for $\text{M} = \text{Sn}, \text{Pb}$ the complexes are formed in which $\text{M}$ possesses a coordination number of 5, 6, 7 and even 8 (for $\text{NH}_3$).

In the case that $\text{M} = \text{Ge}$, such adducts of 1:1 and 1:2 composition appear only at low temperature and are intermediates in the reaction of $\text{Ge}–\text{N}$ bond formation. Organic compounds of tin and lead having $\text{M}–\text{N}$ bonds are less accessible than those of silicon and germanium. They can be obtained by the interaction of the corresponding halides with metal derivatives of ammonia and amines. The $\text{M}–\text{N}$ bonds in $\text{Me}_3\text{MNHMMe}_3$ and $\text{Me}_3\text{MNMe}_2$ ($\text{M} = \text{Si, Ge, Sn, Pb}$) are decomposed by $\text{HX}$ acids ($\text{OH, SH, NH, PH}$ and even $\text{CH}$ acids). The hydrolysis is easier, the larger the atomic number of $\text{M}$. The basicity of the nitrogen atom in the $\text{M}–\text{N}$ bonds increases in the same order.

**H. Compounds Containing a Hypervalent $\text{M}$ Atom**

The ability of the heavier group 14 elements (M) to increase their coordination number rises with the increase of: (a) the atomic number of $\text{M}$, (b) the number of halogen atoms or other electronegative substituents bonded to $\text{M}$. At the same time, many complexes of quadrivalent $\text{Pb}$ compounds are unstable due to redox interactions of the central $\text{Pb}$ atom with the ligands.

Silicon and germanium compounds of the $\text{R}_4–\text{nMX}_n$ ($\text{X} = \text{halogen; } n = 2, 4$) series interact with bases (B) forming complexes of 1:1 and 1:2 composition (the latter are more stable) in which the coordination number of $\text{M}$ is 5 or 6, respectively. However, there exist several intramolecular complexes of Si and Ge in which the coordination number of $\text{M}$ is 7.

Organylhalostannanes form inter- and intra-molecular complexes in which the coordination number of $\text{Sn}$ atom is 5, 6, 7 and even 8.

The range of hypervalent tin derivatives is the broadest. Among these compounds there are, for example, stable coordination compounds such as $\text{R}_2\text{SnX}_2$ · $\text{H}_2\text{NPh}$, $\text{R}_2\text{SnX}_2$ · $\text{2H}_2\text{NPh}$, $\text{R}_2\text{SnX}_2$ · $\text{nNH}_3$ ($n = 2, 3, 4$), $[\text{R}_2\text{SnO}]_{n}·\text{R}_2\text{SnX}_2$ ($n = 1, 2$), $\text{HO(}\text{R}_2\text{SnO})_3\text{H}·\text{R}_2\text{SnX}_2$, ($\text{R}_3\text{Sn})_2\text{O}·\text{R}_2\text{SnX}$ and $\text{R}_3\text{SnOH}·\text{R}_3\text{SnX}$. Similar isostructural complexes of organylhalosilanes and -germanes exist only at very low temperature (if they exist at all).

In contrast to $\text{R}_4–\text{nMX}_n$ ($\text{M} = \text{Si, Ge}$), the compounds with $\text{M} = \text{Sn}$ can form complexes having the $\text{R}_4–\text{nSnX}_n$ · 2$\text{B}·$2$\text{HX}$ composition ($\text{X} = \text{Cl, Br; } \text{B} = \text{pyridine},$
2. Similarities and differences of organic compounds of germanium, tin and lead

quinoline, PhMeNH, PhNH₂; n = 1–4). These complexes correspond to structure \([BH^{+}]_2 \cdot [R_{4-n}SnX_{n+2}]^{2-}\) with a hexacoordinated Sn atom.

While compounds of \(R_3MX\) type with \(M = Si, Ge\) are stable as monomers, the isostructural analogues with \(M = Sn, Pb\) form stable complexes of 1:1 composition with dipolar aprotic solvents (DMF, DMSO, sulpholane). 1-Organylmethallatranes \(RM(OCH_2CH_2)_3N\) are another striking example of the different coordination ability of organic compounds of the silicon subgroup elements. Compounds of this type are always monomeric both in the crystal state and in solution, for \(M = Si, Ge\). The M atom in these compounds does not adopt a hexacoordinated structure under the action of nucleophilic agents. On the contrary, 1-organylstannatranes, \(RM(OCH_2CH_2)_3N\), \(M = Sn\), which have no bulky substituents at the tin atom, are associated in the crystal state and even in solvents (except water), i.e. the Sn atom is hexacoordinated. This is evident from NMR and Mössbauer spectra. Organyplumbatranes \(RPb(OCH_2CH_2)_3N\) remain unknown.

Unlike Si and Ge acetylacetonates (acac), in which the central M atom is hexacoordinated, the coordination number of the Sn atom in \(RSn(acac)_3\) is 7. Hexacoordinated Si, Ge, Sn, Pb complexes with tropolone (Tp) are known. \(Tp_4M\) molecules, where the metal atom is octacoordinated for \(M = Sn, Pb\) or hexacoordinated for \(M = Si, Ge\), are of particular interest. The latter compounds correspond to the structure \(Tp_3M^+Tp^-\) and exist as salts or ion pairs.

I. Compounds Containing a Low-valent M Atom

The majority of organic compounds of group 14 elements, corresponding to the formula \(R_2M\), for which a bivalent state was assigned in the past to the M atom, are in fact cyclic oligomers or linear polymers, in which the M atoms are quadricivalent. In recent years labile monomeric \(R_2M\): compounds (metallenes) have attracted considerable interest. These are six-electron derivatives of divalent C, Si, Sn, Pb — carbenes, silylenes, germynes, stannylenes, and plumbylenes. The carbenes \((M = C)\) differ essentially from the silylenes \((M = Si)\). The reactivity of silylenes also differs from that of the germynes \((M = Ge)\). Diorganylsilylenes are so unstable that it is possible to isolate them only in argon matrix at very low temperature. Diorganylgemermenes are monomeric in the gas phase. Some of them can exist under ordinary conditions as dimers, such as \(R_2Ge=GeR_2\). Diorganylstannylene are more stable, and metallenes are thermochromic. \(R_2M\): (\(M = Ge, Sn, Pb\)) are practically colourless at very low temperature. However, at ordinary temperatures \(R_2Ge, R_2Sn\) and \(R_2Pb\) have canary, terracotta and purple colours, respectively. Their colour is caused by a metal-centred \(p\) electron transition as a result of sp-mixing.

Diorganylmethallenes have both electron-donating (nucleophilic) and weak electron-accepting (electrophilic) properties. They are good \(\pi\)-acceptors. Diorganylmethallenes exhibit Lewis base properties, because they can coordinate with unoccupied orbitals of electrophilic molecules, most often with those of transition metal derivatives. In this case weaker ligands can be displaced by diorganylmethallenes from their coordination compounds (for example, carbonyls).

The first ionization potential of \(R_2M\): is rather low. Its values for \([Me_3Si]_2CH_2M\) (\(M = Ge, Sn, Pb\)) are 7.75, 7.42 and 7.25 eV, respectively. In contrast to the numerous known structures of germylene and especially stannylene complexes, the structures of only a few silylene complexes are known.
Singlet diorganylmetallenes add easily electrophilic agents such as hydrohalogens, halocarbons, acyl halogenides and halogens, according to the general equation 25,

\[ R_2M: + R^1X \rightarrow R_2R^1MX \]  

(25)

where \( R^1 = \text{H, alkyl, acyl, halogen} \); \( X = \text{halogen} \). This reaction can be also considered as an insertion reaction of \( R_2M \) into the \( R^1-X \) bond\(^{176,188} \).

\( R_2M: \) complexes with strong Lewis acids (such as \( BX_3 \) and \( AlX_3 \)) are more stable. \( R_2M: \) can also be added to the 1,4-position of 1,3-dienes, forming the corresponding heterocycles (cyclometallation reaction).

The donor ability (nucleophilicity) of \( R_2M: \), including the stability of complexes being formed, increases as \( M \) becomes heavier. The acceptor properties of \( M \) in \( R_2M: \) (such as the ability to form the adducts with Lewis bases, for example, with pyridine and piperidine at \(-30^\circ\text{C}\)) are determined by the low-lying unoccupied atomic d- and \( p_z \)-orbitals\(^{160} \). Stable free radicals \( R_3M^* \) (\( M = \text{Ge, Sn} \)) are obtained by a photochemical disproportionation reaction of \( R_2M: \) in a hydrocarbon solvent medium\(^{160} \); see equation 26, \( R = (\text{Me}_3\text{Si})_2\text{CH} \).

\[ 2R_2M: \xrightarrow{h\nu} R_3M^* + 1/n(RM)_n \]  

(26)

The very high stability (10 years at room temperature) of \( R_3M^* \) radicals is due to the very bulky \( R \) substituents at \( M \) hindering recombination, as well as the comparatively low values of the \( M-H \) bond energy. Therefore, hydrogen atom abstraction from the hydrocarbon solvent turns out to be unfavourable.

In contrast, the half-life of \( R_3\text{Si}^* \) radicals is 10 min at ordinary temperature. It is noteworthy that a photochemical decomposition of \([\text{(Me}_3\text{Si})_2\text{CH}]_2\text{Pb}\) fails to proceed according to equation 26, but leads instead to homolysis of both \( C-Pb \) bonds and to the formation of a lead mirror deposition (equation 27).

\[ 2R_2\text{Pb} \xrightarrow{h\nu} 2R^* + \text{Pb} \]  

(27)

This result supports the data presented in Section V.A, that of all \( C-M \) bonds, the \( C-Pb \) bonds can undergo homolytic cleavage, forming carbon-centred free radicals most easily.

**VI. BIOLOGICAL ACTIVITY**

The biological activity of organometallic compounds is determined by the nature of the metal atom, the molecular structure and their chemical properties. Biological action of organic compounds of the silicon subgroup can be divided into two groups, Si and Ge derivatives on the one hand and Sn and Pb derivatives on the other, according to certain differences in their chemical properties and molecular structure. The biological activity of these two groups differs sharply.

Silicon is a microbiogenous element and it plays an important role in vital activities of living matter of our planet. Some of its organic compounds are drugs, pesticides and biostimulators\(^{203-206} \). Most organosilicon compounds are slightly toxic, although there are surprising exceptions (1-arylsilatranes are highly toxic\(^{207-209} \)). The role of germanium as a microbiogenous element has not been proved yet, although its presence is established in fungi, plants and animals, as well as in coal formed from plant remains\(^210-212 \). The similarity of the biogeochemical history of germanium and silicon is striking\(^{205-206} \).

The metabolism of silicon and germanium compounds in living organisms is closely related and mutually balanced. It is connected to a high extent with isomorphism of
silicon and germanium, i.e. with the ability of germanium to substitute silicon in biological systems\textsuperscript{205,206}. Organic compounds of germanium are close in their biological action as well as in their chemical properties to isostructural compounds of silicon and differ sharply from toxic organic derivatives of tin and lead\textsuperscript{211,213}. A high-toxic compound has not been found as yet among an abundance of organogermanium compounds. Differences in the toxic action of some isostructural compounds of silicon and germanium can be illustrated by one example: 1-phenylgermatrane (LD\textsubscript{50} = 48 mg/kg)\textsuperscript{214} is almost 150 times less toxic than 1-phenylsilatrane (LD\textsubscript{50} = 0.3 mg/kg)\textsuperscript{207–209}. However, substitution of silicon in organisms of plants and hydrocole by germanium, accompanied by its excess in the environment, can lead to their death.

A large number of organic germanium compounds characterized by different kinds of biological activity have been synthesized and studied\textsuperscript{215,216}. Some of them have already found application in medicine and agriculture as drugs\textsuperscript{212,216} and biostimulants\textsuperscript{212}. Almost all organic compounds of tin and lead have toxic action\textsuperscript{211,213,217–220}. Therefore, their appearance in the environment where they are accumulated\textsuperscript{221–225} is highly dangerous for all living organisms\textsuperscript{221,222,226–229}. Three biochemical mechanisms regarding the influence of organic compounds of tin and lead on the cellular function and viability have been established. They include a cellular lipid metabolism, disruptions of cytosolic calcium homeostasis and a destruction of cytoskeletal components. Man or animals having been poisoned with organic compounds of tin and lead are affected mainly in the central nervous system\textsuperscript{219,230–232}. They are especially dangerous for man, because they are accumulated in the brain and cause degeneration of primitive brain cells, inhibit growth of neurons, disrupt cytoskeletal structures and change lipid metabolism of human cells and cell morphology\textsuperscript{220}.

Cytotoxicity of organic derivatives of tin and lead depends mainly on their topological characteristics and to a lesser extent on the nature of the metal atom.

\( R_3MX \) are the most poisonous in the \( R_{4-n}MX_n \) (M = Sn, Pb) series; this is also observed for the isostructural compounds of silicon\textsuperscript{203}. The toxic action of compounds of tin and lead is similar. Derivatives of \( R_3MX \) inhibit oxidative phosphorylation, whereas \( R_2MX_2 \) binds thiol enzymes groups\textsuperscript{211}. Fungicidal activity of trialkylstannane \( R_3MX \) derivatives is maximal when the number of carbon atoms is 9 in all three \( R \) substituents. On the whole, the toxicity of organic compounds of tin and lead decreases as the bulk of the substituents about the central metal atom increases.

The toxicity of \( R_4M \) (M = Sn, Pb) is caused by decomposition \textit{in vivo} of one \( R-M \) bond with formation of \( R_3M^+ \). This biochemical reaction, proceeding much more easily for \( M = Pb \) than for \( M = Sn \), explains the higher toxicity of isostructural lead compounds. Change in the nature of the \( R \) substituent at the Pb atom affects the toxicity to a lesser extent than for \( M = Sn \).

In spite of its toxicity (and sometimes owing to it) organic compounds of tin and lead have found wide use during the last century as effective fungicides (\( R_3SnX \)), insecticides, antihelmintic and medicinal agents. Other industrial uses of organotin and organolead compounds are as polyvinyl chloride stabilizers, antiknock agents for vehicle fuels (\( Et_4Pb \)), polymeric materials for radiation shielding etc.\textsuperscript{233–235}.

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CHAPTER 9

Radical reaction mechanisms of and at organic germanium, tin and lead

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I. INTRODUCTION

The mechanisms of organometallic reactions and, in particular the processes involving group 14 elements, in principle, do deserve an extensive survey. Interest in the derivatives of the elements of this group is so great and their reactions are so diverse that sometimes they are capable of puzzling any experienced investigator. Having no intention, however, to startle the reader with the mass of available data on reaction mechanisms, we have tried to restrict ourselves to demonstrating the wide potential of spin chemistry methods in investigations of the elementary mechanisms of organic reactions involving radical species with group 14 elements. More than 20 years have passed since the publication of the first review on the applications of chemically induced dynamic nuclear polarization to study organometallic reactions. Since then, the majority of published reviews concerned either directly or indirectly with the application of spin chemistry methods to organometallic reactions were too specialized and therefore could hardly attract the attention of the organometallic community. However, the methods of spin chemistry open new prospects for deeper understanding of the mechanistic features of the broad variety of organometallic reactions.

Despite the spectacular achievements in the organic syntheses of germanium, tin and lead organoelement compounds their reactivity still requires more thorough investigation. As for reliably established reaction mechanisms, one literally could count them on the fingers of one hand. At present the investigations of the structure and properties of short-lived intermediates of organometallic reactions are acknowledged to be among the most topical lines of chemical research. At present, the overwhelming majority of the reaction mechanisms established by means of physical methods involves paramagnetic species such as free element-centered radicals, and biradicals including the heavy carbene analogs, i.e. germylenes. The present chapter is devoted to a description of the elementary mechanisms of the reactions involving these species.

There are several reasons for the interest in homolytic processes. Recent years have witnessed a strong tendency of organic syntheses to employ organometallic reagents in routes to previously unknown or otherwise hardly accessible compounds. From this viewpoint, the reactions of group 14 organoelement compounds are of special interest, in particular, photoinduced reactions of Ge and Sn compounds involving homolytic stages. It is essential that these radical reactions will occur under mild conditions, thus allowing one to obtain a wide range of products with retention of the functional element-containing group — the process characteristic for heterolytic reactions involving organometallic derivatives. These features have stimulated intensive applications of laser pulse photolysis techniques, ESR and spin chemistry methods for the investigation of the reaction mechanisms of homolytic processes involving organic Ge, Sn and Pb compounds. Due to the high informativity of spin chemistry methods the data obtained by means of these methods literally hold a central position among papers devoted to the investigation of homolytic processes involving
9. Radical reaction mechanisms of and at organic germanium, tin and lead

Another goal is to attract the attention of the organometallic community to the options rendered by spin chemistry methods. A major problem is posed by the fact that, at present, these capabilities are mainly exploited by the spin chemistry experts themselves. However, the application of spin chemistry methods would allow organic chemists to obtain more interpretable and unambiguous data on the structure and properties of short-lived paramagnetic intermediates as compared to other physical methods. When comparing different methods, it is necessary to take into account that the method of chemically induced dynamic nuclear polarization combines the simplicity and reliability of the product identification characteristic by NMR spectroscopy with an extremely high sensitivity. Moreover, the rules of qualitative analysis of the polarization effects are straightforward and do not require special training. For those interested, Section II includes an introduction to spin chemistry techniques and their broad potentialities.

II. SPIN CHEMISTRY TOOLS — GENERAL BACKGROUND

Spin chemistry is a comparatively young field of science — about 30 years old — related to the chemistry of radical reactions where the rate and direction of the process depend on the interaction of the electron and nuclear spin of the paramagnetic species which are the precursors of the reaction products. Three phenomena form the foundation of spin chemistry: (1) chemically induced dynamic nuclear (electron) polarization (CIDNP or CIDEP); (2) the magnetic field effect (MFE), which is the influence of the external magnetic field on the product yield and the reaction rates; and (3) the magnetic isotope effect (MIE), dealing with the influence of the external and internal (generated by the magnetic nuclei of the radical) magnetic fields on the distributions of magnetic isotopes (with nonzero nuclear spin) over the reaction products.

One of the most important phenomenon, chemically induced dynamic nuclear polarization (CIDNP), deserves more detailed consideration, since it forms the basis of one of the most powerful modern methods for the investigation of the structure and reactivity of short-lived (from nano- to microseconds) paramagnetic precursors of the reaction products. CIDNP manifests itself in the form of unusual line intensities and/or phases of NMR signals observed when the radical reaction takes place directly in the probe of the spectrometer. These anomalous NMR signals — enhanced absorption or emission — are observed within the time of nuclear relaxation of the diamagnetic molecule (from several seconds to several minutes). Later on, the NMR spectrum re-acquires its equilibrium form.

Theory suggests that the nonequilibrium population leading to the unusual NMR lines is generated as a result of electron–nuclear interactions in the so-called radical pair. Such a pair of paramagnetic particles may originate through the homolysis of a molecule under the action of heating, light or ionizing radiation as well as from single electron transfer between donor and acceptor molecules and occasional radical encounters in the bulk preceding the recombination.

The analysis of CIDNP effects formed in such a radical pair allows one to obtain information on the structure and reactivity of active short-lived paramagnetic species (free neutral and charged radicals), on molecular dynamics in the radical pair and on the geminate (‘in-cage’) and homogeneous (‘escape’) processes of complex chemical reactions, of great importance when studying their mechanisms. CIDNP data are informative of the multiplicity of reacting states, necessary for better understanding the nature of photochemical processes. The observation of CIDNP effects is unambiguous evidence that the relevant product had a radical precursor. One might distinguish two types of CIDNP effects: net effects (enhanced absorption or emission) and multiplet effects which take the form of intensity redistribution between individual components of multiplet signals in the
NMR spectrum. The analysis of CIDNP effects is usually carried out using the existing rules\(^5\). The sign of net CIDNP effect (\(\Gamma_N\)) observed in a high magnetic field is defined by the product of multiplication of the following parameters: \(\Gamma_N = \mu \cdot \varepsilon \cdot \Delta g \cdot A\), where \(\mu\) is the multiplicity of the precursor radical pair (‘+’ for a triplet (T) and uncorrelated (F) pair, and ‘−’ for a singlet (S) precursor), \(\varepsilon\) is ‘+’ for ‘in-cage’ and ‘−’ for ‘escape’ recombination products, \(\Delta g\) is the sign of the difference in \(g\)-factors of the radical with polarized nucleus and radical partner in the RP (radical pair), while \(A\) is the sign of the hyperfine interaction (HFI) constant of the nucleus under study in the radical. The sign of \(\Gamma_N\) reflects the phase of the NMR signal of the nucleus under study: ‘+’ for enhanced absorption (A) and ‘−’ for emission (E). For example, if one considers some group of, say, protons in the product resulting from the recombination (\(\varepsilon\) is ‘+’) of the uncorrelated radical pair or F-pair (\(\mu\) is ‘+’), and if this group belonged to a radical with a \(g\)-factor smaller than that of the partner radical of the radical pair (\(\Delta g\) is ‘−’), and if the sign of the hyperfine interaction for this particular group in the radical is negative (\(A\) is ‘−’), then the multiplication gives

\[
\frac{\mu \cdot \varepsilon \cdot \Delta g \cdot A}{+ \cdot + \cdot - \cdot -} = + (A)
\]

One should then observe an enhanced absorption of the NMR signal of this group.

The qualitative rules for analysis of the multiplet effect (\(\Gamma_M\)) could be written as follows: \(\Gamma_M = \mu \cdot \varepsilon \cdot J_1 \cdot J_2 \cdot A_1 \cdot A_2 \cdot \gamma\), where \(\mu\) and \(\varepsilon\) are the same as for \(\Gamma_N\), \(A_1\) and \(A_2\) are the signs of hyperfine constants of nuclei 1 and 2 in the radicals, \(J\) is the sign of the spin–spin coupling constant of these nuclei in the molecule, while \(\gamma\) is ‘+’ if these nuclei belong to the same radical and ‘−’ if they belong to different radicals constituting the pair. The sign of \(\Gamma_M\) defines two types of multiplet effects, ‘+’ for E/A and ‘−’ for A/E.

The mere fact of CIDNP observation provides no data on the contribution of the radical pathway to the product formation. To obtain this information one should employ another technique, the magnetic field effect (MFE). Basic manifestations of MFE include: (1) the variations of the ratio of geminate (‘in-cage’) and homogeneous (‘escape’) products of radical reaction as a function of the applied external magnetic field; (2) the dependence of the reaction rates (effective rate constants) on the external magnetic field. In itself, the observation of MFE is decisive evidence of the prevalence of the radical pathway of the reaction under study. Theory suggests several model mechanisms of MFE formation\(^6\),\(^7\) and the modeling of the MFE and comparison of theoretical and experimental findings make it possible to reveal the features of the molecular dynamics (in particular, lifetimes) and the structure of reacting states, to discover new reactive intermediates and to get better insight into magnetic properties (\(g\)-factors, hyperfine constants) of the radicals involved. In certain cases, where the MFE are particularly high, one might consider the use of this method to govern the chemical reaction.

### III. REACTIONS OF GERMANIUM AND TIN DERIVATIVES CONTAINING THE ELEMENT–ALKALI METAL BOND

At the very beginning of spin chemistry, the reactions of alkyl lithiums with organic halides were the systems where CIDNP effects\(^8\) and the influence of the external magnetic field\(^9\) (magnetic field effects) were discovered. From the mechanistic viewpoint, the reactions of triorganogermyl derivatives of alkali metals \(R_3\text{GeLi(Na,K)}\) with organic halides should follow a similar sequence of radical stages involving germanium-centered radicals. The reactions of \(R_3\text{GeLi(Na,K)}\) are of special interest not only as a method for the introduction of an organometallic function resulting in the formation of the carbon–metal
9. Radical reaction mechanisms of and at organic germanium, tin and lead bond. It will be demonstrated below how important is the role of supramolecular factors (associated states) for the mechanisms of these reactions.

Similar to the reaction with $n$-BuLi\(^{9}\) the main reaction products of the interaction between benzyl chloride PhCH\(_2\)Cl and Et\(_3\)GeLi, Et\(_3\)GeNa and Et\(_3\)GeK in benzene are the corresponding unsymmetrical (1) and symmetrical (2 and 3) products (equation 1).

$$\text{PhCH}_2\text{Cl} + \text{Et}_3\text{GeLi(Na,K)} \rightarrow \text{PhCH}_2\text{GeEt}_3 + \text{PhCH}_2\text{CH}_2\text{Ph} +$$
$$+ \text{Et}_3\text{GeGeEt}_3 + \text{Li(Na,K)}\text{Cl} \quad (1)$$

Table 1 lists \(^1\)H CIDNP effects detected during mixing of the initial reagents directly in the probe of an NMR spectrometer\(^{10}\). The analysis of the observed chemical polarization effects in accordance with the existing rules\(^{11}\) (see Section II) allows one to propose the radical pathway for the formation of the main reaction products (Scheme 1).

![Scheme 1](image-url)

The significant difference in the $g$-factors\(^{12}\) ($\Delta g = 6.3 \times 10^{-3}$) of the radicals comprising the initial singlet radical pair of $\text{GeEt}_3$ and $\text{CH}_2\text{Ph}$ radicals defines the net character of the observed CIDNP effects (see Table 1). To elucidate the role of the radical pathway, it was necessary to study the dependence of the ratio of the yields of products 1 and 2 on the external magnetic field strength. The difference in $g$-factors and hyperfine interaction in the radical pair of the benzyl and triethylgermyl free radicals allows one to expect a marked influence of the external magnetic field on the recombination probability of this pair. Indeed, the decrease in the external magnetic field from 1.88 T to the geomagnetic value results in the noticeable variation in the ratio 1/2; for the reaction of PhCH\(_2\)Cl with
Et₃GeNa this effect amounts to 28 ± 8%, and in the case of Et₃GeK the influence is even greater and reaches 38 ± 12% (Table 1).10

The observation of a magnetic field effect implies that the radical pathway of the formation of the main reaction products is prevalent. Despite the decrease in the magnitude of the magnetic field effect in the reaction of benzyl chloride with Et₃GeLi (11 ± 5%), the reaction mechanism should be similar for all organogermanium derivatives under study, Et₃GeLi(Na,K). As shown for the case of n-BuLi reactions with benzyl halides⁹, the influence of the external magnetic field has been reliably detected only for rather significant ratios of unsymmetrical and symmetrical (cf 1 and 2) products. This is due to the limited influence of the external magnetic field on the recombination probability of the radical pairs in nonviscous liquids in accordance with the predictions of the radical pair theory.¹³ In the case under study, it is quite reasonable to assume that the increase of the 1/2 ratio in the series Et₃GeLi, Et₃GeNa and Et₃GeK leads to the growth of the observed magnetic field effect (Table 1).

High values of cage effects (Table 1) close to those detected in the reactions of alkyl-lithium compounds⁹ suggest that, similarly to n-BuLi, organogermanium derivatives of alkali metals enter the reaction in the associated state. It is necessary to note that without this assumption it would be difficult to explain the large cage effect values generally uncharacteristic for the reactions of free radicals in solution.¹⁴

The suggested involvement of Et₃GeLi associates has been supported by the results of X-ray analysis in solution.¹⁵ Angular dependence of X-ray scattering intensity (including small angle scattering) as well as analysis of the radical distribution function has allowed one to detect the formation of triethylgermyllithium associates in benzene, cyclohexane and THF. The resulting spatial characteristics—in benzene the diameter of the associate is 12–14 Å and the Ge–Ge distance is about 4.5 Å—allowed one to propose a hexameric structure of the associated units of Et₃GeLi. Similar to the findings of the X-ray structural analysis of the single crystals of Me₃SiLi¹⁶, one might propose a distorted octahedron structure of these associates of Et₃GeLi. Only two faces of such an octahedron are accessible for the attacking benzyl chloride molecule, since the others are blocked by the bulky Et₃Ge- substituents (Figure 1). These steric hindrances justify high values of the experimentally observed cage effects, since under these conditions GeEt₃ radicals enter the reaction in the complex with parent associate.

TABLE 1. 1H CIDNP effects and main products of the reactions of PhCH₂Cl with 0.5 M solutions of Et₃GeLi(Na,K) in various solvents and in different magnetic fields

<table>
<thead>
<tr>
<th>Reagent/Solvent</th>
<th>Viscosity (cP)</th>
<th>Products ratio, 1/2</th>
<th>CIDNP sign of α-CH₂ protons*</th>
<th>Cage effect⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et₃GeLi/Hexane</td>
<td>0.31</td>
<td>—</td>
<td>4.1 ± 0.4</td>
<td>E</td>
</tr>
<tr>
<td>Et₃GeLi/Benzene</td>
<td>0.65</td>
<td>6.0 ± 0.4</td>
<td>5.4 ± 0.3</td>
<td>E</td>
</tr>
<tr>
<td>Et₃GeLi/Dodecane</td>
<td>1.49</td>
<td>—</td>
<td>7.0 ± 0.4</td>
<td>E</td>
</tr>
<tr>
<td>Et₃GeLi/THF</td>
<td>—</td>
<td>—</td>
<td>6.5 ± 0.4</td>
<td>E</td>
</tr>
<tr>
<td>Et₃GeNa/Benzene</td>
<td>0.65</td>
<td>10.0 ± 0.8</td>
<td>7.8 ± 0.4</td>
<td>E</td>
</tr>
<tr>
<td>Et₃GeK/Benzene</td>
<td>0.65</td>
<td>13.6 ± 1.0</td>
<td>9.8 ± 0.8</td>
<td>E</td>
</tr>
</tbody>
</table>

⁶E—emission, A—absorption.
⁷The following relationship was used to estimate the cage effect, e = 1 – P, where P = 2/(1 + 2). P is calculated from the intensities of the corresponding NMR signals (of α-CH₂ protons) observed during the reaction in the magnetic field 1.88 T.
This hypothesis also allows one to explain the differences in the 1/2 products ratio for the series Et₃GeLi, Et₃GeNa and Et₃GeK (Table 1). Indeed, in these different reactions the precursor of the main products is the same singlet radical pair of benzyl and triethylgermyl radicals (Scheme 1), and without the assumption of a reactive complex of *GeEt₃ radical with Et₃GeLi, Et₃GeNa and Et₃GeK associate, it would be difficult to explain the observed trend in the products ratio. Apparently, this is due to the scale of the steric hindrances, dependent on the alkaline metal forming the backbone of the associate (Figure 1, see Plate 1).

Figure 2 shows the magnetic field dependence of the ratio of the yields of symmetrical (2) and unsymmetrical (1) products for the reaction of benzyl chloride with Et₃GeNa in benzene. As earlier observed in the reactions of alkylithiums with dichlorodiphenylmethane, the field dependence pattern qualitatively reflects two basic mechanisms of radical pair theory—HFI and Δg mechanisms. In this particular case, the cage effects in nonviscous media (benzene) create the necessary prerequisites for the

![Graph](image-url)

FIGURE 2. Dependence of the products ratio 2/1 on the external magnetic field strength (H₀) observed for the reaction of benzyl chloride with Et₃GeNa in benzene. The solid line shows the second order polynomial fit of the experimental data.
observation of the magnetic field effect, which is greater than 30%. It is necessary to stress that in the reaction under study, high cage effects are due to the unusual features of the recombination of the radical pair of $^\bullet\text{GeEt}_3$ and $^\bullet\text{CH}_2\text{Ph}$ radicals, i.e. to the reaction in the associated state, and is therefore sine qua non for the observation of the magnetic field effect.

Let us demonstrate how the theoretical modeling of the experimental magnetic field dependence could support the proposed reaction mechanism and prove the involvement of the suggested radical pair—precursor of the main reaction products. According to Scheme 1, the experimentally measured products ratio $2/1$ could be expressed as the following ratio of their formation rates:

$$2/1 = \frac{V_2}{V_1 + V_1^{\text{DIFF}}} \tag{2}$$

where $V_1$ is the in-cage formation rate of $1$, $V_1^{\text{DIFF}}$ is the formation rate of $1$ in the bulk and $V_2$ is the formation rate of $2$; $V_1 = P_S \nu$, where $\nu$ is the generation rate of free $^\bullet\text{GeEt}_3$ and $^\bullet\text{CH}_2\text{Ph}$ radicals and $P_S$ is the recombination probability of the initial radical pair comprised of $^\bullet\text{GeEt}_3$ and $^\bullet\text{CH}_2\text{Ph}$ radicals. The formation rate of $1$ in the bulk is $V_1^{\text{DIFF}} = k_1[^\bullet\text{GeEt}_3][\text{CH}_2\text{Ph}]$ and the formation rate of $2$ is $V_2 = k_2[^\bullet\text{CH}_2\text{Ph}]^2$. Thus, the product ratio $2/1$ could be rewritten in the form:

$$2/1 = \frac{k_2[^\bullet\text{CH}_2\text{Ph}]}{P_S \nu + k_1[^\bullet\text{GeEt}_3][\text{CH}_2\text{Ph}]} \tag{3}$$

Equations 4 and 5 define the time variation of the concentrations of $^\bullet\text{GeEt}_3$ and $^\bullet\text{CH}_2\text{Ph}$ radicals:

$$\frac{d[^\bullet\text{CH}_2\text{Ph}]}{dt} = (1 - P_S) \nu - k_2[^\bullet\text{CH}_2\text{Ph}]^2 - k_1[^\bullet\text{GeEt}_3][^\bullet\text{CH}_2\text{Ph}] \tag{4}$$

$$\frac{d[^\bullet\text{GeEt}_3]}{dt} = (1 - P_S) \nu - k_3[^\bullet\text{GeEt}_3]^2 - k_1[^\bullet\text{GeEt}_3][^\bullet\text{CH}_2\text{Ph}] \tag{5}$$

Assuming that in the first approximation, $k_2 = k_3 = 1/2k_1$, under stationary conditions, we obtain equation 6.

$$2/1 = \frac{1 - P_S}{2(1 + P_S)} \tag{6}$$

This simple kinetic reasoning allows us to draw the interrelation between the experimentally measured products ratio $2/1$ and the recombination probability of the initial singlet radical pair $P_S$ (Scheme 1). Theoretical calculations of $P_S$ in the frame of the semiclassical approximation\(^1\) (which considers the precession of the electron spin of a radical around the vector sum of the external magnetic field vector and the averaged vector of the HFIs of all the magnetic nuclei of this radical) for the radical pair comprised of $^\bullet\text{GeEt}_3$ and $^\bullet\text{CH}_2\text{Ph}$ radicals which take into account the magnetic resonance parameters of these radicals known from the literature\(^1\) demonstrate fairly good agreement between theory and experiment (cf Figures 2 and 3). These conclusions first demonstrate that the radical pathway of this reaction is prevalent, and second, they unambiguously confirm the proposed reaction mechanism and the structure of the radical pair, precursor of the main reaction products. One remarkable fact is noteworthy. The comparison of experimental (Figure 2) and calculated (Figure 3) magnetic field effects shows that, despite excellent reproduction of the field dependence pattern, theory fails to explain the magnitude of the
FIGURE 3. Results of theoretical modeling of the products ratio $2/1$. Calculated dependence of $(1 - P_S)/2(1 + P_S)$ on the external magnetic field strength $H_0$. $P_S$ is the recombination probability of the radical pair comprised of $\cdot$GeEt$_3$ and $\cdot$CH$_2$Ph radicals.

observed magnetic effect. Later efforts$^{19}$ have shown that if the model calculations would account for the associated state (Figure 4, see Plate 2) of the $\cdot$GeEt$_3$ radical entering the reaction with the $\cdot$CH$_2$Ph radical (the association factor could be included in the model as a variable electron exchange interaction between these radicals in the radical pair), it would be possible to reproduce the magnitude of the experimental effect. Thus, the above analysis demonstrates conclusively the potentialities of spin chemistry techniques in investigations of the elementary mechanisms of chemical reactions and the molecular dynamics of the elementary act (the role of electron exchange interaction and steric effects).

Despite the above self-evident demonstration of the radical nature of the intermediate species formed in the reactions of triorganogermyl derivatives of alkali metals, in a
number of papers one yet might find a discussion of other mechanisms, sometimes with
speculations concerning quite unusual intermediates. For instance, similar processes were
observed in the reaction of Ph₃GeLi(Na,K) with aryl halides. However, the radical pro-
cesses are postulated to be prevalent only for aryl fluorides, iodides and bromides, while
in the case of chlorides the discussion considers not only the radical mechanism, but also
a pathway involving an aryne intermediate ⁴²⁰.

\[
\text{(4)}
\]

While it is difficult to ensure the reliable observation of the radical processes during
the mixing of reagents, these are easily detected in the photoinduced reactions of aryl-
substituted compounds of Ge and Sn. Laser pulse photolysis experiments show that direct
photoionization of Ph₃Ge(Sn)⁻ anion results in the neutral radical ²¹,²². The application
of the Chemically Induced Dynamic Electron Polarization (CIDEP) method has allowed
the detection of polarized emission signal of the radicals, thus leading to a conclusion that
direct photoionization of Ph₃Ge(Sn)⁻ anion occurs from the triplet state (equation 7) ²².

\[
\text{R₃MLi} \stackrel{hν}{\rightarrow} (\text{R₃MLi})^S \rightarrow (\text{R₃MLi})^T \rightarrow [\text{R₃M} \cdots \text{e}^-]^T + \text{Li}^+ \hspace{2cm} (7)
\]

M = Ge, Sn

Similar single electron transfer processes were also observed in thermal reactions
if other electron acceptors were used instead of alkyl halides. The main products
of the interaction of R₃GeLi with electron acceptors such as 3,5-di-tert-butyl-o-
quinone, fluorenone, tetracyanoquinodimethane and 2,4,6-tri-tert-butylanitrobenzene include
the corresponding digermane and N(or O)-germyl adducts. ESR spectra of the reaction
mixture demonstrate the formation of germyl radicals as well as the radical anions of the
organic substrates²³. The electron transfer reaction has also been shown to be preferable
for the interaction of trialkylgermyl lithium with a paramagnetic quinoid (R'O⁻) which is
completely transformed into the diamagnetic anion (equation 8)²³.

\[
\text{R₃GeLi} + \text{R'O}^- \rightarrow \text{R₃Ge} + \text{R'O}^- + \text{Li}^+ \hspace{2cm} (8)
\]

The interaction of R₃GeLi (R = Ph, Mes) with conjugated aldo- and keto-forms of
electron acceptors (such as 2-furaldehyde, 2-thiophenecarboxaldehyde and their corre-
sponding nitro derivatives) leads only to germylation of the initial organic compounds.
The formation of the organic radical anions in these reactions has been confirmed by ESR
spectroscopy, and this speaks in favor of an electron transfer process. Further addition
of germyl radicals to the initial organic substrate results in the germylecarbinol formed
through a C-germylation mechanism. In the presence of an excess of the aldehyde, the
germyl ketone is formed; the corresponding nitro compounds mainly lead to O-germyl
derivatives²⁴. However, as opposed to the investigations employing spin chemistry tech-
niques, none of the studies concerns the supramolecular chemistry aspects and considers
the influence of the associated state upon the reaction mechanism.
FIGURE 1. General view of the hexameric units of triethylgermyllithium associate \((\text{Et}_3\text{GeLi})_6\) in solution: • (Li), • (Ge), • (Et), (uncoordinative bond)
FIGURE 4. Schematic presentation of the structure of the radical pair of $^{*}\text{CH}_2\text{Ph}$ radical and associated $^{*}\text{GeEt}_3$ radical: (Li), (Ge), (Et or C), and (uncoordinative bonds)
In conclusion, let us highlight the capabilities of the spin chemistry methods and the necessity to take into account the structural features when applying the magnetic and spin effects to the investigations of the reaction mechanisms. Recent publications provide an illustrative example of the unsuccessful attempt to reproduce the pioneering results\(^9\) of the observation of magnetic field influence on the reactions of \(n\)-BuLi with organic halides where the authors\(^25\) have neglected the role of association and the long-explored fact\(^26–28\) that the interactions of alkyllithiums with organic halides could follow several different mechanisms. In addition to the radical process, depending on the reaction conditions (solvent, temperature and the concentration of the reagents) these mechanisms might involve nucleophilic substitution and an ion exchange reaction. All the mechanisms above lead to identical products, and therefore to ensure the involvement of comparatively long-lived radical pairs which are responsible for the magnetic field effect, it is necessary to check their formation, e.g. by means of CIDNP. These pairs, in turn, appear only in the presence of the associated states of \(n\)-BuLi. However, the authors\(^25\) have neglected all these aspects of the mechanism under study, and if such a superficial approach were used to study a previously unknown process, this would definitely lead to erroneous conclusions about the reaction mechanism.

IV. PHOTOTRANSFORMATIONS OF THE ORGANOELEMENT \(\alpha\)-KETONES

High reactivity, the possibility to fundamentally change the nature of main reaction products through variation of the solvent polarity, excellent radical acceptor properties, unusual photochemical characteristics — all these features of organoelement \(\alpha\)-ketones \(R_3MCOR'\) (\(M = Ge, Sn\)) define the broad prospects of using these compounds in various synthetic applications. The keen interest in organoelement \(\alpha\)-ketones is also stimulated by recent developments in synthetic radical chemistry. For instance, the possibility to use \(R_3MCOR'\) as an excellent equivalent of carbonyl radical acceptor synthon has been demonstrated by the example of acyl germanes\(^29\) in radical cyclization reactions. For using the organoelement \(\alpha\)-ketones in organic syntheses it is necessary to clarify the relevant elementary reaction mechanisms. From the synthetic viewpoint, of special interest are the homolytic processes which ensure less rigid reaction conditions as compared with heterolytic ones.

A. Reaction Mechanisms of the Photolyses of \(\alpha\)-Germyl Ketones in Various Media

Free radical mechanisms of the photolytic decomposition of \(R_3MCOR'\) (\(M = Ge, Sn\)) were considered in a number of earlier fundamental studies\(^30,31\). The nature of the resulting reaction products identified in nonpolar (alkanes, benzene, either in the presence or in the absence of a radical trap) or polar (alcohols, pyridine) media has allowed the proposal of a generalized reaction mechanism of the photolysis of \(R_3GeCOR'\) compounds (Scheme 2).

In the frame of the proposed mechanism, the primary act of the photolysis of \(\alpha\)-germyl ketones in nonpolar media is a \(C-Ge\) bond cleavage (Norrish Type I) leading to element-centered and acyl (aryl) free radicals. The observed main reaction products result from the interaction of the radicals in the bulk and from the halogen abstraction from the corresponding radical trap (e.g. organic halides), if added. In contrast, in polar media (alcohol) the formation of the final reaction products could be explained only by invoking the hypothesis of a photoinduced isomerization of \(R_3GeCOR'\) to the unusual reactive germoxycarbene intermediate, \(R_3GeOCR'\), \(^5\). The insertion of the germoxycarbene into
In nonpolar media

\[
\begin{align*}
\text{Radical reaction products:} \\
R_3\dot{\text{Ge}} + \cdot \text{CR'} & \rightarrow R_3\text{Ge} + \dot{\cdot}X \\
R'\dot{\text{CO}} + \cdot \text{CR'} & \rightarrow R'\text{CO}X + \dot{\cdot}X \\
2 \cdot \text{CR'} & \rightarrow (\cdot \text{CR'})_2
\end{align*}
\]

In polar media

\[
\begin{align*}
R_3\text{GeCOR'} & \rightarrow R_3\text{GeOCR'} + \text{germoxycarbene intermediate} \\
R'\text{OH} & \rightarrow R''\text{OH} \\
R'\text{OH} & \rightarrow \text{OR''} \\
R_3\text{GeO} & \rightarrow \text{R''COR''} \\
R''\text{OH} & \rightarrow \text{R''OH} \\
R''\text{OH} & \rightarrow \text{R''OH} \\
R''\text{OH} & \rightarrow \text{R''OH} \\
R_3\text{GeOR''} & + R_3\text{GeOH} + R'\text{CH(OR''}_2 + R'\text{CHO}
\end{align*}
\]

SCHEME 2

the polar O–H bond of the alcohol results in the unstable semiacetal 6 which decomposes to the main reaction products shown in Scheme 2.

What will happen during the photolysis of R₃GeCOR' in nonpolar, nonhalogenated solvents? Early assumptions concerning the mechanism of photodecomposition of α-germyl ketones in nonpolar solvents in the absence of halogenated radical traps include the addition reaction of photochemically generated R₃M' radicals to the unsaturated C=O bond of the unreacted precursor ketone. Indeed, the application of ESR spectroscopy has allowed one to observe rather stable radical adducts (7) formed even through the thermolysis of the aroyl derivatives R₃MCOAr (M = Ge, Sn) (equations 9 and 10)\(^{33}\).

\[
\begin{align*}
\text{R₃MCOAr} & \xrightarrow{h\nu, \Delta} R₃\dot{\text{M}} + \text{COAr} \\
R₃\dot{\text{M}} + R₃\text{MCOAr} & \rightarrow R₃\text{M} – \cdot \text{C} – \text{Ar} \\
& \xrightarrow{\text{OMR₃}} (7)
\end{align*}
\]

These radical adducts have characteristic resolved ESR spectra which allow the accurate identification of all magnetic properties (g-factors and hyperfine splitting of all magnetic nuclei of the system including \(^{13}\text{C}, {^{73}\text{Ge} and {^{117}\text{Sn and }^{119}\text{Sn of the observed species})}\(^{33}\).

One of the most important implications of these experiments is the conclusion that, due to the high polarity of the C=O bond, organoelement α-ketones R₃MCOR' (M = Ge, Sn) are extraordinary effective radical traps. The electronegative oxygen atom of their carbonyl group could be attacked not only by element-centered radicals R₃M' (M = Ge, Sn), but also by thyl radicals•SR\(^{34}\) and phosphorus-centered\(^{35}\) radicals. Indeed, the experimental estimates of the absolute reaction rate constants of the element-centered radicals with
various radical traps show that the rate constants of the addition of $R_3M^\bullet$ radicals to
the oxygen atom of the carbonyl bond are nearly two orders of magnitude higher than
the reaction rate constants of halogen abstraction from the halogenated traps resulting in
the corresponding halides$^{36}$.

Earlier suggestions of the involvement of free radical intermediates have stimulated the
application of spin chemistry methods to the investigation of the detailed mechanism of
the photolysis of $\alpha$-germyl ketones in either polar or nonpolar solvents, in the presence or
in the absence of traps of element-centered free radicals. Of special interest are problems
of the multiplicity of the reactive state, and the transformations of the element-centered
free radicals in the bulk.

Table 2 lists $^1$H and $^{13}$C CIDNP effects detected during the photolysis of benzoyltri-
ethylgermane $Et_3GeCOPh$ in nonpolar ($C_6D_6$ or $c$-$C_6D_{12}$) and polar ($CD_3OD$) solvents
in the absence and in the presence of the radical traps (benzyl chloride $PhCH_2Cl$ and
bromide $PhCH_2Br$). Both the initial ketone and its decomposition products demonstrate
the effects of chemical polarization$^{37,38}$.

Note that in all the cases considered in Table 2 the ethyl protons of the initial
$Et_3GeCOPh$ demonstrate positive polarization (A). Therefore, the analysis of these effects
in accordance with the existing rules$^{11}$ allows us to conclude that partially reversible
photodecomposition of the ketone both in the presence and in the absence of the radical
traps occurs from the triplet excited state with the formation of the triplet radical pair
comprised of $Et_3Ge^\bullet$ and $^\bulletCOPh$ radicals. The analysis employed the following $g$-factor
and hyperfine interaction values of the radicals: $g(Et_3Ge^\bullet) = 2.0089$, $g(^\bulletCOPh) = 2.0008
and $A_{H}(CH_2) \leq 0.5$ mT (for $Et_3Ge^\bullet$)$^{12}$.

The question of the multiplicity of the reactive state in the photolysis of $\alpha$-germyl
ketones is rather controversial. An attempt to apply laser pulse photolysis techniques

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Reaction products</th>
<th>Chemical shift $\delta$ (ppm)</th>
<th>CIDNP sign$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Et_3GeC(O)Ph$ in $c$-$C_6D_{12}$</td>
<td>$Et_3GeC(O)Ph$</td>
<td>1.07</td>
<td>A</td>
</tr>
<tr>
<td>$Et_3GeC(O)Ph$</td>
<td>$Et_3GeCD(OGeEt_3)Ph$</td>
<td>0.85–1.15</td>
<td>E</td>
</tr>
<tr>
<td>$^{1}$H</td>
<td>$Et_3GeC(O)Ph$</td>
<td>1.07</td>
<td>A</td>
</tr>
<tr>
<td>$Et_3GeC(O)Ph$</td>
<td>$Et_3GeCl$</td>
<td>0.95</td>
<td>E</td>
</tr>
<tr>
<td></td>
<td>$PhCH_2COPh$</td>
<td>3.80</td>
<td>E</td>
</tr>
<tr>
<td>$Et_3GeC(O)Ph$ in $CD_3OD$</td>
<td>$Et_3GeC(O)Ph$</td>
<td>1.07</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>$Et_3GeOCD(OCD_3)Ph$</td>
<td>1.10</td>
<td>E</td>
</tr>
<tr>
<td>$^{13}$C</td>
<td>$Et_3GeC(O)Ph$</td>
<td>239.4</td>
<td>E</td>
</tr>
<tr>
<td>$Et_3GeC(O)Ph$</td>
<td>$Et_3GeC(O)Ph$</td>
<td>136.1</td>
<td>E</td>
</tr>
<tr>
<td>$PhCH_2Br$ in $C_6D_6$</td>
<td>1) $Et_3GeC(O)Ph$</td>
<td>2) $(CH_3CH_2)_3GeBr$</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>3) $PhCOBr$</td>
<td>3) $PhCOBr$</td>
<td>134.0</td>
</tr>
<tr>
<td></td>
<td>4) $PhCH_2COPh$</td>
<td>4) $PhCH_2COPh$</td>
<td>165.1</td>
</tr>
<tr>
<td></td>
<td>5) $PhCH_2COPh$</td>
<td>5) $PhCH_2COPh$</td>
<td>136.9</td>
</tr>
<tr>
<td></td>
<td>6) $PhCH_2COPh$</td>
<td>6) $PhCH_2COPh$</td>
<td>45.2</td>
</tr>
<tr>
<td></td>
<td>7) $PhCH_2COPh$</td>
<td>7) $PhCH_2COPh$</td>
<td>196.1</td>
</tr>
</tbody>
</table>

$^a$Double underline denotes the polarized groups of nuclei.
$^b$E—emission, A—absorption.
to investigate the photochemical transformations of α-germyl ketones failed to detect the reactions of germoxycarbenes, and it was also impossible to observe the addition of germanium-centered radicals to the oxygen atom of the carbonyl group of the unreacted R₃GeCOR' (equation 10). However, transient spectra detected during the photolysis of Ph₃GeCOPh and PhMe₂GeCOPh in cyclohexane show the absorption signals of short-lived intermediates attributed to Ph₃Ge⁺ and PhMe₂Ge⁺ radicals (λ_max = 325–330 nm and λ_max = 315–320 nm, respectively). These experimental findings do not enable us to deduce the multiplicity of the reactive state of the photolyzed α-germyl ketones. Nevertheless, speculations based on the assumption that the lowest n,π* state of Ph₃GeCOPh and PhMe₂GeCOPh (about 440 nm) lies much below the lowest π,π* state (about 295 nm) lead to the wrong conclusion that Norrish Type I photocleavage of these ketones occur from the singlet state.

The decisive evidence of the reaction mechanism is furnished by ¹³C CIDNP observations. The analysis of nuclear polarization effects detected during the photolysis of Et₃GeCOPh in the presence of benzyl bromide (Table 2, Figure 5) unambiguously confirms the formation of an initial triplet radical pair of Et₃Ge⁺ and *COPh. The following magnetic properties of free radicals were employed for the analysis of ¹³C CIDNP effects: Et₃Ge⁺[g = 2.0089, A_C(CH₂) < 0]; *COPh [g = 2.0008, A_C(CO) > 0, A_C(ipso − Ph) > 0]; *CH₂Ph[g = 2.0025, A_C(CH₂) > 0, A_C(ipso − Ph) < 0].

When Et₃GeCOPh is photolyzed in the presence of alcohols, the positive polarization of the unreacted ketone is also observed, and this points to the formation of the triplet radical pair (Et₃Ge⁺ *COPh) in polar solvents, too. The negative polarization (emission) at δ 1.10 ppm is attributed to the ethyl groups of the semiacetal Et₃GeOCD(OCD₃)Ph formed through germoxycarbene Et₃GeOCPh insertion into the O−D (O−H) bond of methanol. The sign of these effects, as well as the mere fact of their formation, imply that the insertion of germoxycarbene includes a stage of H(D) atom abstraction from methanol molecule resulting in the singlet radical pair (Et₃GeOCDPh *OCD₃). Note that an earlier proposed mechanism of the photolysis of R₃MCOR' in polar media (alcohols) has not involved any radical stages (Scheme 2). Since the latter radical pair is incapable of regenerating the ketone, the analysis of nuclear polarization effects makes it clear that the reaction proceeds from the triplet state of the initial triplet radical pair, which is also confirmed by the ¹³C CIDNP observations.

Figure 5. ¹³C CIDNP spectra detected in the photolysis of Et₃GeCOPh in C₆D₆ in the presence of PhCH₂Br: (a) initial spectrum, (b) under UV irradiation. (For line assignment, see Table 2)
9. Radical reaction mechanisms of and at organic germanium, tin and lead

initial benzoyltriethylgermane, while the polarized Et₃GeCOPh is nevertheless observed, we are led to conclude that photodecomposition of Et₃GeCOPh in alcohols involves both reaction mechanisms, i.e. Norrish Type I cleavage and the formation of germoxycarbene intermediate.

As already mentioned, the element-centered radicals formed through the photolysis of organoelement α-ketones are capable of attacking the most electronegative carbonyl group of the initial ketone. The resulting radical adducts R₃MC(OMR₃)R’ disproportionate and/or recombine to the main reaction products. Two polarized signals were observed in the NMR spectra taken during the photolysis of Et₃GeCOPh in c-C₆D₁₂ in the absence of any radical traps (Table 2): the absorption of the initial ketone which is again a manifestation of the starting triplet radical pair, and the emission of Et₃GeCD(OGeEt₃)Ph formed due to the escape of *GeEt₃ radicals into the bulk. Similar to the earlier studied aroyl derivatives, the ESR spectra recorded during the photolysis of Et₃GeCOPh in toluene-d₈ indicate the formation of a rather stable radical with g-factor equal to 2.0033 and hyperfine splitting characteristic for structure 8 (Figure 6). Thus, the detected radical adduct 8 appears to be the product of a sequential addition of two Et₃Ge* radicals to the molecule of the initial ketone.

\[ A(\text{ortho}) = 0.426 \text{ mT}; A(\text{meta}) = 0.16 \text{ mT} \]

All these experimental findings allowed us to propose a comprehensive scheme of the phototransformations of benzoyltriethylgermane in various media (Scheme 3).

![FIGURE 6. ESR spectrum of the radical formed in the photolysis of Et₃GeCOPh in toluene-d₈](image-url)
Initial stage observed in all media:

\[
\text{Et}_3\text{GeCOPh} \xrightarrow{h\nu} (\text{Et}_3\hat{\text{Ge}} \cdot \hat{\text{COPh}})^T \xrightarrow{} (\text{Et}_3\hat{\text{Ge}} \cdot \hat{\text{COPh}})^S \xrightarrow{} \text{Et}_3\text{GeCOPh}
\]

Difffusion into the bulk

\[
\text{Et}_3\hat{\text{Ge}}, \text{PhCO} \xrightarrow{} \text{Et}_3\text{GePh}
\]

The reactions in the bulk result in the following products:

In the presence of PhCH₂X (X = Cl, Br)

\[
\begin{align*}
\text{Et}_3\hat{\text{Ge}} + \text{PhCH}_2\text{X} & \rightarrow \text{Ph}\hat{\text{CH}}_2 + \text{Et}_3\text{GeX} \\
\text{PhCH}_2\text{X} + \text{PhCO} & \rightarrow \text{Ph}\hat{\text{CH}}_2 + \text{XCOPh} \\
\text{PhCH}_2 + \text{PhCO} & \rightarrow \text{PhCH}_2\text{COPh}
\end{align*}
\]

In nonpolar solvents with the initial Et₃GeCOPh

\[
\begin{align*}
\text{Et}_3\hat{\text{Ge}} + \text{Et}_3\text{GeCOPh} & \rightarrow \text{Et}_3\text{Ge} \cdot \hat{\text{C}} \cdot \text{Ph} \\
\text{Et}_3\text{GeCOPh} & \rightarrow \text{Et}_3\text{Ge} \cdot \hat{\text{C}} \cdot \text{Ph}
\end{align*}
\]

In the presence of CD₃OD:

\[
\begin{align*}
\text{Et}_3\text{GeCOPh} \xrightarrow{h\nu} & \text{Et}_3\text{GeOCDPh} \xrightarrow{\text{CD}_3\text{OD}} (\text{Et}_3\text{GeOCDPh} \cdot \text{OCD}_3)^S \rightarrow \text{Et}_3\text{Ge} \cdot \hat{\text{C}} \cdot \text{Ph}
\end{align*}
\]

SCHEME 3
B. Photolysis of $\alpha$-Stannyl Ketones

From the viewpoint of classical organometallic chemistry, $\alpha$-stannyl ketones were always seen like something exotic. Indeed, one could list a dozen papers concerning the failed attempts to identify and trace the reaction mechanisms of $\text{R}_3\text{SnCOR}$'. Some $\alpha$-stannyl ketones could be very unstable and decompose in statu nascendi. Similar to $\text{R}_3\text{GeCOR}$', the anomalous bathochromic shift of n-$\pi^*$ absorption of $\alpha$-stannyl ketones was explained by the inductive effect of the metal which led to an energy increase in the n-orbital with simultaneous preservation of the energy of the $\pi^*$-orbital. This results in a sharp decrease in the energy of the $n \rightarrow \pi^*$ transition. The first suggestions of free radical mechanisms of the reactions involving acylstannanes were based on the experimentally observed acceleration of the autooxidation of $n$-$\text{Bu}_3\text{SnCOR}$' in the presence of azobisisobutyronitrile. Unfortunately, the current literature lacks data on the reaction mechanisms of $\alpha$-stannyl ketones. However, this class of compounds could be very attractive from the viewpoint of spin chemistry techniques due to the high natural abundance of the magnetic isotopes of tin ($^{117}\text{Sn}$ and $^{119}\text{Sn}$) and the extreme magnetic resonance parameters of tin-centered radicals. For instance, the $^{119}\text{Sn}$ hyperfine interaction constant in the corresponding tin-centered radicals which is of the order of 150 mT (nuclear spin $I = 1/2$), and the $g$-factors which differ significantly from the pure spin value (about 2.0160) allow one to expect notable enhancement coefficients for $^1\text{H}$ CIDNP and provide the possibility to observe $^{119}\text{Sn}$ CIDNP.

However, the instability of the simplest $\alpha$-tin ketones precludes the application of CIDNP methods in studying their reaction mechanisms. $\text{Me}_3\text{SnCOMe}$ decomposes on attempted isolation if exposed to daylight. Therefore, to study the mechanisms of the photodecomposition of $\text{R}_3\text{SnCOR}$' it is reasonable to choose more steric hindered derivatives which are relatively stable under ambient conditions. Consequently, the regularities of the reaction mechanisms of $\alpha$-stannyl ketones $\text{R}_3\text{SnCOR}$' have been studied with $2$-methylpropanoyltripropylstannane ($\text{Pr}_3\text{SnCOCHMe}_2$ (9)).

Since one might expect that Norrish Type I cleavage of 9 should result in isopropanoyl $^*\text{COCHMe}_2$, and — after decarbonylation — isopropyl $^*\text{CHMe}_2$ radicals, it was reasonable to expect a similarity between the $^1\text{H}$ CIDNP spectra taken during the photolysis of 9 and those observed in the photolysis of diisopropyl ketone ($\text{Me}_2\text{CH})_2\text{CO}$ (10). Indeed, the experiment (Figure 7) demonstrates a striking similarity between these two reactions. Moreover, analysis of the reaction mixture show the presence of the same reaction products also detected in the photolysis of diisopropyl ketone. Table 3 lists the chemical shifts of the compounds under study and the line assignments of the detected nuclear polarization effects.

This evident similarity of proton polarizations observed for 9 and 10 shows that, in the case of 9, $^1\text{H}$ CIDNP effects could only be employed to trace the fate of $^*\text{COCHMe}_2$ and $^*\text{CHMe}_2$ radicals and the pathways of formation of the reaction products that do not contain organotin function (Table 3). To facilitate analysis of the structure and multiplicity of the initial radical pair and the reaction pathways of tin-centered radicals, it is much more convenient to employ $^{13}\text{C}$ and $^{119}\text{Sn}$ CIDNP techniques.

$^{13}\text{C}$ CIDNP effects (Figure 8) were detected for the carbonyl carbon of the initial 9 (emission, $\delta_C$ 249.8) and carbon monoxide (absorption, $\delta_C$ 183). Polarization of the carbonyl carbon is evidence for the formation of acyl type radicals $^*\text{COR}$ and, in principle, proves that photodecomposition of 9 follows Norrish Type I cleavage resulting in $^*\text{SnPr}_3$ and $^*\text{COCHMe}_2$ radicals. This conclusion is also supported by $^{119}\text{Sn}$ CIDNP effects of the initial $\alpha$-tin ketone and the organotin products of its photodecomposition (Table 4 and Figure 9).
FIGURE 7. $^1$H CIDNP effects detected in the photolysis of Pr$_3$SnCOCHMe$_2$ and diisopropyl ketone (Me$_2$CH)$_2$CO in C$_6$D$_6$ (only the spectra under irradiation are shown): (a) Pr$_3$SnCOCHMe$_2$, (b) (Me$_2$CH)$_2$CO

TABLE 3. $^1$H CIDNP effects observed in the photolysis of Pr$_3$SnCOCHMe$_2$ in C$_6$D$_6$*

<table>
<thead>
<tr>
<th>Reaction product</th>
<th>Group of nuclei</th>
<th>Chemical shift $\delta_H$, ppm (multiplicity)</th>
<th>CIDNP sign$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCH=CH$_2$</td>
<td>$\text{Me}$</td>
<td>1.65 (dd)</td>
<td>A/E + E</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}=$</td>
<td>5.90 (m)</td>
<td>A/E + A</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_2=$</td>
<td>5.10 (m)</td>
<td>A/E + E</td>
</tr>
<tr>
<td>Me$_2$CHC(O)H</td>
<td>$\text{Me}_2$</td>
<td>1.12 (d)</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}=$</td>
<td>2.38 (sp)</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>$\text{C(O)H}$</td>
<td>9.33 (d)</td>
<td>—</td>
</tr>
<tr>
<td>(Me$_2$CH)$_2$CO (10)</td>
<td>$\text{Me}_2$</td>
<td>1.02 (d)</td>
<td>A/E + A</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}=$</td>
<td>2.44 (sp)</td>
<td>A/E + E</td>
</tr>
<tr>
<td>CH$_3$CH$_2$CH$_3$</td>
<td>$\text{CH}_3$</td>
<td>0.93 (t)</td>
<td>A/E + E</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_2$=</td>
<td>0.90–1.25</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_2$=</td>
<td>1.67 (sp)</td>
<td>c</td>
</tr>
<tr>
<td>Pr$_3$SnC(O)CHMe$_2$ (9)</td>
<td>$\text{Me}_2$</td>
<td>0.90–1.25</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_2$=</td>
<td>2.45 (sp)</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>Me$_2$CH$=$</td>
<td>1.35 (d)</td>
<td>c</td>
</tr>
</tbody>
</table>

*aDouble underline denotes the polarized groups of nuclei.

$^b$E — emission, A — absorption.

$^c$The analysis of $^1$H CIDNP effects is hampered by the strong overlap of the signals of the initial Pr$_3$SnCOCHMe$_2$ with those of the reaction products.
9. Radical reaction mechanisms of and at organic germanium, tin and lead

FIGURE 8. $^{13}$C CIDNP spectra detected in the photolysis of Pr$_3$SnCOCHMe$_2$ in C$_6$D$_6$: (a) under UV irradiation, (b) after photolysis

TABLE 4. $^{119}$Sn CIDNP effects observed in the photolysis of Pr$_3$SnCOCHMe$_2$ in C$_6$D$_6$

<table>
<thead>
<tr>
<th>Reaction product</th>
<th>Group of nuclei</th>
<th>Chemical shift $\delta_{Sn}$ (ppm)$^a$</th>
<th>CIDNP sign$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr$_3$SnC(O)Pr-$_i$</td>
<td>$-Sn-$</td>
<td>$-98.0$</td>
<td>A</td>
</tr>
<tr>
<td>Pr$_3$SnPr-$_i$</td>
<td>$-Sn-$</td>
<td>$-8.0$</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>$\overline{-Sn}$</td>
<td>$-82.0$</td>
<td>A</td>
</tr>
<tr>
<td>Pr$_3$SnSnPr$_3$</td>
<td>$-44.0^c$</td>
<td></td>
<td>$A^c$</td>
</tr>
<tr>
<td></td>
<td>$-121.0^c$</td>
<td></td>
<td>$E^c$</td>
</tr>
<tr>
<td>Pr$_3$SnSn(Pr$_2$)SnPr$_3$</td>
<td>Pr$_3$Sn--</td>
<td>$-75.0^d$</td>
<td>$A^d$</td>
</tr>
<tr>
<td></td>
<td>$-Sn(Pr_2)$--</td>
<td>$-225.0^d$</td>
<td>$A^d$</td>
</tr>
</tbody>
</table>

$^a$Chemical shifts relative to Me$_4$Sn.
$^b$E — emission, A — absorption.
$^c$J($^{119}$Sn–$^{117}$Sn) satellites.
$^d$Observed only after prolonged irradiation.

FIGURE 9. $^{119}$Sn CIDNP effects detected in the photolysis of Pr$_3$SnCOCHMe$_2$ in C$_6$D$_6$: (a) 60 scans under UV irradiation, (b) additional 60 scans under light, (c) 2000 scans after photolysis
In accordance with the existing rules\(^\text{11}\) of CIDNP analysis, the observed emission of the \(^{13}\text{C}\) carbonyl group of the initial \(9\) (\(\delta_C 249.8\), Figure 8) shows that this polarization is generated in the triplet initial radical pair. An opposite sign of the polarization of CO (\(\delta_C 183\), Figure 8) suggests that the disproportionation of 2-methylpropanoyl radical \(^\cdot\text{COCHMe}_2\) with CO elimination (decarbonylation) occurs mainly after the separation of the initial radical pair, followed by the diffusion of the partner radicals into the bulk\(^\text{44}\), \(K_{\text{CO}} \sim 10^7 \text{ s}^{-1}\). An identical conclusion about the multiplicity of the initial radical pair could be made from the analysis of the \(^{119}\text{Sn}\) CIDNP effects of the initial \(\alpha\)-tin ketone (absorption, Table 4 and Figure 9). The positive \(^{119}\text{Sn}\) polarization of the tripropylisopropylstannane \(\text{Pr}_3\text{SnCHMe}_2\) also points to its formation from the triplet radical pair. However, since the above-mentioned decarbonylation takes place after the separation of the partners in the bulk, one should conclude that \(\text{Pr}_3\text{SnCHMe}_2\) is a product of the homogeneous recombination of \(^\cdot\text{SnPr}_3\) and \(^\cdot\text{CHMe}_2\) radicals (F-pair). The absorption of the recombination product of two \(^\cdot\text{SnPr}_3\) radicals, i.e. hexapropyldistannane, is easily assigned by means of the observed satellites (Figure 9 and Table 4) from the \(^{119}\text{Sn}–^{117}\text{Sn}\) spin–spin interaction with a characteristic constant \(J^{(119}\text{Sn}–^{117}\text{Sn}) = 2574 \text{ Hz}^{\text{45}}\).

Analysis of the \(^1\text{H}\) CIDNP effects could be most conveniently carried out by comparing the polarizations observed in the photolysis of \(9\) with those detected in phototransformations of \(10\) (Figure 7). It is essential to point out the similarity of the \(^1\text{H}\) CIDNP effects observed in the photolysis of \(9\) (Figure 7a), \(10\) (Figure 7b) and \(9\) in the presence of benzyl chloride \(\text{PhCH}_2\text{Cl}\) (Figure 10). In the latter case, there is no doubt that \(\text{PhCH}_2\text{Cl}\) enters

![Figure 10](image-url)
the reaction as a trap of tin-centered $^\bullet$SnPr$_3$ radicals. The above-mentioned similarity of nuclear polarizations means that $^1$H CIDNP effects in the photolysis of $\mathbf{9}$ are displayed by the radical pair which does not include an $^\bullet$SnPr$_3$ radical. Thus, the integrated analysis of all multinuclear CIDNP effects ($^1$H, $^{13}$C and $^{119}$Sn) allows one to propose a detailed scheme of the photolysis of $\mathbf{9}$ (Scheme 4).

**Reactions in the bulk:**

**In the absence of a radical trap**

\[
\begin{align*}
\text{COCHMe}_2 & \rightarrow \text{CHMe}_2 + \text{CO} \\
(\text{Pr}_3\text{Sn} & \text{CHMe}_2)^F & \rightarrow \text{Pr}_3\text{SnCHMe}_2 \\
(\text{CHMe}_2 & \text{COCHMe}_2)^F & \rightarrow (\text{Me}_2\text{CH})_2\text{CO} \\
(\text{Me}_2\text{CH} & \text{CHMe}_2)^F & \rightarrow (\text{Me}_2\text{CH})_2 \\
(\text{Pr}_3\text{Sn} & \text{SnPr}_3)^F & \rightarrow \text{Pr}_3\text{SnSnPr}_3
\end{align*}
\]

**In the presence of PhCH$_2$Cl**

\[
\begin{align*}
\text{Pr}_3\text{Sn} + \text{PhCH}_2\text{Cl} & \rightarrow \text{Pr}_3\text{SnCl} + \text{PhCH}_2 \\
\text{PhCH}_2 + \text{COCHMe}_2 & \rightarrow \text{PhCH}_2\text{COCHMe}_2 \\
\text{PhCH}_2 + \text{CH}_2\text{Ph} & \rightarrow \text{PhCH}_2\text{CH}_2\text{Ph} \\
\text{PhCH}_2 + \text{CHMe}_2 & \rightarrow \text{PhCH}_2\text{CHMe}_2
\end{align*}
\]

**SCHEME 4**
TABLE 5. Additional $^1$H CIDNP effects (see Table 3) observed in the photolysis of Pr$_3$SnCOCHMe$_2$ in C$_6$D$_6$ in the presence of PhCH$_2$Cl$^a$

<table>
<thead>
<tr>
<th>Reaction product</th>
<th>Group of nuclei</th>
<th>Chemical shift $\delta$, ppm (multiplicity)</th>
<th>CIDNP sign$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCH=CH$_2$</td>
<td>$\text{Me}=\</td>
<td>1.65 (dd)</td>
<td>A/E + A</td>
</tr>
<tr>
<td></td>
<td>$=\text{CH}_2$</td>
<td>5.90 (m)</td>
<td>A/E + E</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_2=\</td>
<td>5.10 (m)</td>
<td>A/E + A</td>
</tr>
<tr>
<td>PhCH$_2$H$_2$</td>
<td>$=\text{CH}_2=\</td>
<td>2.77 (s)</td>
<td>A</td>
</tr>
<tr>
<td>PhCH$_2$C(O)CHMe$_2$</td>
<td>$=\text{CH}_2=\</td>
<td>3.47 (s)</td>
<td>E</td>
</tr>
<tr>
<td></td>
<td>$\sigma=\text{H}</td>
<td>7.20 (s)</td>
<td>E</td>
</tr>
</tbody>
</table>

$^a$Double underline denotes the polarized groups of nuclei.

$^b$E — emission, A — absorption.

Special attention should be paid to the opposite signs of the net polarization of the propene MeCH=CH$_2$ observed in the photolysis of 9 and 10 (cf Figure 7a and Figure 7b). The analysis of the net proton polarizations of MeCH=CH$_2$ formed in the photolysis of 9 in the absence of the radical trap shows that the propene is generated from the radical pair involving the tin-centered *SnPr$_3$ radical (equation 11, Scheme 4). Indeed, the net polarization effects of propene become identical with those observed in the photodecomposition of 10, when 9 is photolyzed in the presence of benzyl chloride — the radical trap of tin-centered radicals, which precludes the participation of the *SnPr$_3$ radical in the reactions in the bulk (cf Table 3 and Table 5, Figure 7 and Figure 10). Evidently, in the absence of PhCH$_2$Cl, proton polarization of propene in the photolysis of 9 is formed at the stage of equation 11 (Scheme 4), while in the presence of benzyl chloride $^1$H CIDNP effects of MeCH=CH$_2$ are generated at the stage of equation 12 (Scheme 4). Theoretical modeling of the polarization kinetics$^{43}$ has allowed us to define the contributions of the stages of equations 11 and 12 to the observed net polarization of propene in the absence and in the presence of PhCH$_2$Cl. It has been shown that in the absence of benzyl chloride the contribution of the stage of equation 11 to the observed net polarization of MeCH=CH$_2$ is 4 orders of magnitude higher than that from the stage of equation 12. However, with PhCH$_2$Cl added, a dramatic drop in the contribution from the stage of equation 11 is observed and the stage of equation 12 becomes prevalent.

Thus, the application of multinuclear CIDNP techniques ($^1$H, $^{13}$C and $^{119}$Sn) has allowed us to obtain detailed information on the elementary mechanisms of the reactions of $\alpha$-germanium and $\alpha$-tin ketones. It has been demonstrated that photodecomposition of all the ketones under study follows the mechanism of Norrish Type I cleavage from the triplet excited state. The CIDNP results confirm the literature data$^{33,36}$ that organoelement $\alpha$-ketones are the most effective traps of element-centered radicals, i.e. that the introduction of the element atom at an $\alpha$-position to the carbonyl group increases its vulnerability toward free radical attack. An important distinction of the organoelement $\alpha$-ketones from their carbon analogs is the tendency of $\alpha$-germanium ketones to form oxycarbene intermediates in polar media, rather than ketyl-type radicals which are characteristic for carbon analogs.

V. REACTIONS OF UNSATURATED ORGANIC DERIVATIVES OF GERMANIUM, TIN AND LEAD

Despite their structural simplicity, allylic derivatives of germanium and tin R$_3$MCH$_2$CH=CH$_2$ (M = Ge, Sn) are, perhaps, among the most intriguing topics for
mechanistic research. One peculiar fact is their capability to enter photoinduced reactions of both homolytic addition and substitution, depending on the nature of the chosen reagent. The reaction mechanisms of the homolytic reactions of $R_3MCH_2CH=CH_2$ are of special interest to organic chemists, since their applications to organic synthesis open the way to hitherto unknown or otherwise almost inaccessible compounds.

A. Reactions of Homolytic Addition

Photoinduced reactions of homolytic addition of bromotrichloromethane $CCl_3Br$ to allylic derivatives of germanium and tin could be an illustrative example of the potentialities of CIDNP application to study processes where the polarization effects have not been generated at the initiation stage. An earlier proposed overall scheme of $CCl_3Br$ addition to the allylic double bond in the $R_3MCH_2CH=CH_2$ molecule was based on the analysis of the reaction products (Scheme 5).

From the viewpoint of the reaction mechanism, the emphasis in Scheme 5 is focused on products with the general formula $R_3MCH_2CHBrCH_2CCl_3$ ($M=Ge, Sn$) with a halogen atom in a $\beta$-position to the element $M$ (the so-called normal addition product). These compounds are believed to be unstable and to decompose with the elimination of an $R_3M^*$ radical. The phenomenon is referred to as $\beta$-decomposition or $\beta$-cleavage (Scheme 5). The mechanism presented in this scheme lacks the radical pair stages, while the experimental results demonstrate CIDNP effects observed for the initial compounds and the main reaction products of the interaction of $R_3MCH_2CH=CH_2$ with $CCl_3Br$ (Table 6). Thus Scheme 5, which is based on the analysis of the reaction products, needs to be refined.

The reaction mechanism of the photoinduced interaction between $Et_3SnCH_2CH=CH_2$ (11) and $CCl_3Br$ was also studied by means of another physical method — the so-called radiofrequency (RF) probing technique. To facilitate the interpretation of CIDNP data and to identify the primary reaction stage which does not involve radical pairs, it is convenient to start from the RF probing technique.

1. The radiofrequency (RF) probing technique — general background

The groundwork for the RF probing technique was laid back in the 1960s when Forsén and Hoffman proposed using the method of RF saturation to study the kinetics of fast
TABLE 6. $^1$H CIDNP effects detected in the photolysis of $R_3MCH_2=CH_2$ ($M = Ge, Sn$) in $c$-$C_6D_{12}$

<table>
<thead>
<tr>
<th>Reaction products</th>
<th>$^1$H CIDNP sign (protons in corresponding positions)$^a$</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_3MCH_2−CH\equiv CH_2$</td>
<td></td>
<td>—</td>
<td>A + A/E</td>
<td>E</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.8, $M = Ge$)$^b$</td>
<td>(5.8)</td>
<td>(4.8, $M = Ge$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.7, $M = Sn$)</td>
<td></td>
<td>(4.6, $M = Sn$)</td>
</tr>
<tr>
<td>$\text{CCl}_3\text{CH}_2\text{CH}=\text{CH}_2$</td>
<td></td>
<td>A</td>
<td>—</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(3.3)</td>
<td></td>
<td>(5.4, $M = Ge$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(5.1, $M = Sn$)</td>
</tr>
<tr>
<td>$R_3MCH_2\text{CHBrCH}_2\text{CCl}_3$</td>
<td></td>
<td>—</td>
<td>E</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.9, $M = Ge$)</td>
<td>(4.8, $M = Ge$)</td>
<td>(3.3, $M = Ge$)</td>
</tr>
<tr>
<td>$R_3\text{MCH}_2\text{CHBrCH}_2\text{CCl}_3$</td>
<td></td>
<td>E</td>
<td>—</td>
<td>E</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2.4, $M = Sn$)</td>
<td></td>
<td>(3.8, $M = Sn$)</td>
</tr>
<tr>
<td>$\text{CHCl}_3$</td>
<td></td>
<td>E</td>
<td></td>
<td>(7.3)</td>
</tr>
</tbody>
</table>

$^a$E — emission, A — absorption.

$^b$Chemical shifts ($\delta$ ppm) of the polarized signals are given in parentheses.

exchange processes. The procedure involves a radiofrequency saturation of the nuclei at one of the positions of the molecule with subsequent tracing of the fate of such a ‘label’ in the NMR spectra. In the version of this technique used in the present investigations of chemical reactions, the additional RF field is applied to a certain group of nuclei in the precursor molecule, and after the reaction the resulting NMR spectrum allows one to identify the product and location of this group of nuclei in the product molecule. In the case of homonuclear decoupling one should expect to observe a decrease in the intensity of the ‘labelled’ nuclei in the product molecule, while the heteronuclear decoupling leads to an increase in this intensity due to the nuclear Overhauser effect. The conditions described below should be met in order to observe the migration of the ‘labelled’ nuclei in the precursor to the reaction products. Let us consider a generalized reaction scheme (equation 13):

$$A \longrightarrow [B] \longrightarrow C$$

where A is the initial molecule, C is the reaction product and B is an intermediate species, free or charged radical, or any other reactive intermediate. The first condition relates to the lifetime $\tau_B$ of the intermediate species B that should be shorter than the relaxation time, i.e. $\tau_B < T_{1B}$, where $T_{1B}$ is the spin–lattice relaxation time of the nuclei B. The second and third conditions relate to the reaction time and observation time, i.e. the yield of ‘labelled’ molecules during a time period comparable to the relaxation time of the diamagnetic product molecule should be sufficient for their detection in the NMR spectrum: $t \leq T_{1C}$, where $T_{1C}$ is the spin–lattice relaxation time of the product C. The recording time also should not exceed the relaxation time of the diamagnetic molecule, otherwise one will observe only equilibrium NMR signals: $t \sim T_{1C}$. All the above possibilities and restrictions of the RF probing technique allow us to use this method to investigate the photoreactions of allylic derivatives of tin and germanium.
2. Homolytic addition of bromotrichloromethane to allyltriorganostannanes

The need to invoke two methods (CIDNP and RF probing) to study the mechanism of the photoinduced addition of CCl$_3$Br to Et$_3$SnCH$_2$CH=CH$_2$ (11) is dictated by the impossibility of analyzing the polarization effects under the assumption of CIDNP formation in a single radical pair. However, application of the RF probing technique has allowed us to ‘label’ the protons in different positions of the initial compounds and then to trace their fate, by identifying their locations in the reaction product molecule. This approach allows us to clarify the structure of at least one of the partner radicals comprising the radical pair responsible for the CIDNP formation.

The photoinduced reaction is given by equation 14:

$$\text{Et}_3\text{SnCH}_2\text{CH}=\text{CH}_2 + \text{CCl}_3\text{Br} \xrightarrow{h\nu} \text{Et}_3\text{SnBr} + \text{CH}_2=\text{CHCH}_2\text{CCl}_3$$

When a radiofrequency field is applied to the individual groups of nuclei of allyltriethylstannane (Et$_3$SnCH$_2$CH=CH$_2$) under simultaneous UV irradiation of the reaction mixture in c-$\text{C}_6\text{D}_{12}$, the NMR spectra demonstrate a peculiar pattern shown in Figure 11. The saturation of the proton signals of the precursor in position 3 leads to a 30–40% decrease in the intensity of the proton signal attributed to position 1’ of the product 4,4,4-trichlorobutene-1 (CCl$_3$CH$_2$CH=CH$_2$). The saturation of the protons in position 1 of the precursor 11 results

![Figure 11: 1H NMR spectra of the reaction mixture of Et$_3$SnCH$_2$CH=CH$_2$ with CCl$_3$Br in c-$\text{C}_6\text{D}_{12}$ under a sequential saturation (application of an RF field) to the proton groups: (a) initial spectrum; (b) under irradiation with saturation of the protons of the precursor at position 3, (c) dark spectrum with saturation of the protons of the precursor at position 3, (d) the resulting equilibrium spectrum. Numerical indices denote the protons of the precursor (Et$_3$SnC$_1$H$_2$C$_2$H= C$_3$H$_2$), and primed indices denote the protons of the reaction product (CCl$_3$C$_1$'H$_2$C$_2'$H= C$_3$'H$_2$). The part of the spectrum associated with the ethyl groups is omitted.](image-url)
in a decrease in the intensity of the NMR signal of the protons in position 3′ of the reaction product (Figure 11). The observed migration of the saturation ‘label’ 1 → 3′ and 3 → 1′ demonstrates that in full accordance with the mechanism of Scheme 5 the initial stages of the reaction involve the addition of a trichloromethyl radical •CCl3 to the terminal carbon atom (at position 3) of the double bond of 11. The formation of the radical adduct suggests that it is this radical which plays a role of one of the partners in the radical pair responsible for the formation of CIDNP effects. Moreover, it is quite reasonable to assume that the •CCl3 radical will be the other partner of this radical pair.

The analysis of the net proton polarization effects (Table 6 and Figure 12) of the main reaction product trichlorobutene Cl3CCH2CH=CH2 (1H NMR: δ = 3.3 and 5.4 ppm in c-C6H12) supports the suggestion47 that this compound might originate from the disproportionation of the diffusion (F-pair) radical pair (Et3SnCH2•CHCH2CCl3 •CCl3)F. 1H CIDNP spectra of the reaction mixture also demonstrate two negatively polarized signals (δ = 2.4 and 3.8 ppm) which are not present in the equilibrium spectrum (Figure 12). Chemical shifts and splitting parameters (doublets, J = 6–7 Hz) allow us to attribute these lines to the so-called normal addition product Et3SnCH2CHBrCH2CCl3 (12). The analysis of CIDNP shows that the observed effects could not originate in the above-mentioned F-pair. Therefore, it is reasonable to conclude that the observed polarizations are formed in the act of radical β-cleavage of the normal addition product 12 which is extremely unstable and could be detected only in its polarized state (Scheme 6).

The protons of 12 are polarized due to partial back recombination of the singlet radical pair (Et3Sn• •CH2CHBrCH2CCl3)S. The analysis of CIDNP effects of trichlorobutene does not preclude the assumption that the polarization of CH2=CHCH2CCl3 is also

FIGURE 12. 1H CIDNP effects detected in the reaction of photoinitiated addition of CCl3Br to Et3SnCH2CH=CH2 in c-C6D12: (a) initial spectrum, (b) under UV irradiation, (c) after the reaction. Numerical indices are the same as in Figure 11.
formed in the above singlet radical pair. Thus, there exist two possible pathways for the trichlorobutene formation: (i) $\beta$-cleavage of 12 and (ii) $\beta$-cleavage of the radical adduct $\text{Et}_3\text{SnCH}_2\text{CHCH}_2\text{CCl}_3$ escaped from the F-pair ($\text{Et}_3\text{SnCH}_2\text{CHCH}_2\text{CCl}_3\text{Cl}_3)^F$. However, the assumption that $\beta$-cleavage of 12 is the main source of trichlorobutene is unacceptable, since it was shown earlier\(^{46}\) that the yield of 12 in the homolytic addition reactions of various reagents to 11 is determined by their reaction rate constants with radical adducts similar to $\text{Et}_3\text{SnCH}_2\text{CHCH}_2\text{CCl}_3$. For instance, in the case of the reactions with $\text{EtSeH}, \text{EtSH}$ and $\text{EtSD}$, the yield of type 12 species decreases from 100% to 33% when passing from ethylselenol to ethyldeuteriothiol in line with their relative reactivity in the chain propagation step of radical reactions. Bromotrichloromethane is a far less reactive reagent than thiols\(^{46}\), and therefore one could hardly expect the formation of significant amounts of 12 in the process under study. An additional argument that 12 is not the main precursor of trichlorobutene are the RF-saturation experiments applied to the NMR spectral range of the protons of 12. The RF field applied during the chemical reaction within the spectral ranges $\delta = 2.3–2.5$ ppm and $3.6–3.8$ ppm (cf Figure 12) under conditions of full saturation has not lead to a decrease in the intensities of the corresponding protons of trichlorobutene. Thus, the main source of trichlorobutene and the other principal reaction product is the process of $\beta$-cleavage of the radical adduct $\text{Et}_3\text{SnCH}_2\text{CHCH}_2\text{CCl}_3$.

### 3. Photolysis of allyltriorganogermanes in the presence of CCl$_3$Br and other polyhalogenated alkanes

Photoinitiated reaction of allyltriorganogermanes with polyhalogenated alkanes is much slower than the reaction of 11 with CCl$_3$Br. The main reaction products with CCl$_3$Br include the normal addition adducts $\text{R}_3\text{GeCH}_2\text{CHBrCH}_2\text{CCl}_3$ ($\text{R}_3 = \text{Me}_3, \text{Me}_2\text{Cl}, \text{MeCl}_2, \text{Cl}_3$) and 4,4,4-trichlorobutene-1, which is present in trace amounts. The normal addition products are stable in solution up to 120°C, but their attempt at isolation by fractional distillation results in a fast cleavage to $\text{R}_3\text{GeBr}$ and trichlorobutene. It should be noted that the rate of decomposition of normal addition products depends on the electronic structure of the $\text{R}_3\text{Ge}$ group. A sequential substitution of methyl groups at the germanium with more electronegative chlorine atoms stabilizes the resulting adducts\(^{48}\).

Table 6 lists the polarization effects of the initial compounds, normal addition products and trichlorobutene observed in the photolysis of allyltriorganogermanes in the presence of CCl$_3$Br. The analysis of the detected $^1\text{H}$ CIDNP shows that, similarly to the reaction of allyltriethylstannane described above, the polarization is formed in the diffusion F-pair.
of the radical adduct $\text{R}_3\text{GeCH}_2\cdot\text{CHCH}_2\text{CCl}_3$ and $\cdot\text{CCl}_3$ radical (Scheme 7). The initial compound $\text{R}_3\text{GeCH}_2\text{CH}=$CH$_2$ is polarized as the ‘in-cage’ product of the same pair, while the polarizations of trichlorobutene CH$_2=$CHCH$_2$C$\equiv$Cl$_3$ and the normal addition product $\text{R}_3\text{GeCH}_2\text{CHBrCH}_2\text{CCl}_3$ are formed in the escape of the radicals into the bulk.

\[
\begin{align*}
(R_3\text{GeCH}_2\cdot\text{CHCH}_2\text{CCl}_3) + \text{Cl}_3\text{F} & \rightarrow R_3\text{GeCH}_2\text{CH} = \text{CH}_2 + \text{Cl}_3\text{CCl}_3 \\
R_3\text{GeCH}_2\text{CHCH}_2\text{CCl}_3 & \xrightarrow{\text{Diffusion into the bulk}} R_3\text{GeCH}_2\text{CHBrCH}_2\text{CCl}_3 \\
R_3\cdot\text{Ge} + \text{CH} = \text{CHCH}_2\text{CCl}_3 & \xrightarrow{\beta\text{-cleavage}} R_3\text{GeCH}_2\text{CHBrCH}_2\text{CCl}_3
\end{align*}
\]

SCHEME 7

The photochemical interaction of Et$_3$GeCH$_2$CH=$\text{CH}_2$ (13) with CCl$_3$Br is also accompanied by the formation of trace amounts of polarized chloroform CHCl$_3$ (Table 6 and Figure 13). The sign of chloroform polarization (emission) allows one to suggest that CHCl$_3$ is a product of the ‘in-cage’ disproportionation of the initial

\[\text{Et}_3\text{GeCH}_2\text{CH} = \text{CH}_2 + \text{CCl}_3\text{Br} \rightarrow \text{Et}_3\text{GeCH}_2\text{CHBrCH}_2\text{CCl}_3\]

**FIGURE 13.** $^1$H CIDNP effects in the photolysis of Et$_3$GeCH$_2$CH=$\text{CH}_2$ (13) in the presence of CCl$_3$Br in $c$-C$_6$D$_{12}$: (a) initial spectrum, (b) under UV irradiation, (c) dark spectrum, (d) after the photolysis. The part of the spectrum associated with the ethyl groups is omitted
diffusion pair (Scheme 7). Another product of this disproportionation is definitely Et₃GeCH₂CH=CHCCl₃, which is observed in trace amounts in the NMR spectra after completion of the reaction (equation 15).

\[
\text{(Et₃GeCH₂•CHCH₂CCl₃•CCl₃)}^\text{F} \rightarrow \text{Et₃GeCH₂CH=CHCCl₃ + CHCl₃}
\] (15)

Thus, the detailed investigations by means of spin chemistry techniques and RF probing demonstrate that the homolytic addition reactions of bromotrichloromethane to allylic derivatives of germanium and tin R₃MCH₂CH=CH₂ proceed via mechanisms that somewhat differ for M = Sn and M = Ge. Comparison of all the experimental results leads to the conclusion that all these differences are determined by both the nature of the element and the electron-donating properties of the R₃M group. However, the general feature of these processes is the involvement of free radical stages in the β-cleavage reaction as well as the radical addition to the terminal carbon to give the radical adducts R₃MCH₂CHCH₂CCl₃.

B. Homolytic Substitution Reactions

Photoinduced homolytic addition reactions of various reagents to multiple bonds of unsaturated organic derivatives of group 14 elements, particularly to the corresponding tin derivatives, are of extreme importance as synthetic routes to a number of rather complex alicyclic and heterocyclic compounds. Analysis of the basic features of these processes allows us to conclude that otherwise almost inaccessible unusual products could be formed in the homolytic substitution reactions of the hydrogen atom in the organic moiety of the organotin species, in particular, if a hydrogen atom is substituted by halogen. A major challenge is to select a proper reagent capable of entering a regiospecific reaction with the substrate which would proceed solely via a free-radical mechanism, since the ionic reactions usually lead to the elimination of an organic moiety. One example of these unusual transformations is the photoinitiated reaction of allyltriestannane Et₃SnCH₂CH=CH₂ (11) with N-bromohexamethyldisilazane (Me₃Si)₂NBr (14), leading to a high yield of allene CH₂=C=CH₂ (ca 92%). The literature shows that the reaction of 14 with olefins results in allylic bromination products. It has been suggested that the reaction with olefins proceeds via a free-radical mechanism, and this provides grounds to assume that the reaction of (Me₃Si)₂NBr with 11 will also follow the allylic bromination mechanism.

However, analysis of the main reaction products has unexpectedly revealed 92% allene and equimolar amounts of bromotriethylstannane Et₃SnBr and hexamethyldisilazane (Me₃Si)₂NH (equation 16).

\[
\text{Et₃SnCH₂CH=CH₂} + \text{(Me₃Si)₂NBr} \xrightarrow{hν} \text{Et₃SnBr} + \text{(Me₃Si)₂NH} + \text{CH₂=C=CH₂}
\] (16)

The direct photolysis of the reaction mixture of 11 and 14 in the probe of the NMR spectrometer has allowed one to detect ¹H CIDNP effects (Figure 14) of the methyl protons of (Me₃Si)₂NBr and hexamethyldisilazane, and the methylene protons of allene. The spectrum also demonstrates polarization effects in the region of olefin protons of precursor 14.

According to earlier published data, the primary act of the process is the homolytic decomposition of N-bromodisilazane 14 (Scheme 8, equations 17 and 18). Further reaction stages include the interactions of 11 with the (Me₃Si)₂N• radical and bromine atom. The above-discussed CIDNP studies of the photoinduced interaction of 11 with CCl₃Br
have shown that bromine adds to the least hydrogenated carbon atom of \( \text{11} \). It has been shown\(^{47} \) that the brominated product with the bromine atom in a \( \beta \)-position to the triethyltin substituent (\( \text{12} \)) undergoes a fast \( \beta \)-cleavage — only polarized signals of this product were detected, and no traces could be seen in the NMR spectrum after photolysis. In the present case, CIDNP effects of the allene protons suggest that, similarly to the main product of the photolysis of \( \text{11} \) with \( \text{CCl}_3\text{Br} \), i.e. \( \text{CH}_2=\text{CH}\text{CH}_2\text{CCl}_3 \), \( \text{CH}_2=\text{C}=\text{CH}_2 \) results from a \( \beta \)-cleavage of the brominated product \( \text{Et}_3\text{SnCH}_2\text{CBr}=\text{CH}_2 \) (\( \text{15} \), Scheme 8). Compound \( \text{15} \) originates from the disproportionation of the radical pair of \( \cdot \text{CH}_2\text{CHBrCH}_2\text{SnEt}_3 \) and \( (\text{Me}_3\text{Si})_2\text{N}^* \); another product of this pair is a polarized hexamethyldisilazane \( (\text{Me}_3\text{Si})_2\text{NH} \), since the \( (\text{Me}_3\text{Si})_2\text{N}^* \) radical readily abstracts hydrogen\(^{52} \) from the partner radical in the pair and it does not enter the recombination reaction.

\[
\begin{align*}
\text{Me}_3\text{Si} & \quad \text{N} \quad \text{Br} \quad \xrightarrow{\text{hv}} \quad \text{Me}_3\text{Si} \quad \text{N}^* \quad + \quad \text{Br} \\
(14) \\
\text{Me}_3\text{Si} & \quad \text{N} \quad \text{Br} \quad \xrightarrow{\text{hv}} \quad \text{Me}_3\text{Si} \quad \text{N}^* \quad + \quad \text{Br} \\
(17) \\
\text{Et}_3\text{Sn} & \quad + \quad \text{Br} \quad \xrightarrow{} \quad \text{Et}_3\text{Sn} \quad \text{Br} \\
(18)
\end{align*}
\]
Another polarized product, the precursor \( N \)-bromohexamethyldisilazane (14), could result from a chemical exchange reaction between the polarized \((\text{Me}_3\text{Si})_2\text{N}\) radical and the initial \((\text{Me}_3\text{Si})_2\text{NBr}\) (Scheme 8, equation 19).

It is necessary to emphasize the unusual character of the observed results. It is common belief that radicals usually attack the terminal \( \gamma \)-carbon atom of an allylic moiety. Indeed, the CIDNP effects detected in the photolysis of 11 in the presence of bromotrichloromethane\textsuperscript{47} unambiguously point to the formation of the radical adduct \( \text{Et}_3\text{SnCH}_2\text{•CHCH}_2\text{CCl}_3 \) resulting from the addition of the \( \text{•CCl}_3 \) radical to the terminal \( \gamma \)-carbon. However, in the present case we observe neither the products that could stem from the analogous addition of \((\text{Me}_3\text{Si})_2\text{N}\) radical to allylic \( \gamma \)-carbon, nor CIDNP effects that could be ascribed to certain unstable para- or diamagnetic intermediates formed through this addition. Instead, the \( \text{•Br} \) attacks the least hydrogenated \( \beta \)-carbon atom of the allyl-stannane and the resulting \( \text{•CH}_2\text{CHBrCH}_2\text{SnEt}_3 \) radical becomes the precursor of the unusual products of the homolytic substitution reaction.

As demonstrated earlier\textsuperscript{48}, compounds with a \( \beta \)-bromine atom to \( \text{R}_3\text{Ge} \) groups (in contrast to their tin analogs) are quite stable in solution, and the \( \beta \)-cleavage reaction is observed only during an attempt at their separation. If the above assumptions on the mechanism of \( \text{CH}_2=\text{C}=\text{CH}_2 \) formation are correct (Scheme 8), a high yield of allene should not be observed in the photoreactions of 11 and \( \text{Et}_3\text{GeCH}_2\text{CH}==\text{CH}_2 \) with 14. The experiments have indeed shown that the mixture obtained after the reaction does not contain \( \text{CH}_2=\text{C}=\text{CH}_2 \) at all. These results suggest the following regularity observed when analyzing the mechanisms of formation of the products of the photoinduced reaction of 14 with allylic tin (11) and germanium derivatives. The definitive stage of formation of the products are the interactions in the uncorrelated radical F-pair of \( \text{•CH}_2\text{CHBrCH}_2\text{M} \) and \((\text{Me}_3\text{Si})_2\text{N} \) radicals (cf Schemes 8 and 9).
When $M = \text{Sn}$ the disproportionation of the radical pair becomes the main reaction pathway, while for $M = \text{Ge}$ a recombination of the pair is also possible. Undoubtedly, this difference is caused by the influence of the element atom, and this is in agreement with the evidences obtained earlier that the effect of germanium-containing substituents on the radical addition reactions is distinctly different from that of tin-containing groups\(^47,48\).

Thus, there are two instances of the influence of the organoelement on the radical reactivity. Despite the apparent triviality, these results are unusual and the nature of the influence of organoelement function on the hydrogen atom abstraction by another radical or a recombination process is of special interest. As of now, one might only suggest that the organotin substituent, having more pronounced donor properties as compared to an organogermanium substituent, facilitates the homolytic C−H bond cleavage.

C. Other Examples of Reactions of Homolytic Addition and Substitution

Allylic derivatives $\text{R}_3\text{MCH}_2\text{CH} = \text{CH}_2$ ($M = \text{Ge, Sn, Pb}$) react with a number of element-centered radicals $\cdot\text{YPh}$ ($Y = S, \text{Se, Te}$) formed in the decomposition of the corresponding dichalcogen compounds $\text{PhYYPh}\(^53\). $\text{R}_3\text{MCH}_2\text{CH} = \text{CH}_2$ also reacts with the isopropyl free radical generated by the decomposition of $i\text{-PrHgCl}$. It has been found
that allylic derivatives of lead and, under certain conditions, the similar germanium
derivatives, undergo $S_{2H}$ or $S_{2H}'$ radical substitution reactions which follow a chain
mechanism similar to that described above for allyltriethylstannane (equation 20).

\[
\begin{align*}
\text{MR}_3 + \cdot \text{SPh} & \rightarrow \text{MR}_3 \cdot \text{SPh} \\
\end{align*}
\]  

Analysis of the yield of the product reveals the following trend—the reactivity
of the allylic derivatives of group 14 elements increases in the sequence: Ge < Sn < Pb. Comparison with the reactivity of the vinyl derivatives, in particular, with the
$\beta$-metallostyrenes, shows that $R_3MCH_2CH=CH_2$ have higher reactivity in the substitution
reactions of the $R_3M$ group by allyl or chalcogen moiety. The reactivity of the chalcogen-
centered radicals toward the allylic derivatives is given by the following sequence:
$S > Se > Te$.

Radical substitution reactions involving allylic tin derivatives could be accompanied
by a photoinduced 1,3-rearrangement. A photostationary mixture of cinnamyl(triphenyl)stannane with its regioisomer 1-phenylprop-2-enyl(triphenyl)stannane has been
shown to form in the photolysis of $(E)$-cinnamyl(triphenyl)stannane in benzene under
aerobic conditions, or in the presence of halogenated organic compounds or radical-
trapping reagents (equation 21).

\[
\begin{align*}
\text{SnPh}_3 & \stackrel{\hbar}{\rightarrow} \text{SnPh}_3 \\
\end{align*}
\]  

It is noteworthy that this rearrangement was not observed in pure benzene under anaer-
obic conditions. It is suggested that the rearrangement is intramolecular and occurs via
a $\pi-\pi^*$ excitation of the cinnamyl group. The simultaneous homolytic cleavage of the
C$-$Sn bond resulting in $\text{Ph}_3\text{Sn}^*$ and cinnamyl radicals was also observed. In the case of
crotyl- and phenyl(tributyl)stannanes, this rearrangement appears to be inefficient, while
the triphenyl and dibutylphenyl substituted derivatives undergo this 1,3-rearrangement
via photoexcitation of the phenyl substituent at the tin atom resulting in a regiosomeric
mixture of the initial linear and isomerized stannane. In both the above cases, the content
of the isomerized compound in the photostationary mixture is greater than that of the
precursor allylstannane.

Of special interest are also the reactions of allyl-substituted element-centered radicals.
For instance, AllBu$_2$Ge$^*$ and dibutyl(2-methylallyl)germyl radicals undergo disproportion-
ation reactions leading to derivatives of tetra- and divalent germanium.

\[
\begin{align*}
\text{GeBu}_2 \cdot \text{Bu}_2 \text{Ge} + \text{GeBu}_2 \cdot \text{Bu}_2 \text{Ge} & \rightarrow \text{GeBu}_2 + \cdot \text{Bu}_2 \text{Ge} \\
\end{align*}
\]  

Note that while homolysis of the element–carbon bond is as a rule not characteris-
tic for allylic derivatives, similar cyclopentadienyl tin and lead derivatives undergo a
direct photolysis with $\text{Cp}^*$ radical abstraction. ESR spectra taken in the photolysis of
CpMe₃Pb, CpPh₃Pb and Cp₂Ph₂Pb have shown the formation of the cyclopentadienyl radical. Interestingly, under the same conditions the photolysis of CpEt₃Pb results in the Cp⁺ radical only at temperatures above −50°C. Below −100°C only the formation of the ethyl radical has been observed. The properties of the resulting lead-centered radicals are similar to those of the tin-centered species, though the former demonstrate lower reactivity toward alkyl bromides and alkenes. It has been found that lead-centered radicals are effectively trapped by α,β-diketones, in particular by biacetyl, resulting in the formation of radical adducts which could be observed by means of ESR spectroscopy. The interaction of lead-centered radicals with 2-methyl-2-nitropropane leads to the corresponding radical adduct Me₃C(R₃PbO)NO⁺, which is observed in the ESR spectrum.

From the viewpoint of the electronic structure, the benzyl-substituted derivatives could demonstrate a certain similarity with the allylic species. However, their properties are close to that of the above-mentioned cyclopentadienyl derivatives, i.e. their photolysis results in the homolysis of the element–carbon bond. Both stationary and time-resolved ¹H CIDNP techniques were used to study the mechanism of photolysis of Me(PhCH₂)₃Sn and (PhCH₂)₃SnCl. The analysis of the detected nuclear polarization effects demonstrates that the decomposition of Me(PhCH₂)₃Sn occurs from a triplet excited state. The reaction mechanism and hence the observed polarizations are independent of the solvent. On the contrary, CIDNP detected in the photolysis of (PhCH₂)₃SnCl shows a marked dependence on the nature of the solvent. The analysis of polarization effects observed in benzene favors the conclusion that photodecomposition of (PhCH₂)₃SnCl occurs from the singlet excited state. When CDCl₃ is used as a solvent, the detected polarizations correspond to the simultaneous formation of both singlet and triplet radical pairs. The formation of singlet radical pairs in the photolysis of (PhCH₂)₃SnCl was taken as compelling evidence for the formation of stannylene. Similar results have stimulated discussions on the possibility of the involvement of germynes in the photolyses of benzyl-substituted digermanes.

VI. REACTIONS INVOLVING GERMYLENES AND DIGERMENES

In the last decade, reactions involving short-lived para- and diamagnetic organogermanium derivatives, i.e. germynes and unsaturated germanium derivatives containing a multiple bond Ge=X (X = Ge, N, P, O), have attracted considerable attention. Of special interest are the elementary reaction mechanisms involving these intermediates which pose a challenging problem for modern physical chemistry. For the most part, the solution amounts to a choice between radical and ionic mechanisms, since the experimental data often cannot distinguish between the two options. It is clear that the most reliable way to find a solution is to identify these short-lived intermediates, the precursors of the end reaction products.

When analyzing the literature data on reactive intermediates in organometallic reactions, two basic approaches to solve this fundamental problem are used. In the first approach, which is characteristic for classical organic chemistry, the conclusion is reached on the structure of the short-lived intermediate species and on their involvement in the process under study on the basis of analysis of the end reaction products. Another approach, more typical for physical chemistry, is based on time-resolved techniques, which allow one to measure the rate constants of the reactions of intermediates. However, in this case, one usually refrains from analysis of the reaction products. Unfortunately, it should be noted that inconsistency is often observed between the spectroscopic and kinetic data on the intermediates in reactions involving short-lived derivatives of group 14 elements. Table 7 exemplifies the discrepancies of spectral data for the simplest alkyl-substituted short-lived carbenoid, dimethylgermylene Me₂Ge: (16).

At the same time, spin chemistry techniques are capable of providing reliable information on the nature of the generated intermediates and their consequent transformations.
TABLE 7. Spectroscopic parameters of dimethylgermylene Me₂Ge:

<table>
<thead>
<tr>
<th>λ&lt;sub&gt;max&lt;/sub&gt; (nm)</th>
<th>Precursor</th>
<th>Conditions&lt;sup&gt;a&lt;/sup&gt;</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>420</td>
<td>Me₂Ge(SePh)₂</td>
<td>21 K, Ar</td>
<td>61</td>
</tr>
<tr>
<td>506</td>
<td>(Me₂Ge)&lt;sub&gt;5&lt;/sub&gt;</td>
<td>77 K, 3-MP</td>
<td>62</td>
</tr>
<tr>
<td>430</td>
<td>(Me₂Ge)&lt;sub&gt;6&lt;/sub&gt;</td>
<td>77 K, 3-MP</td>
<td>63</td>
</tr>
<tr>
<td>420</td>
<td>Me₂Ge(SePh)₂</td>
<td>77 K, 3-MP</td>
<td>61</td>
</tr>
<tr>
<td>490</td>
<td>(Me₂Ge)&lt;sub&gt;5&lt;/sub&gt;</td>
<td>293 K, c-C₆H₁₂</td>
<td>62</td>
</tr>
<tr>
<td>450</td>
<td>(Me₂Ge)&lt;sub&gt;6&lt;/sub&gt;</td>
<td>293 K, c-C₆H₁₂</td>
<td>63</td>
</tr>
<tr>
<td>425</td>
<td>PhGeMe₂SiMe₃</td>
<td>293 K, c-C₆H₁₂</td>
<td>64</td>
</tr>
<tr>
<td>420</td>
<td>Me₂Ge(SePh)₂</td>
<td>293 K, c-C₆H₁₂</td>
<td>61</td>
</tr>
<tr>
<td>420</td>
<td>Me₂Ge(SePh)₂</td>
<td>293 K, CCl₄</td>
<td>61</td>
</tr>
<tr>
<td>380</td>
<td></td>
<td>293 K, C₇H₁₆</td>
<td>65</td>
</tr>
<tr>
<td>480</td>
<td>Me₃GeGeHMe₂</td>
<td>293 K, gas phase</td>
<td>66</td>
</tr>
</tbody>
</table>

<sup>a</sup>3-MP, 3-methylpentane.

From this perspective, the combination of spin chemistry techniques and laser pulse photolysis should allow one to obtain the most valuable information on the formation and decay reactions of such active short-lived derivatives as alkyl-substituted germynes and digermynes, as well as on germanium-centered free radicals<sup>67,68</sup>.

A. Generation of Dimethylgermylene

7-Germanorbornadienes are among the most convenient and commonly used germynene precursors<sup>67–71</sup>. Under mild thermal conditions or UV irradiation these compounds decompose to the inert aromatic molecule and a short-lived germynene. Equation 23 shows the generation of Me₂Ge: from 7,7′-dimethyl-1,4,5,6-tetraphenyl-2,3-benzo-7-germanorbornadiene (17).

\[
\begin{align*}
\text{MeMe} & \begin{array}{c}
\begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array}
\end{array} \\
\text{Ph} & \begin{array}{c}
\begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array}
\end{array} \\
\text{Ph} & \begin{array}{c}
\begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array}
\end{array}
\end{align*}
\]

\[\text{hv and/or } \Delta \rightarrow \text{Me}_2\text{Ge: + (16)}\]

(17)

(16)

(18)

It is necessary to mention the ongoing discussion about the hypothesis of the involvement of a biradical species resulting from breaking of one of the Ge–C bonds in the process described by equation 23. It has been found that the thermal decomposition of 17...
monitored by the NMR spectra or by the absorption spectra of 1,2,3,4-tetraphenylnaphthalene (18) obeys a first order kinetics and is characterized by a reaction rate constant \( k = 1.1 \times 10^{-3} \text{ s}^{-1} \) (78 °C, in toluene). The order of magnitude of the activation parameters of this reaction (\( \Delta H^\neq = 116.5 \text{ kJ mol}^{-1}, \Delta S^\neq = 28.5 \text{ J mol}^{-1} \text{ K}^{-1} \) in the range 65–85 °C) are in agreement with the literature data on reactions involving biradicals. Photogeneration of 16 from 17 was also studied by pulse photolysis and matrix isolation. In addition to 16, an absorption band at \( \lambda_{\text{max}} = 420 \text{ nm} \) is observed in the photolysis of 17 at 77 K. The band was attributed to a germanium-centered 1,5-biradical. This conclusion is based on the fact that the annealing of the species with a \( \lambda_{\text{max}} \) at 420 nm did not result in germanium-containing products and it reverted to the initial 17. Thus, the mechanism of the generation of 16 in equation 24 has been proposed.

Application of the \(^1\text{H CIDNP} \) technique has allowed us to confirm the hypothesis of the biradical formation and to propose a detailed scheme of the photolysis of 17.

It is also known that 16 might react with the initial 17 at a rather high reaction rate constant, \( k = 1.2 \times 10^7 \text{ mol}^{-1} \text{ s}^{-1} \). However, the formation of the addition product of 16 to 17, 7,7',8,8'-tetramethyl-1,4,5,6-tetraphenyl-2,3-benzo-7,8-digermabicyclo[2.2.2]octadiene (19), has been observed in the NMR spectra only in the photolysis of 17 in the presence of CCl₄.
Figure 15 shows the nuclear polarization effects detected in the photolysis of 17 in deuteriobenzene, emissions of the Me groups of the initial 17 ($\delta = 0.22$ and 0.94 ppm) and the absorption of tetraphenylnaphthalene 18 ($\delta = 7.43$ ppm). CIDNP effects of the initial 17 provide direct evidence of the reversibility of the photodecomposition of 17 and confirm the hypothesis of the formation of a biradical proposed on the basis of the above-mentioned annealing experiments. Indeed, the formation of nuclear polarization effects of the initial 17 and the reversibility of the process could be explained only through the generation of the 1,5-biradical resulting from the cleavage of one of the endocyclic Ge–C bonds. The analysis of $^1$H CIDNP effects detected in the photolysis of 17 points to the formation of a germanium-centered 1,5-biradical in the singlet state. Its recombination results in the regeneration of the initial compound 17, and the methyl protons demonstrate negative (emission) polarization (Figure 15). In this case, the observed positive (absorption) polarization of the protons of the main stable reaction product 18 suggests that tetraphenylnaphthalene originates from the triplet state of this 1,5-biradical. Regarding the formation of the 1,5-biradical, one should take into account that in accordance with the requirement of the retention of total spin of the system, a certain product resulting from the decomposition of the triplet biradical (equation 24) should be formed in the triplet excited state. It is quite reasonable to assume that this triplet excited product is germylene 16, resulting from the cleavage of the second Ge–C bond in the biradical accompanied by simultaneous formation of 18. Laser pulse photolysis studies of the analogous 7-silanorbornadiene$^{73}$ confirm that 18 is formed in the singlet state, thus another product of the cleavage of the triplet biradical should be generated in a triplet excited...
The combination of CIDNP and laser pulse photolysis data allows us to propose the mechanism of the formation of 16 shown in Scheme 10.

However, attempts to detect CIDNP effects of the initial compound in the thermal decomposition of 17 have been unsuccessful. Only the polarizations formed in the radical pairs involving germyl free radicals resulting from the reaction of singlet 16 with the germylene trapping agents were observed. Possible reasons for this inconsistency might include both lower concentrations of the paramagnetic species formed in the reactions of thermal generation as compared to photoinduced decomposition, and CIDNP methodology which employed greater delays prior to the registration pulse of the NMR spectrometer. Certainly, the possibility of changes in the reaction mechanism of the thermolysis of 17 must not be ruled out, e.g. a simultaneous cleavage of both Ge—C bonds (synchronous mechanism). In this case, polarization effects will be generated only in the reactions of 16 with the trapping agents.

In concluding of this section, it is necessary to discuss some additional aspects of the process under study. In principle, as an alternative to Scheme 10 one might suggest an additional pathway for the formation of polarization effects of the initial compound 17, namely, the regeneration of 17 via the reaction of 16 with the final reaction product 18. However, since the reaction occurs in the bulk, the presence of the additional trapping agents of germylene should affect the observed CIDNP efficiency. However, it has been reliably established that polarization effects of the initial 17 appear to be independent of...
the presence of the scavengers of 16. Similar reaction of 16 with substituted naphthalenes was also not observed in the thermal decomposition of 17\textsuperscript{60,72}.

The nature of polarization effects of the initial 17 and of the tetraphenylnaphthalene 18 points to the realization of the so-called S-T\textsubscript{0} mechanism of CIDNP formation\textsuperscript{13}, characteristic for rigid biradicals. In the present case, one might expect a relatively rigid fixation of the unpaired electron orbital at the germanium atom with respect to the carbon skeleton of the 1,5-biradical 20. These structural features of the biradical 20 resulting from 7-heteronorbornadienes have been additionally confirmed by theoretical calculations of the geometry and electron exchange interaction parameters\textsuperscript{75}. Due to the lack of literature data on the structure and lifetimes of element-centered biradicals, the information obtained in CIDNP experiments is of obvious mechanistic interest. For instance, the observation of CIDNP effects allows one to estimate the lifetime of the biradical 20. In accordance with radical pair theory\textsuperscript{13}, to generate the nonequilibrium population (CIDNP) in the radicals with HFI constants not greater than 0.5 mT (typical for Me protons in the biradical 20) the lifetime of the intermediate should be longer than several nanoseconds.

It is reliably established that the singlet state is the ground state of the germylenes\textsuperscript{65}. Therefore, the consequent stages of the process under study (Scheme 10) will include triplet to singlet conversion of germylene 16 (\(\text{GeMe}_2^T\) in the triplet excited state) as well as the reactions of its triplet and singlet states with the trapping agents. Note that a wide variety of approaches has been used to study the reactions of singlet germylene, while only the application of CIDNP techniques has allowed us to identify the processes involving triplet germylene. We now discuss the reactions of 16 in various spin states.

**B. Reaction of Dimethylgermylene with Various Trapping Agents**

Insertion processes into a C–X bond (X = OH, Hal or element) are known to be characteristic of alkyl-substituted germynes\textsuperscript{60}. Application of the laser pulse photolysis technique has allowed one to determine the reaction rate constants of these processes. However, all these results characterize the reactions of germynes in the ground singlet state, and there are no literature data on the reactions of triplet germynes identified by conventional methods of physical chemistry. The insertion reactions of germynes in nonpolar solvents are thought\textsuperscript{60} to follow two alternative mechanisms: (i) formation of a three-centered intermediate state and its synchronous decomposition, and (ii) a free radical pathway involving abstraction and recombination steps. It is quite difficult to distinguish these alternatives only on the basis of analysis of the end products, while the application of CIDNP techniques often allows us to elucidate the reaction mechanism and to determine the multiplicity of the reacting state of the germylene. CIDNP methods were used to study the reactions of both thermally\textsuperscript{67,74} and photochemically\textsuperscript{68,76} generated germylene 16. First, it is noteworthy that the addition of the trapping agent does not affect the rate of thermolysis of 17\textsuperscript{67,69}. The above-described CIDNP effects of the initial compound\textsuperscript{68} detected in the photolysis of 17 also remain essentially unchanged. Hence, these trapping agents do not participate in the reaction with the element-centered 1,5-biradical 20.

The insertion reactions of 16 into the C-Hal bond of alkyl halides were found to be the most convenient model for CIDNP studies. Since in accordance with Scheme 10 the photolysis of 17 leads to the formation of triplet germylene 16, we start with the first evidence of the reactions of triplet excited 16\textsuperscript{76}.

1. **Reactions with thiacycloheptyne**

3,3,6,6-Tetramethyl-1-thiacyclohept-4-yn (21) is known to be one of the most effective trapping agents of 16, since this germylene readily inserts into its triple bond with the
formation of the corresponding germacyclopene (22) (equation 25). The rate constant of this process is \( k = 5 \times 10^8 \text{ mol}^{-1} \text{ s}^{-1} \). Figure 16 and Table 8 show the polarization effects of the initial compound and 21 (emissions of Me protons) and the positively polarized protons of the reaction product 22.

\[
\text{Me}_2\text{Ge:} + \quad \text{SMeMeMeMeMeMe} \quad \rightarrow \quad \text{SMeMeMeMeMeMeGeMeMe} \quad \text{(22)}
\]

Observation of the polarization effects of the reaction product, germacyclopene 22, confirms its formation from paramagnetic precursors. However, in the case under study, one could hardly imagine the generation of a radical pair, and therefore it is reasonable to suggest that the intermediate step of the insertion of 16 into the triple bond of thiacycloheptyne 21 involves the formation of a 1,3-biradical. Analysis of the observed proton polarization effects (Table 8 and Figure 16) in accordance with the existing rules allows us to propose the reaction mechanism in Scheme 11.

**FIGURE 16.** \(^1\text{H} \) CIDNP effects detected in the photolysis of 7-germanorbornadiene (17) in the presence of thiacycloheptyne (21) in C\(_6\)D\(_6\) (only the aliphatic part of the NMR spectra is present): (a) initial spectrum, (b) under UV irradiation, (c) after the photolysis
TABLE 8. $^1$H CIDNP effects observed in the photolysis of $\gamma$-germanorbornadiene 17 in the presence of thiacycloheptyne 21 in C$_6$D$_6$

<table>
<thead>
<tr>
<th>Reaction product</th>
<th>Chemical shift $\delta$ (ppm)</th>
<th>CIDNP effects$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>21 (Me)</td>
<td>1.15 (s, 12 H)</td>
<td>E</td>
</tr>
<tr>
<td>22 (Me)</td>
<td>1.22 (s, 12 H)</td>
<td>A</td>
</tr>
<tr>
<td>22 (Me$_2$Ge&lt;)</td>
<td>0.48 (s, 6H)</td>
<td>A</td>
</tr>
</tbody>
</table>

$^a$E, emission; A, absorption.

![Scheme 11](image)

Thus, the sign of the observed polarization of the Me protons of the product 22 (absorption) is unambiguous evidence of the formation of an intermediate triplet 1,3-biradical $23^T$, and this fact, in turn, means that 16 enters the reaction with 21 in the excited triplet state. The end product 22 is formed after the triplet–singlet conversion of the triplet biradical $23^T$ followed by cyclization of the singlet biradical $23^S$ (Scheme 11), while the triplet biradical $23^T$ also reverts to the initial reagents. Only this reverse reaction could explain the negative polarization (emission) of the Me protons of the initial thiacycloheptyne 21. It should be noted that the process described in Scheme 11 is the first example of a reaction of the excited triple state of germylene 16$^{76}$. 
2. Reactions with carbon tetrachloride

The main products of the reaction between germylene 16 and CCl₄ include the insertion product ClMe₂GeCCl₃ (24), Me₂GeCl₂ (25) and hexachloroethane C₂Cl₆. The yield of the insertion product 24 in the reaction of photochemically generated 16 is not greater than 20–30%, and the yield of 25 is 70–80%⁶⁵. In the case of thermally generated 16, the yield of 25 increases up to 95%, and this is believed to be due to thermal decomposition of 24⁶⁷. The kinetic parameters of this reaction were also studied by means of laser pulse photolysis, and Table 9 summarizes the reaction rate constants for different precursors of 16.

Both thermal⁶⁷ and photochemical⁷⁷ decomposition of 17 demonstrate CIDNP effects of the methyl protons of 24 and 25 (Table 10). In addition, the above-mentioned polarization effects of the initial 17 have been also observed in the photodecomposition of 17.

### TABLE 9. Rate constants of reactions of Me₂Ge: with CCl₄ at an ambient temperature

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Precursor/Solvent</th>
<th>k (mol⁻¹ s⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>16 + CCl₄</td>
<td>17/C₇H₁₆</td>
<td>1.2 × 10⁷</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>PhMe₂GeSiMe₃/c-C₆H₁₂</td>
<td>3.2 × 10⁸</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>(Me₂Ge)₆/c-C₆H₁₂</td>
<td>4.9 × 10⁸</td>
<td>63</td>
</tr>
</tbody>
</table>

### TABLE 10. ¹H CIDNP effects observed in the photolysis and thermolysis of 17 in the presence of halogenated traps

<table>
<thead>
<tr>
<th>Reaction mixture/solvent</th>
<th>Reaction products</th>
<th>Chemical shift δ (ppm)</th>
<th>CIDNP effects⁶⁸</th>
</tr>
</thead>
<tbody>
<tr>
<td>17 + CCl₄/MePh (1:3) (thermolysis at 80°C)</td>
<td>ClMe₂GeCCl₃</td>
<td>0.80</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>Me₂GeCl₂</td>
<td>0.90</td>
<td>E</td>
</tr>
<tr>
<td>17 [10⁻² M] + CCl₄/C₆D₆ (1:1) (photolysis at 20°C)</td>
<td>Me₂Ge₂CCl₃</td>
<td>0.98</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>Me₂GeCl₂</td>
<td>1.00</td>
<td>E</td>
</tr>
<tr>
<td>17 + Me₃SnCl/C₆D₆ (photolysis at 20°C)</td>
<td>ClMe₂GeSnMe₃</td>
<td>0.68</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>ClMe₂GeSnMe₃</td>
<td>0.74</td>
<td>A</td>
</tr>
<tr>
<td>17 + PhCH₂Br/PhCl (thermolysis at 80°C)</td>
<td>BrMe₂GeCH₂Ph</td>
<td>0.55</td>
<td>E</td>
</tr>
<tr>
<td></td>
<td>BrMe₂GeCH₂Ph</td>
<td>2.57</td>
<td>E</td>
</tr>
<tr>
<td></td>
<td>Me₂GeBr₂</td>
<td>1.06</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>PhMe</td>
<td>2.22</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>(PhCH₂)₂</td>
<td>2.84</td>
<td>—</td>
</tr>
<tr>
<td>17 + PhCH₂Br/c-C₆D₁₂ (photolysis at 20°C)</td>
<td>Me₂GeBr₂</td>
<td>0.95</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>PhMe</td>
<td>2.30</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>(PhCH₂)₂</td>
<td>2.80</td>
<td>—</td>
</tr>
</tbody>
</table>

⁶⁸E, emission; A, absorption.

* NMR spectra after the photolysis show a single line at δ = 1.00 ppm; the addition of 25 to the reaction mixture allows us to assign the signal to this compound.

* In accordance with the literature data, the sole NMR signal at δ = 0.72 ppm observed after the reaction corresponds to the main reaction product 25.
CIDNP effects of the main reaction products 24 and 25 suggest that the first stage of the interaction of 16 with the trapping agent (CCl₄) is the abstraction of a halogen atom. The resulting radical pair of •GeMe₂Cl and •CCl₃ radicals recombines to give the product 24 of insertion of 16 into the C—Cl bond. The escape of the radicals into the bulk followed by the abstraction of a second halogen atom leads to 25. The analysis of CIDNP effects observed in the presence of excess amounts of CCl₄ (Table 10) shows that the initial radical pair has triplet multiplicity. Thus, 16 generated in the photolysis of 17 enters the reaction with CCl₄ in the excited triplet state (Scheme 12).

![Scheme 12](image)

An interesting feature of these reactions observed only in CIDNP experiments is the formation of chloroform (Table 10). It is reasonable to assume that a methyl group of the •GeMe₂Cl radical is the source of the polarized proton of CHCl₃, and chloroform is the second cage product of the disproportionation of the singlet radical pair (Scheme 12). It is seen from Table 10 that the increase in concentration of the initial 17 results in alteration of the CIDNP signs of the ‘in-cage’ and ‘escape’ products. This effect is most likely due to the reactions of both singlet and triplet states of 16. It could be also explained by the competitive reactions of 16 with CCl₄ and the initial 17. As already mentioned, this reaction yields 7,8-digermabicyclo[2.2.2]octadiene 19.

3. Reactions with chlorotrimethylstannane

According to the literature data, the rate constant of the reaction of 16 with Me₃SnCl is high enough (k = 3.5 × 10⁸ mol⁻¹ s⁻¹) to expect that this scavenger will be also capable of trapping triplet germylene 16. Indeed, the polarization effects (Table 10) observed in the reaction of photogenerated 16 with chlorotrimethylstannane in the absorption of both methyl groups at Sn and Ge atoms of the insertion product Me₃SnGeMe₂Cl could not be ascribed only to the reaction of singlet 16, since in this case the Me₃Sn protons would demonstrate emission. On the other hand, if the reaction of triplet 16 would prevail, one should expect to observe opposite signs of the ClMe₂Ge and Me₃Sn protons of the insertion product (emission and absorption, respectively). Taking into account the
sufficiently high rate constant of the reaction of 16 with Me₃SnCl, one might suggest that chlorotrimethylstannane reacted with both spin states of 16, and that the observed CIDNP is essentially the superposition of the polarization effects formed in the triplet and singlet radical pairs. This hypothesis could be corroborated or discounted only by analysis of the dependence of the efficiency of the CIDNP of Me₃SnGeMe₂Cl on the Me₃SnCl concentration. However, the literature lacks this kind of data.

4. Reaction with benzyl bromide

CIDNP techniques have been successfully applied to investigations of the detailed mechanism of the reaction of 16 with benzyl bromide. The yield of the end products depends on the mode of generation of 16. In the case of thermal reaction, the reaction mainly results in the insertion product, PhCH₂GeMe₂Br, together with amounts of Me₂GeBr₂ (5%), PhMe (5%) and (PhCH₂)₂ (15%). The analysis of ¹H CIDNP effects of PhCH₂GeMe₂Br and Me₂GeBr₂ (Table 10) allows one to propose the mechanism involving the reactions of ground singlet state of 16 shown in Scheme 13.

![Scheme 13](image)

However, in the reaction involving photogenerated 16, only one polarized product (Me₂GeBr₂, Table 10) is observed. In accordance with Scheme 13 it is formed in the bulk and demonstrates polarization effects identical to those detected in the thermolysis. It could be suggested that in both cases the reaction follows the same mechanism, and the ‘in-cage’ product PhCH₂GeMe₂Br appears to be unstable under the UV irradiation. Analogous singlet radical pairs are also shown to form in the reactions of singlet 16 with bromotrichloromethane, benzyl iodide and chlorodiphenylmethane.

C. Generation of a Digermene from a 7,8-Digermabicyclo[2.2.2]octadiene

Bicyclic molecules with a Ge–Ge bond are considered to be potential precursors of another family of active short-lived germanium derivatives, the digermenes. Photochemical decomposition of 1,4-diphenyl-7,7′,8,8′-tetramethyl-2,3-benzo-7,8-digermabicyclo[2.2.2]octadiene (26) results in 1,4-diphenynaphthalene (27) and supposedly in tetramethyldigermene (28) identified on the basis of the products derived by its reaction with trapping agents (equation 26). The existing views of the reaction mechanisms of the decomposition of such bicyclic compounds are based on
9. Radical reaction mechanisms of and at organic germanium, tin and lead analogies with the schemes proposed for 7-heteronorbornadienes.

Similar to the case of 7-heteronorbornadienes, the application of the $^1$H CIDNP method has allowed us to identify the elementary stages of the photolytic decomposition of 26. In addition to 27, the main reaction products also include oligogerananes and the product of photorearrangement of the initial 26, namely 6,6',7,7'-tetramethyl-2,5-diphenyl-3,4-benzo-6,7-digermatricyclo[3.3.0.0]octane. Table 11 and Figure 17 show the polarization effects of methyl and aromatic 5,6-protons of the initial 26 observed in the photolysis in C₆D₆; similar effects were also observed in c-C₆D₁₂ and in CCl₄-C₆D₆ mixtures.

It is apparent that the polarization effects observed in this reaction (Table 11) are similar to those detected in the photolysis of 7-germanorbornadiene 17 (see Section IV.A). In this case, the opposite sign of the effects of the initial 7,8-digerma­bicyclooctadiene 26 and 1,4-diphenynaphthalene 27 most likely indicate an S-T₀ mechanism of CIDNP formation. Thus, CIDNP data confirm the suggestion that photodecomposition of digerma­bicyclo derivatives follows a mechanism analogous to that proposed for 7-germanorbornadiene, i.e. via a cleavage of one endocyclic C–Ge bond with formation of the intermediate 1,6-biradical. The mechanism in Scheme 14 has been proposed on the basis of the analysis of the observed CIDNP effects.

Analysis of the observed polarization effects (Table 11 and Figure 17) shows that 26 is regenerated through the recombination of the singlet 1,6-biradical 29, while the cleavage of the second C–Ge bond in triplet biradical 29 results in a triplet excited diphenynaphthalene 27 and tetramethyldigermane 28. Note that the formation of a triplet excited state of a diamagnetic molecule from the triplet biradical 29 follows from the requirement of retention of the total spin of the system. The formation of the excited triplet state of diphenynaphthalene 27 has been confirmed in laser pulse photolysis experiments.

An intensive absorption band is detected immediately after the first laser pulse in the photolysis of a solution of 26. Its characteristic maximum band ($\lambda_{\text{max}} = 420$ nm

<table>
<thead>
<tr>
<th>Reaction product</th>
<th>Chemical shift $\delta$ (ppm)</th>
<th>CIDNP effects$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>26 (GeMe₂)</td>
<td>0.35, 0.51 (both s)</td>
<td>E</td>
</tr>
<tr>
<td>26 (H(5),H(6))</td>
<td>6.15 (s)</td>
<td>E</td>
</tr>
<tr>
<td>27 (H(2),H(3))</td>
<td>7.43 (s)</td>
<td>A</td>
</tr>
<tr>
<td>27 (H(6-9))</td>
<td>7.20–8.20 (m)</td>
<td>—</td>
</tr>
<tr>
<td>27 (Ph)</td>
<td>7.25 (s, 10 H)</td>
<td>—</td>
</tr>
</tbody>
</table>

$^d$E, emission; A, absorption.
FIGURE 17. $^1$H CIDNP effects detected in the photolysis of 7,8-digermbicyclooctadiene (26) in C$_6$D$_6$: (a) initial spectrum, (b) under UV irradiation

SCHEME 14
in hexane\textsuperscript{79} and $\lambda_{\text{max}} = 430$ nm in cyclohexane\textsuperscript{80}) is effectively quenched in the presence of oxygen ($k = 3.5 \times 10^9$ mol\textsuperscript{-1}s$^{-1}$). These observations are in good agreement with the literature data on the T-T absorption of 1,4-diphenynaphthalene\textsuperscript{81}, and this has enabled the experimentally detected absorption band to be ascribed to the triplet excited 27 (Scheme 14).

At the same time, the use of an excimer laser as a light source ($\lambda = 308$ nm) precludes the detection of the absorption signal at $\lambda = 380$ nm which is observed with an excitation light at $\lambda = 266$ nm and ascribed to tetramethyldigermene\textsuperscript{80}. This discrepancy could be also explained by the relatively low yield of 28 when $\lambda = 308$ nm is used for the excitation due to the significant difference in the molar extinctions of 26 in these two spectral regions.

Unfortunately, the above results do not allow one to determine unequivocally the mechanism presented in Scheme 14 as the sole possible pathway for the photodecomposition of 26, or if there exists a possibility of a parallel reaction with sequential generation of two germylenes 17 (Scheme 15). In this case, one should expect a Ge–Ge bond cleavage in the 1,6-biradical 29 and the resulting 1,5-biradical might display two alternative pathways: (i) a recombination resulting in the corresponding 7-germanorbornadiene, or (ii) a cleavage of a second C–Ge bond generating one more germylene 16 and a triplet excited diphenynaphthalene 27 (Scheme 15). If the latter possibility is realized, one might expect to
observe the polarized signals of the corresponding 7-germanorbornadiene. However, these have not been detected experimentally\(^\text{79}\). This does not necessarily mean that dimethylgermylene 16 is not formed in the process under study, since 7-germanorbornadiene most likely will not accumulate under the stationary UV irradiation. Moreover, the possibility of mutual transformations of germylene and digermene should not be excluded. Similar reactions are well-explored for the so-called Lappert’s digermenes with \((\text{Me}_3\text{Si})_2\text{CH}\) substituents. These compounds dissociate spontaneously to the corresponding germynes\(^3,^4\) and, according to theoretical predictions, analogous reactions are also possible for the simplest digermenes.

In order to gain a deeper understanding of the reaction mechanism of the photolysis of 26, it is reasonable to study this process in the presence of trapping agents capable of reacting with the expected intermediate, i.e. with germylene and/or digermene. Thus, comparison of the CIDNP effect detected in the photolysis of 17 and 26 in the presence of trapping agents will allow us to study the consecutive formation of digermene 28 and germylene 16 generated from 26 and to define the spin of the generated intermediates and their reactive states involved in the reactions with the trapping agents.

**D. Reactions of the Intermediates Formed in the Photolysis of a 7,8-Digermabicyclooctadiene with Various Trapping Agents**

Because of the known capability of digermenes to insert into multiple bonds\(^3,^4\), it is reasonable to start the present discussion with the reactions which occur in the photolysis of 26 in the presence of unsaturated trapping agents. Similarly to germylene 16, digermene 28 could insert into the triple bond of thiacycloheptyne 21 with the formation of digermacyclobutene 30.

![Diagram](image)

Table 12 and Figure 18 show the polarization effects detected in the photolysis of 26 in the presence of thiacycloheptyne 21 which could be compared with the effects observed under analogous conditions in the photodecomposition of 7-germanorbornadiene 17 (Table 8).

Two polarized lines \((\delta = 1.22 \text{ and } 0.48 \text{ ppm})\) strictly coincide with the signals earlier assigned to germacyclopentene 22 resulting from the insertion of germylene 16 into the triple bond of thiacycloheptyne 21 (Table 8 and Table 12). According to the literature\(^82\), signals at \(\delta = 1.13 \text{ and } 0.65 \text{ ppm}\) are attributed to the digermacyclobutene 30. Signals from 30 could be observed only at the initial stages of the photolysis and, after prolonged UV irradiation, germacyclopentene 22 remains the major reaction product (Figure 18). This points to the low stability of 30 under conditions of stationary photolysis. Photodecomposition of digermacyclobutene 30 might result in germylene 16 and germacyclopentene 22. Another reaction resulting in the polarized germacyclopentene 22 involves the insertion of triplet excited germylene 16 into the triple bond of thiacycloheptyne 21 via the biradical intermediates (Scheme 11). A major question is to decide
TABLE 12. $^1$H CIDNP effects observed in the photolysis of 7,8-digermabicyclooctadiene 26 in the presence of thiacycloheptyne 21

<table>
<thead>
<tr>
<th>Reaction product</th>
<th>Chemical shift $\delta$ (ppm)</th>
<th>CIDNP effects$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>21 (Me)</td>
<td>1.15 (s, 12H)</td>
<td>E</td>
</tr>
<tr>
<td>22 (Me)</td>
<td>1.22 (s, 12H)</td>
<td>A</td>
</tr>
<tr>
<td>22 (GeMe$_2$)</td>
<td>0.48 (s, 6H)</td>
<td>A</td>
</tr>
<tr>
<td>30 (Me)</td>
<td>1.13 (s, 12H)</td>
<td>A</td>
</tr>
<tr>
<td>30 (GeMe$_2$)</td>
<td>0.65 (s, 12H)</td>
<td>—</td>
</tr>
</tbody>
</table>

$^a$E, emission; A, absorption.

FIGURE 18. $^1$H CIDNP effects observed in the photolysis of 7,8-digermabicyclooctadiene 26 in the presence of thiacycloheptyne 21 in C$_6$D$_6$: (a) under UV irradiation, (b) after the photolysis between two possible sources of triplet germylene in the system under study: the decomposition of digermacyclobutene 30 or of tetramethyldigermene 28? The possibility of forming both triplet and singlet germylene in the decomposition of Me$_2$Ge=GeMe$_2$ is determined by certain features of the double bond in digermene which is characterized by weak side overlap of the p-electron orbitals of germanium atoms (see equation 27)$^{3,4}$.

\[
\begin{align*}
\text{Me}_2\text{Ge=GeMe}_2 & \rightarrow \text{Me}_2\text{Ge}^S + \cdot\text{GeMe}_2^T \\
(28) & \rightarrow (16^S) + (16^T)
\end{align*}
\]

In any case, the identical polarization effects of germacyclopene 22 observed in the photolysis of 17 and 26 in the presence of thiacycloheptyne 21 confirm the involvement of triplet excited germylene 16. CIDNP effects of the methyl groups of digermacyclobutene 30 suggest that its formation follows a mechanism analogous to that presented in Scheme 11, though involving the corresponding 1,3-biradical. The comparison with the polarization effects detected in the presence of halogenated trapping agents could be helpful for a better understanding of the possibility of generating germylene 16 from digermene 28.
It has been found that 7,8-digermabicyclooctadiene 26 reacts spontaneously with CCl₄ and benzyl bromide at ambient temperatures. However, these reactions are in fact much slower than the photolysis and do not preclude the observation of CIDNP. Moreover, the presence of these halogenated trapping agents does not hamper the detection of CIDNP effects formed in the photolysis of the initial 26. Thus, the trapping agents do not enter the reaction with the intermediate 1,6-biradical 29 which is responsible for the CIDNP formation (Scheme 14). CIDNP effects detected in these reactions are summarized in Table 13 and the experimental spectra are shown in Figure 19.

Photoinitiated reaction of 7,8-digermabicyclooctadiene 26 with carbon tetrachloride yields diphenylnaphthalene 27 (95%), hexachloroethane C₂Cl₆ (37%), dichlorotramethylgermane ClMe₂GeGeMe₂Cl (71%) and dichlorodimethylgermane Me₂GeCl₂ (27%)⁸⁰. The formation of a significant amount of ClMe₂GeGeMe₂Cl is explained by the

| Reaction mixture/solvent | Reaction products | Chemical shift δ (ppm) | CIDNP effects
|--------------------------|-------------------|------------------------|----------------
| 26 + CCl₄/C₆D₆ (1:3)     | Me₂ClGeCCl₃       | 0.67                   | E (weak)       |
|                          | Me₂GeCl₂          | 0.70                   | A (weak)       |
|                          | CHCl₃             | 6.45                   | E              |
|                          | Me₂GeBr₂          | 1.10                   | E              |
|                          |                   | 4.30                   | E              |

| 26 + PhCH₂Br/C₆D₆ | [intermediates] | 3.50, (dd J = 7.0 Hz; J = 4.0 Hz) | A |
|                   |                 | 5.20, (t, J = 7.0 Hz)             | E |

⁸⁰E, emission; A, absorption.

FIGURE 19. ¹H CIDNP effects observed in the photolysis of 7,8-digermabicyclooctadiene 26 in C₆D₆ in the presence of benzyl bromide
reaction of digermene 28 with CCl₄, resulting in a sequential abstraction of two chlorine atoms. However, it has been shown that this product might also result from the insertion of germyle 16 into the Ge−Cl bond of dichlorodimethylgermane. On the other hand, the presence of monogermanium derivatives as well as polarized CHCl₃ points to the involvement of dimethylgermylene 16 (cf Tables 10 and 13). Note that chloroform demonstrates noticeable CIDNP effects with a sign identical to that observed in the photolysis of 7-germanorbornadiene 17 against the background of a rather weak polarization of the Me protons of ClMe₂GeCCl₃ and Me₂GeCl₂.

Thus, the formation of polarized chloroform and monogermanium compounds in the photolysis of 7,8-digermabicycloclooctadiene 26 in the presence of CCl₄ shows that the generated germyle 16 enters the reaction with CCl₄ in a triplet excited state (Scheme 12). However, judging from the weak polarizations of ClMe₂GeCCl₃ and Me₂GeCl₂ one should not exclude also reactions of the ground singlet state of 16. The possibility of generating both singlet and triplet excited germyle 16 has already been mentioned (equation 27). In fact, the CIDNP technique allows one to detect only the reaction of 16 with CCl₄ and no signs of interaction between the digermene 28 and carbon tetrachloride were observed despite the known fact that the rate constant of this process measured in laser pulse photolysis experiments is rather high (k = 1.2 × 10⁷ mol⁻¹ s⁻¹).

The reverse situation has been observed when the photolysis of 7,8-digermabicycloclooctadiene 26 is performed in the presence of benzyl bromide. These observations are markedly different from the CIDNP pattern detected in the photolysis of 7-germanorbornadiene 17 with PhCH₂Br (Tables 10 and 13). Dibromodimethylgermane is a characteristic product of the photolysis of both 17 and 26 in the presence of PhCH₂Br and, similarly to the reactions with CCl₄, the sign of the polarization effects of Me₂GeBr₂ (Table 13) suggests the involvement of triplet excited germyle 16. However, the major distinction between these two processes is the appearance of polarized signals close to the methylene protons of PhCH₂Br (δ = 4.30 ppm) and in the range characteristic for the double bond protons (Figure 19). The chemical shift of the polarized protons suggests that the reactive intermediates generated by the photolysis of 7,8-digermabicycloclooctadiene 26 do not enter the C−Br bond cleavage reaction of benzyl bromide which is characteristic for germylenes, but rather attack the benzene ring, leading to the loss of aromaticity. It is known that digermenes could insert into the double bonds of aromatic molecules (anthracene, benzene derivatives, heterocycles, etc.) to form the corresponding bicyclic compounds, but these reactions have not been detected for germylenes. Therefore, it is quite reasonable to assume that the observed CIDNP effects are generated in the reaction of digermene 28 and PhCH₂Br. However, the resulting products are unstable, and it was impossible to accumulate detectable amounts under UV irradiation. The mass spectra of the reaction mixture demonstrate only the presence of Me₂GeBr₂, (PhCH₂)₂ and oligogermanes. Unfortunately, only polarized signals lead to certain information on the nature of these intermediate products (Figure 19) and, at present, it is impossible to propose a reliable structure for these species. The absence of analogous polarization effects in the photolysis of 17 where 28 could be generated only through the dimerization of germyle 16 definitely supports the hypothesis that in the photolysis of 26, germyle 16 is formed through the decomposition of digermene 28 (equation 27).

VII. CONCLUSION

The achievements of mechanistic studies employing spin chemistry methods convincingly demonstrate the potential of these techniques in revealing the detailed reaction mechanisms of a number of homolytic processes involving organic Ge, Sn and Pb compounds. The role of short-lived paramagnetic (and sometimes diamagnetic) intermediates, such as free...
radicals, biradicals, germylenes and digermenes, has been conclusively elucidated. The application of spin chemistry techniques, in particular, in combination with laser pulse photolysis methods allows us to attain much deeper insight into the organometallic chemistry of highly reactive species. From our viewpoint, progress in the investigation of the elementary mechanisms could be achieved only when applying a combination of physical and chemical analytical techniques. This is particularly true since the processes described in the present chapter do not compare with the rapidly growing number of newly synthesized organometallic compounds and with reactions in which they participate. If our efforts to attract the attention of the organometallic community to the spectacular potential of spin chemistry techniques turn out to be successful, we will consider our goal to have been achieved.

**VIII. REFERENCES**

CHAPTER 8

Structural effects on germanium, tin and lead compounds

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I. THE NATURE OF STRUCTURAL EFFECTS

A. Introduction

This article is a supplement to the chapter entitled ‘Substituent effects of germanium, tin, and lead groups’1. Included is work published after the appearance of the original chapter, topics which were not discussed previously and topics for which further examples would be useful. Readers should consult the glossary in the original chapter for the definitions of terms and variables. Those terms and variables which are new will be defined in Appendix I of this supplement. A list of abbreviations used is given below. The objective of both the original chapter and this supplement is to describe methods and parameters for the quantitative description of structural effects on chemical reactivity, chemical and physical properties, and biological activities of germanium, tin and lead compounds.

ABBREVIATIONS

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B. Structure–Property Quantitative Relationships (SPQR)

Structural variations in a chemical species (molecule, ion, radical, carbene, benzyne etc.) generally result in changes in some measured property of the species. The property measured may be a chemical reactivity (rate or equilibrium constant, oxidation potential etc.), chemical property (resulting from a difference in intermolecular forces between an
initial and a final state), a physical property (either of the ground state or of an excited state) or a biological activity. The change in the measured property that results from a structural variation is a structural effect. Structural effects within a set of related species can be modeled by the correlation of the measured properties with appropriate parameters using statistical methods. The resulting equation is called a structure–property quantitative relationship (SPQR). The parameters required for modeling structural effects may be obtained from physicochemical reference data sets, quantum chemical calculations, topological methods, comparative molecular field analysis (COMFA) or molecular mechanics (restricted to steric effects). An alternative to statistical methods is the use of neural networks.

SPQR have three functions:

1. They are predictive. Once the SPQR has been determined, the value of the property can be calculated for any chemical species for which the structural effect parameters are available. This makes possible the design of chemical species with specific chemical, physical or biological properties.

2. They are explicative. SPQR can be used to explain structural effects on a measured property. In the case of chemical reactivity they can provide information useful in determining reaction mechanisms.

3. They are archival. Information regarding structural effects on measurable properties can easily and concisely be stored in this way.

It must be noted that in order to be explicative, SPQR must be obtained either by using pure parameters or by using composite parameters of known composition. A pure parameter is a parameter which represents a single structural effect. A composite parameter is a parameter that represents two or more structural effects.

Data sets are of three types. The most frequently encountered type has the form XGY in which X is a variable substituent, Y is an active site (an atom or group of atoms responsible for the observed phenomenon) and G is a skeletal group to which X and Y are bonded. A second type has the form XY; the substituent X is directly bonded to the active site Y. In the third type, designated X_Y, the entire chemical species is both active site and variable substituent.

Structural effects are of three types: electrical effects, steric effects and intermolecular force effects.

II. ELECTRICAL EFFECTS

It has long been known that a substituent X in an XGY system can exert an electrical effect on an active site Y. It is also well known that the electrical effect which results when X is bonded to an sp³ hybridized carbon atom differs from that observed when X is bonded to an sp² or an sp hybridized carbon atom. As electron delocalization is minimal, in the first case, it has been chosen as the reference system. The electrical effect observed in systems of this type is a universal electrical effect which occurs in all systems. In the second type of system, a second effect (resonance effect) occurs due to delocalization, which is dependent both on the inherent capacity for delocalization and on the electronic demand of the active site. In systems of the second type the overall (total) electrical effect is assumed to be a combination of the universal and the delocalized electrical effects. For many years an argument has sometimes raged (and at other times whimpered) concerning the mode of transmission of the universal electrical effect. Two models were proposed originally by Derick², a through bond model (the inductive effect) and a through space model (the field effect). These proposals were developed into the classical inductive effect (CIE)³ and the classical field effect (CFE)⁴ models. As the CIE model could not account
for the observed dependence of the electrical effect on path number, a modified version
was introduced (the MIE model)\(^5\). The matter has recently been treated in some detail\(^6,7\).
The dependence on molecular geometry is in best agreement with a modified field effect
(MFE) model\(^8\).

Electrical effects are conveniently described by the triparametric (three independent
variables) LDR equation (equation 1):

\[
Q_X = L\sigma_{lX} + D\sigma_{dX} + R\sigma_{eX} + h
\]  

(1)
or relationships derived from it. The parameters are described below.

\(\sigma_l\) is the localized (field) electrical effect parameter; it is identical to \(\sigma_I\) and \(\sigma_F\). Though
other localized electrical effect parameters such as \(\sigma_q\) have been proposed, there is no
advantage to their use. The \(\sigma^*\) parameter and the \(F\) parameter have sometimes been
used as localized electrical effect parameters; such use is generally incorrect as both of
these parameters contain a small but significant delocalized effect contribution. As was
noted above, the available evidence is strongly in favor of an electric field model for
transmission of the localized effect.

\(\sigma_d\) is the intrinsic delocalized (resonance) electrical effect parameter; it represents the
delocalized electrical effect in a system with no electronic demand.

\(\sigma_e\) is the electronic demand sensitivity parameter; it adjusts the delocalized effect of a
group to meet the electronic demand of the system.

The electrical effect is characterized by two quantities derived from equation 1:

The electronic demand, \(\eta\), is a property of a system or of a composite electrical effect
parameter that is itself a function of both \(\sigma_d\) and \(\sigma_e\). It is defined as \(R/D\) where \(R\) and
\(D\) are the coefficients of \(\sigma_e\) and \(\sigma_d\), respectively.

The percent delocalized effect, \(P_D\), is defined by equation 2:

\[
P_D = \frac{100D}{L + D}
\]  

(2)

Diparametric equations can be obtained from equation 1 in two ways. One alternative is
to combine \(\sigma_l\) and \(\sigma_d\) to form a composite parameter with a fixed value of \(P_D\). The other
is to combine \(\sigma_d\) and \(\sigma_e\) to form a composite parameter with a fixed value of \(\eta\). These
composite substituent constants are designated \(\sigma_{Ck'}\) (where \(k' = P_D\) and \(\sigma_D\), respec-
tively. A monoparametric equation results when a composite electrical effect parameter is
obtained by combining all three pure electrical effect parameters with fixed values of both
\(P_D\) and \(\eta\). The Hammett substituent constants are of this type. The choice of electrical
effect parameterization depends on the number of data points in the data set to be mod-
eled. When using linear regression analysis, the number of degrees of freedom, \(N_{DF}\), is
equal to the number of data points, \(N_{dp}\), minus the number of independent variables, \(N_{iv}\),
minus one. When modeling physicochemical data, \(N_{DF}/N_{iv}\) should be at least 2, and
preferably 3 or more. As the experimental error in the data increases, \(N_{DF}/N_{iv}\) should
also increase. Values of electrical effect substituent constants used in Section V are given
in Table 1.

III. STERIC EFFECTS

A. Introduction

A short review of the origins and early development of steric effects is given elsewhere\(^1\).
Steric effects are proximity effects that result from and are related to substituent size.
TABLE 1. Electrical effect substituent constants used in applications

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### 8. Structural effects on germanium, tin and lead compounds

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\(^a\)For abbreviations see Section I.A. In the \(\sigma_{c,k'}\) values \(k' = P_D\). Thus \(\sigma_{c14.3}\) had 14.3% delocalized effect.

#### B. The Nature of Steric Effects

1. **Primary steric effects**

   These effects are due to repulsions between electrons in valence orbitals on adjacent atoms which are not bonded to each other. They supposedly result from the interpenetration of occupied orbitals on one atom by electrons on the other, resulting in a violation of the Pauli exclusion principle. *All primary steric interactions raise the energy of the system in which they occur.* Their effect on chemical reactivity is to either decrease or increase a rate or equilibrium constant, depending on whether steric repulsions are greater in the reactant or in the product (equilibria) or transition state (rate).

2. **Secondary steric effects**

   These effects on chemical reactivity can result from the shielding of an active site from the attack of a reagent, from solvation, or both. They may also be due to a steric effect that determines the concentration of the reacting conformation of a chemical species. The secondary steric effect of a nonsymmetric group will also depend on its conformation.

3. **Direct steric effects**

   Direct steric effects can occur when the active site at which a measurable phenomenon occurs is in close proximity to the substituent. Among the many skeletal groups exhibiting direct steric effects are vicinally (1,2) substituted skeletal groups such as *ortho*-substituted...
benzenes, 1, cis-substituted ethylenes, 2, the ortho (1,2-, 2,1- and 2,3-) naphthalenes, 3, 4 and 5, respectively, and peri skeletal groups such as 1,8-substituted naphthalenes, 6. Other vicinal examples are cis-1,2-disubstituted cyclopropanes, cis-2,3-disubstituted norbornanes and cis-2,3-disubstituted [2.2.2]bicyclooctanes, 7, 8 and 9, respectively. Some skeletal groups do not always show steric effects. 2,3-Disubstituted five-membered ring heteroarenes such as thiophenes and selenophenes are generally free of steric effects. This is probably due to the larger XCC angle in these systems as compared with ethene and benzene systems. Geminally substituted (1,1) skeletal groups such as disubstituted methanes, 10, and 1,1-disubstituted ethenes, 11, are also generally free of steric effects.
4. Indirect steric effects

These effects are observed when the steric effect of the variable substituent is relayed by a constant substituent between it and the active site, as in 12, where Y is the active site, Z is the constant substituent and X is the variable substituent. This is a type of buttressing effect.

\[
\text{Y} \quad \text{Z} \quad \text{X}
\]

(12)

5. The directed nature of steric effects

This is easily shown by considering, for example, the ratio \( r \) of the steric parameter \( \nu \) for any five carbon alkyl group to that for 1-pentyl. Values of \( r \) are: 1-Pe, 1; 2-Pe, 1.54; 3-Pe, 2.22; CH₂Bu-s, 1.47; CH₂Bu-i; 1.00; CH₂Bu-t, 1.97; CMe₂Pr, 2.40; CHMePr-i, 1.90. All of these groups have the same volume and therefore the same bulk, but they differ in their steric effect\(^9\). In order to account for this it is necessary to consider what happens when a nonsymmetric substituent is in contact with an active site. We consider the simple case of a spherical active site Y in contact with a nonsymmetric substituent \( CZ^LZ^MZ^S \), where the superscripts L, M and S represent the largest, the medium-sized and the smallest Z groups, respectively. The C–G bond and the Y–G bond are of comparable length. There are three possible conformations of this system (Figure 1). As all steric repulsions raise the energy of the system, the preferred conformation will be the one that results in the lowest energy increase. This is the conformation which presents the smallest face to the active site, conformation (a). From this observation we have the minimum steric interaction (MSI) principle which states: a nonsymmetric substituent prefers that conformation which minimizes steric interactions. The directed nature of steric effects results in a conclusion of vital importance: that in general the volume of a substituent is not an acceptable measure of its steric effect\(^10\). There are still some workers who are unable to grasp this point. It is nevertheless true that group volumes are not useful as steric parameters except in the case of substituents that are roughly spherical, and not always then. They are actually measures of group polarizability. In short, for a range of different substituent shapes in a data set steric effects are not directly related to bulk, polarizability is.

![Figure 1](image-url)

FIGURE 1. Possible conformations of a \( \text{cis}-1,2 \)-substituted ethene having a spherical reaction site in contact with a tetrahedral substituent consisting of a central atom M bearing large (\( Z^L \)), medium (\( Z^M \)) and small (\( Z^S \)) sized groups. The energies of the conformations are (a) lowest and (c) highest. The same types of confirmation occur in other 1,2- and 1,3-disubstituted systems in which substituent and reaction site are in contact.
van der Waals radii, \( r_v \), have long been held to be an effective measure of atomic size\(^{11}\). Charton proposed the use of the van der Waals radius as a steric parameter\(^{12}\) and developed a method for the calculation of group van der Waals radii for tetracoordinate symmetric top substituents MZ\(^3\) such as the methyl and trifluoromethyl groups\(^{13a}\). In later work the hydrogen atom was chosen as the reference substituent and the steric parameter \( \nu \) was defined by equation 3:

\[
\nu_X \equiv r_{vX} - r_{vH} = r_{vX} - 1.20
\]

where \( r_{vX} \) and \( r_{vH} \) are the van der Waals radii of the X and H groups in Angstrom units\(^{13b}\).

Expressing \( r_v \) in these units is preferable to the use of picometers, because the coefficient of the steric parameter is then comparable in magnitude to the coefficients of the electrical effect parameters. Whenever possible, \( \nu \) parameters are obtained directly from van der Waals radii or calculated from them. An equation has been derived which makes possible the calculation of \( \nu \) values for nonsymmetric tetrahedral groups of the types MZ\(^2\)SZL and MZSZM\(^3\)ZL in which the Z groups are symmetric\(^{14}\). These are considered to be primary values. For the greater number of substituents, however, \( \nu \) parameters must be calculated from the regression equations obtained for correlations of rate constants with primary values. The values obtained in this manner are considered to be secondary \( \nu \) values. All other measures of atomic size are a linear function of van der Waals radii\(^{10b}\). There is therefore no reason for preferring one measure of atomic size over another. As values of \( \nu \) were developed for a wide range of substituent types with central atoms including oxygen, nitrogen, sulfur and phosphorus as well as carbon, these parameters provide the widest structural range of substituents for which a measure of the steric effect is available.

1. Steric classification of substituents

Such classification is useful in understanding the way in which different types exert steric effects\(^9\). Substituents may be divided into three categories based on the degree of conformational dependence of their steric effects:

1. No conformational dependence (NCD). Groups of this type include monoatomic substituents such as hydrogen and the halogens, M\(^a\) \( \equiv \) M\(^b\) substituents such as ethynyl and cyano and MZ\(^3\) groups.

2. Minimal conformational dependence (MCD). Among these groups are: (a) Non-symmetric substituents with the structure MH\(_n\)(lp)\(_{3-n}\), such as the hydroxyl and amino groups (lp is a lone pair). (b) Nonsymmetric substituents with the structure MZ\(^2\)SZL, where S stands for small and L for large.

3. Strong conformational dependence (SCD). These groups have the structures: (a) MZ\(^1\)Z\(^5\) and MZ\(^1\)ZMZ\(^5\), where the superscript M indicates medium. (b) Planar \( \pi \)-bonded groups MZ\(^1\)Z\(^5\) where M and either or both Zs are sp\(^2\) hybridized, such as phenyl, acetyl, nitro (X\(_{p\pi}\) groups). (c) Quasi-planar \( \pi \)-bonded groups such as dimethylamino and cyclopropyl.

The steric parameter for NCD groups can be obtained directly from van der Waals radii or calculated from them. The values for MCD groups are often obtainable from van der Waals radii, although in some cases they must be derived as secondary values.
from regression equations obtained by correlating rate constants with known values of the steric parameter. Steric parameters for SCD groups of the nonsymmetric type are usually obtainable only from regression equations.

2. Planar $\pi$-bonded groups

In the case of planar $\pi$-bonded groups, the maximum and minimum values of the steric parameter are available from the van der Waals radii (Figure 2). A more detailed discussion is provided elsewhere.

D. Multiparametric Models of Steric Effects

In some cases a simple monoparametric model of the steric effect is insufficient. Examples are when the active site is itself large and nonsymmetric, or alternatively when the phenomenon studied is some form of bioactivity in which binding to a receptor determines the activity. The failure of the monoparametric model is due to the fact that a single steric parameter cannot account for the variation of the steric effect at various points in the substituent. The use of a multiparametric model of steric effects that can represent the steric effect at different segments of the substituent is required. Five multiparametric models are available: that of Verloop and coworkers, the simple branching model, the expanded branching model, the segmental model and the composite model. The Verloop model will not be discussed.

1. The branching equations

The simple branching model\textsuperscript{10b} for the steric effect is given by equation 4:

$$S\psi = \sum_{i=1}^{m} a_i n_i + a_b n_b$$

where $S\psi$ represents the steric effect parameterization, $a_i$ and $a_b$ are coefficients, $n_i$ is the number of branches attached to the $i$-th atom, and $n_b$ is the number of bonds between the first and last atoms of the group skeleton. It follows that $n_b$ is a measure of group length. Unfortunately, it is frequently highly collinear in group polarizability, which greatly limits its utility. For saturated cyclic substituents it is necessary to determine values of $n_i$ from an appropriate regression equation. For planar $\pi$-bonded groups $n_i$ is taken to be 1 for each atom in the group skeleton. For other groups $n_i$ is obtained simply by counting branches. The model makes the assumption that all of the branches attached to a skeleton atom are equivalent. This is at best only a rough approximation. Distinguishing between branches
results in an improved model called the expanded branching equation (equation 5):

$$S\psi = \sum_{i=1}^{m} \sum_{j=1}^{3} a_{ij} n_{ij} + a_{b} n_{b}$$

which allows for the difference in steric effect that results from the order of branching. This difference follows from the MSI principle. The first branch has the smallest steric effect, because a conformation in which it is rotated out of the way of the active site is preferred. In this conformation the active site is in contact with two hydrogen atoms. The preferred conformation in the case of a second branch has the larger of the two branches directed out of the way. The smaller branch and a hydrogen atom are in contact with the active site. When there are three branches, the largest will be directed out of the way and the other two will be in contact with the active site. The problem with the expanded branching method is that it requires a large number of parameters. Data sets large enough to permit its use are seldom seen.

2. The segmental model

This model is often the simplest and most effective of the multiparametric models. In this model each atom of the group skeleton together with the atoms attached to it constitutes a segment of the substituent. Applying the MSI principle, the segment is considered to have that conformation which presents its smallest face to the active site. The segment is assigned the \(\nu\) value of the group which it most resembles. Values of the segmental steric parameters \(\nu_{i}\), where \(i\) designates the segment number, are given in Table 2. Numbering starts from the first atom of the group skeleton which is the atom that is attached to the rest of the system. The segmental model is given by equation 6:

$$S\psi = \sum_{i=1}^{m} S_{i} \nu_{i}$$

When only steric effects are present, equation 7 applies:

$$Q_{X} = S\psi_{X}$$

In the general case, electrical effects are also present and the general form of the LDGRS equation (equation 8):

$$Q_{X} = L\sigma_{lX} + D\sigma_{dX} + R\sigma_{eX} + S\psi_{X} + h$$

is required.

3. The composite model

This model is a combination of the monoparametric \(\nu\) model with the simple branching model. This method has proven useful in modelling amino acid, peptide and protein properties. It is an improvement over the simple branching model and requires only one additional parameter.

E. Bond Length Difference as a Factor in Steric Effects

The steric effect exerted by some group \(X\) is a function of the lengths of the substituent-skeletal group \((X-G)\) and active site-skeletal group \((Y-G)\) bonds. The steric parameters
### Table 2. Steric effect parameters used in applications

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<th>Parameter</th>
<th>( \nu )</th>
<th>( \nu_1 )</th>
<th>( \nu_2 )</th>
<th>( n_1 )</th>
<th>( n_2 )</th>
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\(^a\)For abbreviations, see section I.A.

\(^b\)The bond length of the CM bond.

---

FIGURE 3. The effect of bond length on steric effects. (a) A system in which substituent and X and reaction site Y have comparable X−G and Y−G bond lengths; \( G^1 \), \( G^2 \) and \( G^3 \) are atoms of the skeletal group. (b), (c) A system in which X−G and Y−G bond lengths are significantly different described above function best when they are of comparable length. In that case the contact between X and Y is that shown in Figure 3a. If the YG bond is much shorter than the XG bond, the contact is as shown in Figure 3b. In that case, the distance from Y to the X−G bond is less in Figure 3b than it is in Figure 3a although the XY distance in both Figures 3a and 3b is the sum of the van der Waals radii, \( r_{VX} \) and \( r_{VY} \). The effective size of the van der Waals radius of X is reduced. Steric parameters were originally derived for systems like that in Figure 3a. In a system like Figure 1b, corrected steric parameters are needed. An approximate value of the effective van der Waals radius of X, \( r_{CVX} \), can be calculated for the case in which the X−G and Y−G bonds are parallel to each other.
from a consideration of Figure 3c and Scheme 1, where \( l_{XG} \) and \( l_{YG} \) are the lengths of the X–G and Y–G bonds, respectively.

\[
\begin{align*}
\overline{XY} &= r_{yx} + r_{vy} \\
\overline{XD} &= l_{XG} - l_{YG} \\
\overline{DY} &= \left( (\overline{XY})^2 - (\overline{XD})^2 \right)^{1/2} \\
\overline{DY} &= (r_{yx} + r_{vy})^2 - (l_{XG} - l_{YG})^2 \right)^{1/2} \\
\overline{DY} &= r_{vy} + r_{yx}^c \\
r_{yx}^c &= [(r_{yx} + r_{vy})^2 - (l_{XG} - l_{YG})^2]^{1/2} - r_{vy}
\end{align*}
\]

SCHEME 1

Values of steric effect substituent constants used in the applications are given in Table 2.

IV. INTERMOLECULAR FORCES

A. Introduction

Inter- and intramolecular forces (IMF) are of major importance in the quantitative description of structural effects on bioactivities and chemical properties. They may make a significant contribution to chemical reactivities and some physical properties as well. Common types of intermolecular forces and their parameterization are given in Table 7 of Reference 1.

B. Parameterization of Intermolecular Forces

1. Hydrogen bonding

Two parameters are required for the description of hydrogen bonding. One is required to account for the hydrogen atom donating capacity of a substituent and another to account for its hydrogen atom accepting. The simplest approach is the use of \( n_H \), the number of OH and/or NH bonds in the substituent, and \( n_n \), the number of lone pairs on oxygen and/or nitrogen atoms as parameters\(^{17}\). The use of these parameters is based on the argument that if one of the phases involved in the phenomenon studied includes a protonic solvent, particularly water, then hydrogen bonding will be maximized. For such a system, hydrogen bond parameters defined from equilibria in highly dilute solution in an ‘inert’ solvent are unlikely to be a suitable model. This type of parameterization accounts only for the number of hydrogen donor and hydrogen acceptor sites in a group. It does not take into account differences in hydrogen bond energy. An improved parameterization would result from the use of the hydrogen bond energy for each type of hydrogen bond formed\(^{18}\). For each substituent, the parameter \( E_{hbx} \) would be given by equation 9:

\[
E_{hbx} = \sum_{i=1}^{m} n_{hbi} E_{hbi}
\]

where \( E_{hbx} \) is the hydrogen bonding parameter, \( E_{hbi} \) is the energy of the \( i \)-th type of hydrogen bond formed by the substituent X and \( n_{hbi} \) is the number of such hydrogen bonds. The validity of this parameterization is as yet untested. In any event, the site number parameterization suffers from the fact that, though it accounts for the number of hydrogen
bonds formed, it does not differentiate between their energies and can therefore be only
an approximation. A recent definition of a scale of hydrogen bond acceptor values from
1-octanol–water partition coefficients of substituted alkanes shows that the site number
method strongly overestimates the hydrogen acceptor capability of the nitro group and
seriously underestimates that of the methylsulfoxy group\textsuperscript{19}. Much remains to be done in
properly parameterizing hydrogen bonding.

2. \textit{van der Waals interactions}

These interactions (dipole–dipole, dd; dipole–induced dipole, di; and induced dipole–
induced dipole, ii) are a function of dipole moment (\(\mu\)) and polarizability. It has been
shown that the dipole moment cannot always be replaced entirely by the use of electrical
effect substituent constants as parameters\textsuperscript{17,18}. This is because the dipole moment has
no sign. Either an overall electron donor group or an overall electron acceptor group
may have the same value of \(\mu\). It has also been shown that the bond moment rather
than the molecular dipole moment is the parameter of choice. The dipole moments of
MeX and PhX were taken as measures of the bond moments of substituents bonded
to sp\textsuperscript{3} and sp\textsuperscript{2} hybridized carbon atoms, respectively, of a skeletal group. Application to
substituents bonded to sp hybridized carbon atoms should require a set of dipole moments
for substituted ethynes.

The polarizability parameter used here, \(\alpha\), is given by equation 10:

\[
\alpha \equiv \frac{MR_X - MR_H}{100} = \frac{MR_X}{100} - 0.0103
\]  

where \(MR_X\) and \(MR_H\) are the group molar refractivities of X and H, respectively\textsuperscript{16,18}.\nThe factor \(1/100\) is introduced to scale the \(\alpha\) parameter so that its coefficients in the
regression equation are roughly comparable to those obtained for the other parameters
used. Many other polarizability parameters have been proposed, including parachor, group
molar volumes of various kinds, van der Waals volumes and accessible surface areas. Any
of these will serve as they are all highly collinear in each other\textsuperscript{20,21}. The advantage of
\(\alpha\) is that it is easily estimated either by additivity from the values for fragments or from
group molar refractivities calculated from equation 11:

\[
MR_X = 0.320n_c + 0.682n_b - 0.0825n_n + 0.991
\]  

where \(n_c\), \(n_b\) and \(n_n\) are the numbers of core, bonding and nonbonding electrons, respec-
tively, in the group X\textsuperscript{20}.

3. \textit{Charge transfer interactions}

These interactions can be roughly parameterized by the indicator variables \(n_A\) and \(n_D\),
where \(n_A\) takes the value 1 when the substituent is a charge transfer acceptor and 0 when
it is not, and \(n_D\) takes the value 1 when the substituent is a charge transfer donor and 0
when it is not. An alternative parameterization makes use of the first ionization potential
of MeX (ipMeX) as the electron donor parameter and the electron affinity of MeX as the
electron acceptor parameter. Usually, the indicator variables \(n_A\) and \(n_D\) are sufficient.
This parameterization accounts for charge transfer interactions directly involving the sub-
stituent. If the substituent is attached to a \(\pi\)-bonded skeletal group, then the skeletal group
is capable of charge transfer interaction the extent of which is modified by the substituent.
This is accounted for by the electrical effect parameters of the substituent.
### TABLE 3. Intermolecular force substituent constants used in applications

<table>
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<tr>
<th>Substituent</th>
<th>$\alpha$</th>
<th>$\mu(sp^2)$</th>
<th>$\mu(sp^3)$</th>
<th>$n_H$</th>
<th>$n_n$</th>
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<tbody>
<tr>
<td>Me</td>
<td>0.046</td>
<td>0.37</td>
<td>0</td>
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<tr>
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<td>0.37</td>
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<td>0</td>
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<tr>
<td>c-Pr</td>
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<td>Pr</td>
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### CH$_2$Z

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### CZ$_3$

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### VnX

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### C$_2$Z

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### Ar

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### PnZ

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continued overleaf
4. Intermolecular force equation

The intermolecular force (IMF) equation is a general relationship for the quantitative description of intermolecular forces. It is written as equation 12:

\[
Q_X = L \sigma_{lX} + D \sigma_{dx} + R \sigma_{eX} + M \mu_X + A \alpha_X + H_1 n_{H_X} \\
+ H_2 n_{nX} + I i_X + B_{DX} n_{DX} + B_{AX} n_{AX} + S \psi_X + B^o
\]

Values of intermolecular force substituent constants used for the substituent applications are set forth in Table 3.

V. APPLICATIONS

A. Chemical Reactivities (QSRR)

We now consider the application of the methods and parameters described above to substituents and/or active sites containing Si, Ge, Sn and Pb.

Eaborn and Singh\textsuperscript{22} have reported rate constants for H-T exchange in tri(4-substituted phenyl)-tritio-germanes, \((4 - XPn)_3GeT\), with methoxide ion in methanol at 20, 30 and 40 °C (set CR1, Table 4). The data were correlated with the LDRT equation which has the form of equation 13:

\[
Q_X = L \sum \sigma_{lX} + D \sum \sigma_{dx} + R \sum \sigma_{eX} + T \tau + h
\]

where \(\tau\) is defined as 100 divided by \(T_K\), the temperature in degrees Kelvin. This model was chosen to permit the inclusion of every available rate constant. All of the regression equations presented in this section are the best obtained. In this case the regression equation is equation 14:

\[
\log \frac{k_X}{T} = 3.19(\pm 0.268)\sigma_{lX} + 2.98(\pm 0.247)\sigma_{dx} - 62.3(13.5)\tau + 23.5(\pm 4.45)
\]

\(100 R^2, 95.54; A 100 R^2, 94.73; F, 71.44; S_{est}, 0.363; S^o, 0.250; N_{dp}, 14; P_D, 48.2(\pm 4.92), \eta, 0; r_{ld}, 0.487; r_{l\tau}, 0.000; r_{d\tau}, 0.000.\)

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\(a\) For abbreviations, see Section I. A.
TABLE 4. QSRR data sets

CR1. $10^6 k_1$ (l mol$^{-1}$ s$^{-1}$), $4 \cdot X_1 Pn \cdot 4 \cdot X_2 Pn \cdot 4 \cdot X_3 Pn Ge T + Me O^{-}$ in MeOH. $X_1$, $X_2$, $X_3$, $T$ (°C), $10^6 k_1$: H, H, H, 20, 148; H, H, H, 30, 530; H, H, H, 40, 1520; Me, Me, Me, 20, 14.2; Me, Me, Me, 30, 41.5; Me, Me, Me, 40, 161; MeO, MeO, MeO, 30, 13.2; Ph, Ph, Ph, 30, 570; Ph, Ph, Ph, 40, 17500; NO$_2$, H, H, 30, 680000; CN, H, H, 30, 360000; F, H, H, 30, 600.

CR2. $10^4 k_2$ (dm$^3$ mol$^{-1}$ s$^{-1}$). Me$_3$SnOPn$^-\cdot X^-$ in various solvents $s_v$ at 130°C $S_v$, X, $10^4 k_2$: CCl$_4$, OMe, 5.37; CCl$_4$, Me, 3.99; CCl$_4$, Cl, 2.81; CCl$_4$, NO$_2$, 0.417; CH$_2$Cl$_2$, OMe, 5.13; CH$_2$Cl$_2$, Me, 3.23; CH$_2$Cl$_2$, H, 1.20; CH$_2$Cl$_2$, Cl, 0.466; CH$_2$Cl$_2$, NO$_2$, 0.174; PhCN, OMe, 17.3; PhCN, Me, 9.67; PhCN, H, 7.56; PhCN, Cl, 6.18; PhCN, NO$_2$, 7.58; MeCN, OMe, 5.04; MeCN, Me, 6.28; MeCN, H, 8.58; MeCN, Cl, 13.4; MeCN, NO$_2$, 56.8.

CR3. $k_{rel}$, (MeO)$_3$SiOCH$_2$X methanolysis catalyzed by Et$_2$NH. X, $k_{rel}$: Me, 1.00; Et, 0.60; Pr, 0.53; Bu, 0.54; $t$-Bu, 0.049; GeMe$_3$, 0.30; SiMe$_3$, 0.15; SiMe$_2$Et, 0.11; CH$_2$SiMe$_3$, 0.49; CH$_2$GeMe$_3$, 0.54; CH$_2$OMe, 2.10; CH$_2$Cl, 3.23; CH$_2$Ph, 1.48; CH$_2$Vi, 3.27.

CR4. $k_{rel}$, (MeO)$_3$SiOCH$_2$CH$_2$X methanolysis catalyzed by Et$_2$NH. X, $k_{rel}$: H, 1.00; Me, 0.60; Et, 0.53; Pr, 0.54; $t$-Bu, 0.52; CH$_2$Bu-$t$, 0.52; GeMe$_3$, 0.54; SiMe$_3$, 0.50; CH$_2$SiMe$_3$, 0.50; CH$_2$GeMe$_3$, 0.52; OMe, 2.10; Cl, 3.23; CH$_2$Cl, 0.82; CH$_2$OMe, 0.87.

CR5. $10^2 k_2$ (l mol$^{-1}$ s$^{-1}$), Ak$_1$SnAk$_2$ + I$_2$ in MeOH at 20°C. Ak$_1$, Ak$_2$, $10^2 k_2$: Me, Me, 1.77; Et, Me, 0.256; Pr, Me, 0.132; $i$-Pr, Me, 0.01; Me, Et, 3.58; Et, Et, 0.22; Pr, Et, 0.065; Bu, Et, 0.600; $i$-Pr, Et, 0.004.

CR6. $10^2 k_2$ (l mol$^{-1}$ s$^{-1}$), AkSnMe$_3$ + Hgl$_2$ in AcOH at 20°C. Ak, $Hgl_2$, $10^2 k_2$: Me, 24.9, 1.15; Et, 24.9, 0.80; Pr, 24.9, 0.225; Bu, 24.9, 0.31; $i$-Pe, 24.9, 0.30; Me, 49.8, 17.1; Et, 49.8, 10.9; Pr, 49.8, 3.1; Bu, 49.8, 4.3; $i$-Pe, 49.8, 4.2; Me, 60.0, 41.2; Et, 60.0, 28.2; Pr, 60.0, 8.2; Bu, 60.0, 10.6; $i$-Pe, 60.0, 12.2.

---

$a$ For abbreviations, see Section I.A.

$b$ Sets CR2a, CR2b, CR2c and CR2d are rate constants in CCl$_4$, CH$_2$Cl$_2$, PhCN and MeCN, respectively.

c Excluded from the best regression equation.

d $\phi$ is the mole fraction.

There is no dependence on $\sigma_e$, thus the electronic demand is zero, contrary to the conclusions of Eaborn and Singh.

Kozuka and coworkers$^{23}$ have reported second-order rate constants for the reaction

$$Me_3SnOPnX-4 + MeSO_2Cl \rightarrow Me_3SnCl + MeSO_2OPnX-4$$

in the solvents tetrachloromethane, dichloromethane, benzonitrile and acetonitrile. The number of data points in each solvent is only five though at least they are well chosen (sets CR2a to CR2d in Table 4). Plots of log $k$ against $\sigma_p X$ show that the reactions in tetrachloromethane and dichloromethane go by a different mechanism from that in acetonitrile. Furthermore, 3-nitrophenoxytrimethylstannanes in benzonitrile reacts by a different mechanism from that which characterizes the other members of set CR2c. Sets CR2a, CR2b, CR2d and, on exclusion of the nitro compound, set CR2c were all correlated.
separately with the CR equation 15:

\[ Q_X = C \sigma_{cX} + R \sigma_{eX} + h \]  \hspace{1cm} (15)

where \( \sigma_{cX} \) is a composite substituent constant obtained by combining \( \sigma_l \) and \( \sigma_d \) so as to have a particular \( P_D \) value. The regression equations obtained for sets CR2a through CR2d, respectively, are equations 16–19:

\[
\log k_{2X} = -0.725(\pm 0.0265)\sigma_{e60X} + 3.22(\pm 0.433)\sigma_{eX} + 0.546(\pm 0.0197) \]

\[ 100R^2, 99.81; A \] 100\( R^2 \), 99.75; \( F \), 530.3; \( S_{est} \), 0.0273; \( S^o \), 0.0686; \( N_{dp} \), 5; 

\[ P_D , 60; \eta, -2.96(\pm 0.384); r_{ce}, 0.324. \]

\[
\log k_{2X} = -1.48(\pm 0.163)\sigma_{e50X} + 5.94(\pm 2.14)\sigma_{eX} + 0.0151(\pm 0.0925) \]

\[ 100R^2, 97.67; A \] 100\( R^2 \), 96.89; \( F \), 41.89; \( S_{est} \), 0.130; \( S^o \), 0.241; \( N_{dp} \), 5; 

\[ P_D , 50; \eta, 4.01(\pm 1.37); r_{ce}, 0.409. \]

\[
\log k_{2X} = -1.04(\pm 0.247)\sigma_{e60X} + 3.02(\pm 2.32)\sigma_{eX} + 0.847(\pm 0.0553) \]

\[ 100R^2, 99.37; A \] 100\( R^2 \), 99.04; \( F \), 78.38; \( S_{est} \), 0.0268; \( S^o \), 0.159; \( N_{dp} \), 4; 

\[ P_D , 60; \eta, -1.94(\pm 1.42); r_{ce}, 0.972. \]

\[
\log k_{2X} = 1.14(\pm 0.163)\sigma_{e50X} - 1.17(\pm 0.343)\sigma_{eX} + 0.921(\pm 0.0153) \]

\[ 100R^2, 99.87; A \] 100\( R^2 \), 99.82; \( F \), 752.1; \( S_{est} \), 0.0215; \( S^o \), 0.0576; \( N_{dp} \), 5; 

\[ P_D , 50; \eta, -1.03(\pm 0.301); r_{ce}, 0.331. \]

The results are uncertain due to the small number of data points in each set. It seems likely, however, that sets CR2a through CR2c, all of which have a negative value of \( C \) and about the same \( P_D \) value, possess the same mechanism. Set CR2d, which has a positive value of \( C \), seems to have a different mechanism. None of the four solvents studied is a hydrogen donor in hydrogen bonding; none of the substituents studied has this capacity. Then the solvent effect should be dependent only on dipole moment and polarizability. The data for sets CR2a, CR2b and CR2c excluding nitrophenoxytrimethylstannanes were combined into a single data set and correlated with equation 20:

\[ Q_{X/Sv} = C\sigma_{cX} + R\sigma_{eX} + A\alpha_{Sv} + M\mu_{Sv} + b^o \] \hspace{1cm} (20)

The best regression equation was obtained on exclusion of the value for Cl in dichloromethane; it is equation 21:

\[
\log k_{2,X/Sv} = -0.890(\pm 0.0666)\sigma_{e60X} + 3.52(\pm 0.556)\alpha_{Sv}
\]

\[ + 0.0468(\pm 0.0202)\mu_{Sv} - 0.412(\pm 0.121) \] \hspace{1cm} (21)

\[ 100R^2, 97.15; A \] 100\( R^2 \), 96.58; \( F \), 102.3; \( S_{est} \), 0.108; \( S^o \), 0.203; \( N_{dp} \), 13; 

\[ P_D , 60; \eta, 0; r_{ce\alpha}, 0.168; r_{ce\mu}, 0.205; r_{a\mu}, 0.428; C_{\sigma c}, 49.1; C_{\sigma a}, 46.8; C_{\mu}, 4.10. \]

None of the zeroth-order partial correlation coefficients involving \( \sigma_e \) was significant. It seems fairly certain that the electronic demand in the reaction in set CR2abc is 0. The rate of the reaction is accelerated by electron donor substituents and decelerated by electron acceptor groups. This situation is reversed in set CR2d. The best explanation of these observations is that the mechanism in the most polar solvent, acetonitrile, is different
from that in the least polar solvents, tetrachloromethane and dichloromethane, while in benzonitrile which is intermediate in polarity a change in mechanism is occurring with nitrophenoxytrimethylstannanes. A mechanism in accord with these results is shown in Scheme 2. If, in less polar media, $S-O$ bond formation is more advanced than $Sn-O$ bond breaking, there will be a partial positive charge on oxygen and the reaction will be favored by electron donor groups. If, in the more polar medium, this situation is reversed, then there will be a partial negative charge on oxygen and the reaction will be favored by electron acceptor substituents.

\[ Me_3Sn-O X \]
\[ Me_3SnCl + MeSO_2O \]
\[ \xrightarrow{\text{‡}} \]
\[ MeSO_2Cl + Me_3Sn-O \]

**SCHEME 2**

Pola, Bellama and Chvalovsky$^{24}$ have reported relative rates for the methanolysis in methanol catalyzed by ethylamine of $X(\text{CH}_2)_n\text{OSi(OMe)}_3$ ($n = 1$, set CR3; $n = 2$, set CR4; Table 4). Correlation with the LDRS equation is in the form of equation 22:

\[ Q_X = L\sigma_{lX} + D\sigma_{dX} + R\sigma_{eX} + S\nu_X + h \] (22)

The regression equation for $n = 1$, obtained on the exclusion of the value for $X = t$-Bu, is equation 23:

\[ \log k_{rel,X} = 4.85(\pm 0.449)\sigma_{lX} - 0.209(\pm 0.0393) \]

\[ 100r^2, 91.39; F, 116.8; S_{est}, 0.141; S^0, 0.319; N_{dp}, 13; P_D, 0; \eta, 0. \]

The regression equation for $n = 2$, obtained on the exclusion of the value for $X = H$, is equation 24:

\[ \log k_{rel,X} = 1.54(\pm 0.112)\sigma_{lX} - 0.230(\pm 0.0190) \]

\[ 100r^2, 94.48; F, 186.4; S_{est}, 0.0641; S^0, 0.255; N_{dp}, 13; P_D, 0; \eta, 0. \]
We now consider structural effects in the halodealkylation of tetraalkylstannanes\textsuperscript{25} (sets CR5 and CR6), their reaction with HgCl\textsubscript{2}\textsuperscript{26} (set CR7) and the reaction of tetraalkylplumbanes with acetic acid\textsuperscript{27} (set CR8). The data sets are given in Table 4. As only alkyl groups vary in these data sets and the electrical effects of alkyl groups are constant, only steric effects and polarizability need to be considered for parameterization. In order to provide a sufficiently large data set for analysis, rate constants for bromo- and iodo-dealkylation were combined into a single data set by means of the Zeta method. In this method the parameterization needed to combine data sets is obtained by choosing a data point from each set to be combined for which all the other parameters are the same. The quantity ζ was defined as \( \log k_2 \) for the methyl group and the simple branching equation (equation 4) was used to account for the steric effect. Only branching at the first and second carbon atoms of the alkyl group was parameterized. The correlation equation is equation 25:

\[
Q_{Ak/Hl} = a_1 n_1 + a_2 n_2 + Zζ + a^0
\]  

(25)

The regression equation is equation 26:

\[
\log k_{2,Ak/Hl} = -1.03(±0.0592)n_1 - 0.287(±0.152)n_2 + 1.19(±0.0879)ζ + 0.213(±0.146)
\]  

(26)

100\( R^2 \), 98.23; A 100\( R^2 \), 97.79; \( F \), 129.7; \( S_{est} \), 0.239; \( S^0 \), 0.167; \( N_{dp} \), 11;
\( r_{12} \), 0.165; \( r_{1ζ} \), 0.199; \( r_{2ζ} \), 0.069; \( C_{n1} \), 59.0; \( C_{n2} \), 15.4; \( C_ζ \), 29.6; \( B_1/B_2 \), 3.59.

There is a clear dependence on steric effects with branching at C\textsuperscript{1} having a much greater effect than branching at C\textsuperscript{2}.

The same method has been applied to the iododealkylation of Ak\textsuperscript{1}SnAk\textsuperscript{2} with Ak\textsuperscript{2} equal to Me or Et. Again, ζ was defined as \( \log k_2 \) for the methyl group. Correlation of the data set with equation 25 gave regression equation 27:

\[
\log k_{2,Ak^1/Ak^2} = -1.30(±0.107)n_1 - 0.327(±0.138)n_2 + 0.492(±0.138)
\]  

(27)

100\( R^2 \), 95.67; A 100\( R^2 \), 95.13; \( F \), 77.30; \( S_{est} \), 0.213; \( S^0 \), 0.248; \( N_{dp} \), 10;
\( r_{12} \), 0.000; \( C_{n1} \), 79.1; \( C_{n2} \), 12.1; \( B_1/B_2 \), 3.98.

Steric effects account completely for the observed reactivity; there is no dependence on the nature of Ak\textsuperscript{2}. Again, the effect of branching at C\textsuperscript{1} predominates over that at C\textsuperscript{2}.

Second-order rate constants for the reaction of mercury(II) chloride with tetraalkylstannanes according to equation 28:

\[
Ak_4Sn + HgCl_2 \rightarrow Ak_3SnCl + AkHgCl
\]  

(28)

in aqueous methanol of varying concentrations were correlated with equation 29:

\[
Q_{Ak/Sv} = a_1 n_1 + a_2 n_2 + F φ + a^0
\]  

(29)

where φ is the mole fraction of methanol and \( F \) is its coefficient. The regression equation is equation 30:

\[
\log k_{Ak/Sv} = -2.59(±0.320)n_1 - 1.08(±0.261)n_2 - 2.63(±0.853)φ + 4.794(±0.781)
\]  

(30)
8. Structural effects on germanium, tin and lead compounds

Steric effects account for the result of structural variation. Though the steric effect of branching at C1 is again predominant, the extent is significantly less.

First-order rate constants for the acetolysis of tetraalkylplumbanes in acetic acid at various temperatures according to equation 31:

\[
\text{Ak}_4\text{Pb} + \text{AcOH} \rightarrow \text{Ak}_3\text{PbOAc} + \text{AkH}
\]  

were correlated with equation 32:

\[
Q_{\text{Ak}/T} = a_1n_1 + a_2n_2 + T\tau + \alpha^o
\]  

The regression equation is equation 33:

\[
\log k_{\text{Ak}/T} = -0.174(\pm 0.0495)n_1 - 0.454(\pm 0.0404)n_2 - 43.5(\pm 1.03)\tau
+ 14.7(\pm 0.327)
\]  

The structural effect is again accounted for by steric effects. What is unusual is that, contrary to the results obtained for the three previous data sets, steric effects are predominantly due to branching at C2.

B. Chemical Properties (QSCR)

1. Phase change properties

a. Melting points \((T_m)\). The melting points of MX\(^1\)X\(^2\)X\(^3\)X\(^4\), where M is a group 14 element other than carbon\(^28\), can be modeled by a relationship derived from the IMF equation. The melting points of the subset MX\(^4\), where X is H, Cl, Br, I or Me (set CP1a, Table 5), is a particularly simple case as the dipole moment is zero for these compounds and hydrogen bonding is not possible. As all of these compounds have similar molecular geometry they are likely to have similar crystal lattices; this packing effect should be constant. Then only induced dipole–induced dipole interactions are possible and the correlation equation is equation 34:

\[
Q_X = A\alpha + \alpha^o
\]  

Correlation of the data subset with equation 34 gives equation 35:

\[
T_m = 613(\pm 19.9)\alpha + 17.3(\pm 8.05)
\]  

Clearly, the assumptions made in the choice of equation 34 were justified. In order to include the remainder of the data set, it is necessary to introduce a term in the dipole moment \(\mu\). Another necessary term results from the fact that while all four surfaces of the tetrahedral molecule MX\(^4\) are equivalent, those of related molecules are not. Thus, MX\(^1\)X\(^2\)X\(^2\) has two sets of two equivalent faces while MX\(^3\)X\(^2\) has a set of three equivalent
### TABLE 5. QSCR data sets

**CP1.** $T_m$, K, MX$^1$X$^2$X$^3$X$^4$. MX$^1$X$^2$X$^3$X$^4$, $T_m$: SiH$_4$, 88.5; SiCl$_4$, 203; SiBr$_4$, 279; SiI$_4$, 394; SiMe$_4$, 174; GeH$_4$, 107; GeCl$_4$, 224; GeBr$_4$, 299; GeI$_4$, 407; GeMe$_4$, 185; SnH$_4$, 123; SnCl$_4$, 239; SnBr$_4$, 303; SnI$_4$, 418; SnMe$_4$, 218; PbCl$_4$, 258; PbMe$_4$, 246; SiH$_3$Br, 179; SiH$_3$Cl, 155; SiH$_3$I, 216; SiH$_3$Me, 117; SiCl$_3$Me, 195; SiCl$_3$H, 147; SiBr$_3$H, 200; SiF$_3$H, 142; SiF$_3$Cl, 135; SiH$_2$Cl$_2$, 151; SiMe$_2$H$_2$, 123; GeH$_3$Br, 241; GeH$_3$Cl, 221; GeH$_3$Cl$_2$, 205.

**CP1a.** This set consists of those members of set CP1 that have the formula MX$_4$.

**CP1b.** This set consists of all other members of set CP1.

**CP2.** $T_m$, K, MX$^1$X$^2$X$^3$X$^4$. MX$^1$X$^2$X$^3$X$^4$, $T_m$: SiH$_4$, 161; SiF$_4$, 331; SiCl$_4$, 460; SiBr$_4$, 621; GeH$_4$, 185; GeF$_4$, 356; GeCl$_4$, 460; GeBr$_4$, 621; GeMe$_4$, 317; SnH$_4$, 221; SnF$_4$, 576; SnCl$_4$, 300; SnBr$_4$, 460; SnI$_4$, 621; SnMe$_4$, 351; PbF$_4$, 383; PbCl$_4$, 460; PbBr$_4$, 621. SiF$_3$H, 368; SiCl$_3$H, 306; GeH$_3$Cl, 325; GeH$_3$Br, 241; GeH$_3$Cl, 301; GeH$_3$Cl$_2$, 343.

**CP2a.** This set consists of those members of set CP2 that have the formula MX$_4$.

**CP2b.** This set consists of all other members of set CP2.

**CP3.** $\Delta v_{OH}$ (cm$^{-1}$), XC$_2$SiMe$_3$ + PhOH in CCl$_4$. X, $\Delta v_{OH}$: H, 99; Me, 122; t-Bu, 131; Ph, 106; C$_6$F$_5$, 49; Me, 107; Et, 107; Cl, 70; Br, 75; I, 79; SiMe$_3$, 121; GeMe$_3$, 145; GeEt$_3$, 146; SnMe$_3$, 158; SnEt$_3$, 162; CH$_2$SiMe$_3$, 145.

**CP4.** $\Delta v_{OH}$ (cm$^{-1}$), XC$_2$SnMe$_3$ + PhOH in CCl$_4$. X, $\Delta v_{OH}$: H, 136; Me, 154; Et, 160; t-Bu, 170; Ph, 140; C$_6$F$_5$, 74; Me, 135; Et, 136; Cl, 90; Br, 99; C$_6$F$_5$, 160; CH$_2$OE, 140; CH$_2$Cl, 111; CH$_2$Br, 110; SiMe$_3$, 158; SiEt$_3$, 163; GeMe$_3$, 181; GeEt$_3$, 183; SnMe$_3$, 194; CH$_2$SiMe$_3$, 181.

**CP5.** $\Delta v_{CH}$ (cm$^{-1}$), XC$_2$H in dimethylformamide. X, $\Delta v_{CH}$: i-Pr, 66; Bu, 64; i-Bu, 64; t-Bu, 67; Ph, 75; Ph, 80; CH$_2$OME, 80; Et, 77; CO$_2$Et, 100; C$_6$F$_5$, 107; CH$_2$Cl, 86; CH$_2$Br, 84; SiMe$_3$, 121; GeMe$_3$, 145; GeEt$_3$, 146; SnMe$_3$, 158; SnEt$_3$, 162; CH$_2$SiMe$_3$, 145.

**CP6.** $\Delta v_{CH}$ (cm$^{-1}$), XC$_2$H in tetrahydrofuran. X, $\Delta v_{CH}$: i-Bu, 56; t-Bu, 58; CH$_2$Ph, 62; Ph, 73; CH$_2$OME, 67; Et, 67; CH$_2$Cl, 78; CH$_2$Br, 77; C$_6$F$_5$, 100; SiMe$_3$, 66; SiEt$_3$, 63; GeMe$_3$, 61; SnMe$_3$, 56; SnEt$_3$, 54; CH$_2$SiMe$_3$, 58; CH$_2$GeMe$_3$, 59.

**CP7.** $A$ (KJ mol$^{-1}$) values for c-HxX$^b$. X, A: CMe$_3$, 21; SiMe$_3$, 10.5; GeMe$_3$, 8.8; SnMe$_3$, 3.9; PbMe$_3$, 2.8.

For abbreviations, see Section I.A.


faces and a set of one face. We assume that the face with the largest value of $\Sigma \alpha X$ will preferentially bind to the crystal surface. Then we assign values of the probability $\omega$ as 1 for all MX$_4$, 0.75 to MX$_1$X$_2$X$_3$X when the set of three equivalent faces has the higher value of $\Sigma \alpha X$, 0.25 when the reverse is the case and 0.50 to MX$_1$X$_2$X$_2$. Thus, the correlation equation becomes equation 36:

$$ T_m = A \alpha + M \mu + P \omega + a_o $$

(36)

Correlation of the entire data set (sets CP1a and CP1b) with equation 36 gave, on the exclusion of the values for SiCl$_3$Me and GeH$_3$Br, the regression equation 37:

$$ T_m = 594(\pm 18.7)\alpha + 52.3(\pm 5.63)\mu + 97.6(\pm 18.1)\omega - 72.2(\pm 18.5) $$

(37)

$$ 100R^2, 97.97; A 100R^2, 97.80; F, 385.4; S_{est}, 13.5; S^\circ, 0.154; N_{dp}, 28; r_{\alpha \mu}, 0.504; r_{\alpha \omega}, 0.402; r_{\mu \omega}, 0.726; C_{\alpha}, 44.2; C_{\mu}, 19.5; C_{\omega}, 36.3. $$

For abbreviations, see Section I.A.

8. Structural effects on germanium, tin and lead compounds

As a hypothetical reference compound for calculating \( C \), we have chosen that for which \( \alpha = 0.2, \mu = 1 \) and \( \omega = 1 \). Though \( \alpha \) and \( \mu \) are highly significant, the zeroth-order partial correlation coefficient of \( \mu \) with \( \omega \) indicates collinearity and casts some doubt on the validity of a dependence on \( \omega \). That dependence is likely but uncertain. Polarizability makes the greatest contribution. The coefficients of \( \alpha \) in equations 35 and 37 do not differ significantly. There is, of course, a considerable difference in the intercepts.

b. Boiling points (\( T_b \)). The \( T_b \) values for MX4 compounds\(^{28} \) (set CP2a, Table 5) were correlated with equation 34 to give the regression equation 38:

\[
T_b = 836(\pm 20.0)\alpha + 78.0(\pm 7.87) 
\]

\[100R^2, 99.15; F, 1251; S_{est}, 14.0; S^o, 0.0981; N_{dp}, 17.\]

Again, in order to include compounds in which not all the X groups are the same, it is necessary to introduce a term \( M\mu \), so that the correlation equation becomes equation 39:

\[
T_b = A\alpha + M\mu + a_o 
\]

Correlation of the combined data sets (sets CP2a and CP2b) with equation 38 gives the regression equation 40:

\[
T_b = 831(\pm 21.5)\alpha + 30.9(\pm 4.50)\mu + 78.8(\pm 8.21) 
\]

\[100R^2, 98.32; A 100R^2, 98.26; F, 788.8; S_{est}, 16.4; S^o, 0.137; N_{dp}, 30; 
\]

\[
r_{a\mu}, 0.401; C\alpha, 84.3; C\mu, 15.7. 
\]

Clearly, polarizability is the major factor in determining the boiling point in these compounds. There is no significant difference in the values of \( A \) or in the intercepts of equations 39 and 40.

2. Hydrogen bonding

Egorochkin and coworkers\(^{29} \) have measured the change in \( \nu_{OH} \) for solutions of 1-substituted-2-trimethylsilylectylene and 1-substituted-2-trimethylstannylectylene containing phenol (sets CP3 and CP4, Table 5). These data sets were correlated with the LDRA equation 41:

\[
Q_X = L\sigma_{IX} + D\sigma_{dX} + R\sigma_{eX} + A\alpha + h 
\]

For set CP3 the regression equation is equation 42:

\[
\Delta \nu_{OH,X} = -145(\pm 21.3)\sigma_{IX} - 80.6(\pm 23.4)\sigma_{dX} + 109(\pm 32.6)\alpha + 100(\pm 8.46) 
\]

\[100R^2, 87.07; A 100R^2, 85.34; F, 31.41; S_{est}, 13.1; S^o, 0.408; 
\]

\[N_{dp}, 18; P_D, 35.8(\pm 11.5), \eta, 0; \eta_{d}, 0.641; \eta_{\alpha}, 0.557; r_{da\alpha}, 0.504; 
\]

\[C_I, 58.6; C_d, 32.6; C\alpha, 8.80. 
\]

For set CP4 it is equation 43:

\[
\Delta \nu_{OH,X} = -184(\pm 20.8)\sigma_{IX} - 93.0(\pm 22.5)\sigma_{dX} + 75.8(\pm 30.9)\alpha + 139(\pm 7.46) 
\]

\[100R^2, 88.49; A 100R^2, 87.05; F, 38.42; S_{est}, 12.6; S^o, 0.382; 
\]

\[N_{dp}, 19; P_D, 33.6(\pm 8.92), \eta, 0; \eta_{d}, 0.627; \eta_{\alpha}, 0.491; r_{da\alpha}, 0.483; 
\]

\[C_I, 63.0; C_d, 31.8; C\alpha, 5.19. 
\]
The goodness of fit is in accord with the experimental error in the data. Both equations 42 and 43 are significant at the 99.9% confidence level. Though $\sigma_l$ is significantly collinear in $\sigma_d$, a dependence on both parameters is fairly certain. Electrical effects are the predominant factor in the structural effect with the localized effect making the greater contribution.

In another paper, Egorochkin and coworkers$^{30}$ have reported $\Delta \nu_{CH}$ values for the interaction of substituted acetylenes with dimethylformamide and with tetrahydrofuran (sets CP5 and CP6 respectively, Table 5). Correlation of set CP5 with the LDRA equation gave the regression equation 44:

$$\Delta \nu_{CH,X} = 73.0(\pm 7.61)\sigma_{lX} + 37.5(\pm 6.29)\sigma_{dX} + 72.9(\pm 1.25)$$  \hspace{1cm} (44)

$100R^2$, 85.38; $A$ 100$R^2$, 84.57; $F$, 49.65; $S_{est}$, 4.91; $S^o$, 0.415; $N_{dp}$, 20; $P_D$, 34.0(\pm 6.45), $\eta$, 0; $r_{ld}$, 0.358; $r_{la}$, 0.449; $r_{da}$, 0.179; $C_l$, 66.0; $C_d$, 34.0.

For set CP6, the regression equation is given by equation 45:

$$\Delta \nu_{CH,X} = 81.7(\pm 10.2)\sigma_{lX} + 33.9(\pm 8.38)\sigma_{dX} + 64.8(\pm 1.41)$$  \hspace{1cm} (45)

$100R^2$, 83.19; $A$ 100$R^2$, 82.00; $F$, 32.18; $S_{est}$, 5.14; $S^o$, 0.455; $N_{dp}$, 16; $P_D$, 29.3(\pm 7.99), $\eta$, 0; $r_{ld}$, 0.378; $r_{la}$, 0.633; $r_{da}$, 0.329; $C_l$, 70.7; $C_d$, 29.3.

In sets CP3 and CP4 the 1-substituted-2-trimethylsilylacetylenes and 1-substituted-2-trimethylstannylacetylenes are acting as hydrogen bond acceptors while in sets CP5 and CP6 they are acting as hydrogen bond donors. Electrical effects are similar in all four sets, however. The $P_D$ values show no statistically significant difference and $\eta$ is zero in all four data sets. The major difference between the donor and acceptor sets is that the latter show a dependence on polarizability while the former do not.

3. Conformation

Monosubstituted cyclohexanes, $c$-$HxX$, exist in two conformations, axial and equatorial. In the axial conformation the substituent X is in close proximity to the cis hydrogen atoms at positions 3 and 5 ($H^3c$ and $H^5c$). It has been shown$^{16}$ that when X is a tetrahedral group of the type $MZ^1ZS^1MZ^2S^2$ ($L$, $M$, and $S$ are large, medium, and small, respectively), the $A$ values for $c$-$HxX$ ($AX \equiv -\Delta G_X$) are a function of electrical and steric effects when $M$ is a second period element ($X_{12}$ group) but solely a function of steric effects when $M$ is a third period element ($X_{13}$ group). The electrical effect is the result of a weak hydrogen bond between $Z^S$ and $H^3c$ and $H^5c$. This effect may occur only when these atoms are in contact. When $M$ is a third or higher period element, $H^3c$ and $H^5c$ are in contact only with M. It will not be observed in tetrahedral groups with M of any period greater than second.

The predominant effect on $A$ in tetrahedral groups of a given period is a steric effect due to $Z^S$. The steric effect due to M is much smaller. The magnitude of the $Z^S$ steric effect decreases as the covalent radius of M, $r_{CM}$, decreases. Thus we obtain equation 46:

$$S_{Z^S(p)} = a_1/r_{CM(n)} + a_o$$  \hspace{1cm} (46)

where $S_{Z^S(p)}$ is the coefficient of the steric parameter and $p$ is the period of M, while $r_{CM}$ is the covalent radius of M.
To test the hypothesis, we consider the set of $c$-HxX for which X is MMe$_3$ and M is C, Si, Ge, Sn or Pb, for all of which $A$ values are available (set CP7, Table 5). The $A$ values for the set of interest should obey equation 47:

$$A_{MMe_3} = S_1 \vartheta_M + S_2 \vartheta_Z + A_0$$  \hspace{1cm} (47)

As no value of $r_{CM}$ for Pb was available, it was replaced by $l_{CM}$, the bond length of the C–M bond. This is equal to the sum of the covalent radii of C and M. The value of $\vartheta_M$ for C, Si, Ge, Sn and Pb is linear in $l_{CM}$. Equation 48 then exists:

$$\vartheta_M = a_2 l_{CM} + a_0$$  \hspace{1cm} (48)

Then $A$ values for MMe$_3$ groups should be linear in $l_{CM}$. Correlation with equation 49:

$$A_{MMe_3} = b_1 l_{CM} + B_0$$  \hspace{1cm} (49)

gives the regression equation 50:

$$A_{MMe_3} = -24.5(\pm 2.76)l_{CM} + 57.4(\pm 5.40)$$  \hspace{1cm} (50)

These results support our arguments concerning the effect of tetrahedral groups on $A$ values.

**C. Physical Properties (QSPR)**

**1. Dipole moments of X$_n$MZ$_{4-n}$**

The dipole moments $\mu$ of X$_n$MZ$_{4-n}$ were correlated with the LDR equation (equation 1), and in some cases the CR equation (equation 15) and the LD equation 51:

$$Q_X = L \sigma_{lX} + D \sigma_{dX} + h$$  \hspace{1cm} (51)

M may be Si, Ge, Sn or Pb; Z is constant throughout a given data set and may be Me, Et or H, while X varies. The data sets studied are reported in Table 6.

Correlation of $\mu$ in benzene for XSiMe$_3$ (set PP1) with the LDR equation gave the regression equation 52:

$$\mu_X = 4.75(\pm 0.460)\sigma_{lX} - 0.890(\pm 0.405)\sigma_{dX} + 0.270(\pm 0.133)$$  \hspace{1cm} (52)

Correlation of $\mu$ for XGeMe$_3$ (set PP2) with the CR equation and the $\sigma_{c14.3}$ and $\sigma_{c16.7}$ constants gave the regression equations 53 and 54:

$$\mu_X = 5.56(\pm 0.513)\sigma_{c14.3,X} + 0.430(\pm 0.144)$$  \hspace{1cm} (53)

$$\mu_X = 5.61(\pm 0.519)\sigma_{c16.7,X} + 0.474(\pm 0.142)$$  \hspace{1cm} (54)
TABLE 6. QSPR data sets

| PP1. | µ in PhH, XSiMe3. X, µ: H, 0.58; Cl, 2.02; Br, 2.31; I, 2.46; Ph, 0.42; Vi, 0.33; 2-ViVn, 0.29; CH2Vi, 0.82; C2H, 0.45b, Me, 0; Bu, 0; t-Bu, 0; CH2Ph, 0.68b; OMe, 1.18; OEt, 1.17; OPh, 1.17; OAc, 1.86; SiMe, 1.73; NMe2, 0.67. |
| PP2. | µ in PhH, XGeMe3. X, µ: H, 0.668; F, 2.51; Cl, 2.89; Br, 2.84; I, 2.81; Ph, 0.58; Me, 0; CH2Ph, 0.63; C2H, 0.79b, OMe, 1.73; OEt, 1.60. |
| PP3. | µ in PhH, XSnMe3. X, µ: Cl, 3.46; Br, 3.45; I, 3.37; Ph, 0.51; Me, 0; CH2Ph, 0.91; NMe2, 1.09; NEt2, 0.85; Vi, 0.45. |
| PP4. | µ in PhH, XSiEt3. X, µ: H, 0.76; F, 1.74; Cl, 2.09; Br, 2.42; Ph, 0.71d; 2-ViVn, 0.47; CH2Vi, 0.2; Et, 0; OH, 1.21. |
| PP5. | µ in PhH, XSiEt3. X, µ: H, 0.76; F, 1.74; Cl, 2.09; Br, 2.42; Ph, 0.71d; 2-ViVn, 0.47; CH2Vi, 0.2; Et, 0; OH, 1.21. |
| PP6. | µ in PhH, XGeH3. X, µ: H, 0; F, 1.268; Cl, 1.292; Br, 1.31; I, 1.62c; N3, 2.17; SiH3, 0; Me, (−) 0.7351; Et, (−) 0.76; i-Bu, (−) 0.75. |
| PP7. | µ in PhH, X2SiMe2. X, µ: H, 0.75; Cl, 1.89; Br, 2.45; OH, 1.94f; OMe, 1.29; OEt, 1.39; OPh, 1.278f; SiMe3, 0; Me, 0; Pr, 0.3. |
| PP8. | µ in PhH, X2GeMe2. X, µ: H, 0; F, 1.268; Cl, 1.292; Br, 1.31; I, 1.62c; N3, 2.17; SiH3, 0; Me, 0; Pr, 0.3. |
| PP9. | µ in PhH, X2SnMe2. X, µ: Cl, 3.14; OMe, 1.63; OEt, 1.51; OPr, 1.49; OPh, 1.45; Me, 0. |
| PP10. | µ in PhH, X3SnMe. X, µ: H, 0.68; Cl, 10.36; Et, 10.09; Bu, 10.05; t-Bu, 9.97; CH2Bu-t, 9.80; F, 9.35; Me, 9.69; Et, 9.72; Pr, 9.52; Bu, 9.48; CH2Vi, 9.62; CH2Ph, 9.71; CH2CN, 10.18; CH2OH, 10.16; CH2Cl, 10.34; CH2Br, 10.16; NH2, 8.64; OMe, 9.05; OEt, 9.15; OMe, 9.85; I, 10.08; CO2H, 10.91; CO2Me, 11.12; CHO, 10.95; SiMe3, 9.56; SiH3, 10.37; CH2GeMe3, 8.85. |
| PP11. | µ in PhH, X2SnMe2. X, µ: Cl, 4.22; Br, 3.86; I, 3.76; OEt, 2.19; NMe2, 1.33; Me, 0. |
| PP12. | µ in PhH, X3SnMe. X, µ: H, 0.68; Cl, 3.62; Br, 3.77; I, 2.64; NMe2, 1.36; Me, 0. |
| PP13. | Ionization potentials (eV), BiX. X, IP: Bi, 9.69; Me, 9.69; Et, 9.72; Pr, 9.52; Bu, 9.48; CH2Vi, 9.62; CH2Ph, 9.71; CH2CN, 10.18; CH2OH, 10.16; CH2Cl, 10.34; CH2Br, 10.16; NH2, 8.64; OMe, 9.05; OEt, 9.15; OMe, 9.85; I, 10.08; CO2H, 10.91; CO2Me, 11.12; CHO, 10.95; SiMe3, 9.56; SiH3, 10.37; CH2GeMe3, 8.85. |
| PP14. | Ionization potentials (eV), HC2X. X, IP: H, 11.40; Me, 10.36; Et, 10.18; Pr, 10.09; Bu, 10.05; t-Bu, 9.97; CH2Bu-t, 9.80; F, 9.35; Me, 9.69; Et, 9.72; Pr, 9.52; Bu, 9.48; CH2Vi, 9.62; CH2Ph, 9.71; CH2CN, 10.18; CH2OH, 10.16; CH2Cl, 10.34; CH2Br, 10.16; NH2, 8.64; OMe, 9.05; OEt, 9.15; OMe, 9.85; I, 10.08; CO2H, 10.91; CO2Me, 11.12; CHO, 10.95; SiMe3, 9.56; SiH3, 10.37; CH2GeMe3, 8.85. |
| PP15. | Vertical ionization potentials (eV), π3 (b1) orbital of PhX. X, IP (eV): H, 9.24; Me, 8.84; t-Bu, 8.83; CH2Bu-t, 8.77; F, 9.35; Cl, 9.10; Br, 8.99; I, 8.67; N3, 8.72b; NH2, 8.05; NHMe, 7.65; NMe2, 7.37; OH, 8.56; OMe, 8.39; SH, 8.17; SMe, 8.07; SPh, 7.89; CH2Cl, 9.27; CH2Br, 9.23; CH2OMe, 9.12; CH2OH, 8.90; CH2Vi, 8.65; c-Pr, 8.66; Vi, 8.49; Ph, 8.39; C2H, 8.82; CF3, 9.90; CCl3, 9.32; Ac, 9.51; CO2Me; 9.50; CN, 9.72; SO2Me, 9.74; SO2Ph, 9.37; NO2, 9.99; SiH3, 9.18; SiMe3, 9.05; SiF3, 10.23b; SiCl3, 9.46; SiBr3, 9.06b; SiMeF2, 9.55; SiMeCl2, 9.52; SiMe2F2, 9.55; SiMe2Br2, 10.10; SiMe2Cl2, 9.30; SiMe2Ph, 8.98; SiPh3, 8.96; GeMe3, 9.00; GePh2Br, 9.19; GePh3, 8.95; SnMe3, 8.94; SnPh2Cl, 9.39; SnPh3, 9.04; PbPh3, 8.95; CH2SiMe3, 8.42; (C(SiMe3)3, 8.10; CH2SnMe3, 8.21b. |
| PP16. | A1/2 (/ mol1/2 cm−1) of the C ≡ C stretching frequency (IR) of Me3GeC2X. A1/2, X: NH2, −131.9; OMe, −121.8; OH, −114.2; F, −99.0; Me, −38.3; Vi, −25.6; H, −13.0; CF3, 12.3; CN, 9.8; CHO, 47.7; Ac, 42.7; NO2, 30.3; CH2Ph, −40.2; CH2OMe, −24.5; CH2Br, −11.4; Ph, −37.7. |
TABLE 6. (continued)

<table>
<thead>
<tr>
<th>PP17. $\delta^{13}C^a$ (NMR) of Me$_3$SiC$_2$X. X, $\delta^{13}C^a$: H, 89.78; Me, 83.89; t-Bu, 82.14; Ph, 94.05; C$_6$F$_5$, 109.40; SMe, 96.90; SEt, 95.21; Cl, 74.76; Br, 86.99; I, 104.2; CH$_2$OEt, 90.99; GeMe$_3$, 113.79; SnMe$_3$, 111.20; SnEt$_3$, 111.20; SnMe$_3$, 117.78; SnEt$_3$, 118.97; CH$_2$SiMe$_3$, 83.87.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP18. $\delta^{29}Si$ (NMR) of Me$_3$SiC$_2$X. X, $\delta^{29}Si$: H, $-17.6$; Me, $-19.6$; t-Bu, $-19.4$; Ph, $-18.0$; C$_6$F$_5$, $-15.3$; SMe, $-18.5$; SEt, $-18.5$; Cl, $-16.1$; Br, $-16.0$; I, $-16.2$; CH$_2$Cl, $-17.3$; CH$_2$Br, $-17.3$; SiMe$_3$, $-19.4$; GeMe$_3$, $-20.1$; GeEt$_3$, $-20.1$; SnMe$_3$, $-20.8$; SnEt$_3$. $-20.3$; CH$_2$SiMe$_3$, $-20.1$.</td>
</tr>
<tr>
<td>PP19. $\delta^{119}Sn$ (NMR) of Me$_3$SiC$_2$X. X, $\delta^{119}Sn$: H, $-68.3$; Me, $-73.7$; Et, $-73.2$; t-Bu, $-72.8$; Ph, $-67.7$; C$_6$F$_5$, $-57.8$; SMe, $-68.8$; SEt, $-68.4$; Cl, $-58.5$; Br, $-58.8$; CH$_2$OEt, $-69.5$; CH$_2$Cl, $-65.5$; CH$_2$Br, $-65.6$; SiMe$_3$, $-77.0$; SiEt$_3$, $-77.1$; GeMe$_3$, $-77.3$; GeEt$_3$, $-78.9$; SnMe$_3$, $-80.9$; CH$_2$SiMe$_3$, $-74.0$.</td>
</tr>
</tbody>
</table>

\[ \mu_X = 7.47(\pm 0.727)\sigma_{c14.3} - 0.0193(\pm 0.200) \]  
\[ 100r^2, 93.78F, 105.6; S_{est}, 0.381, S^0, 0.283; N_{dp}, 9; P_D, 0; \eta, 0. \]

Correlation of $\mu$ for XSiEt$_3$ (set PP4) with the CR equation gave the regression equation 56:

\[ \mu_X = 4.11(\pm 0.494)\sigma_{c16.7} + 0.365(\pm 0.128) \]  
\[ 100r^2, 90.83; F, 69.34; S_{est}, 0.280, S^0, 0.343; N_{dp}, 9; P_D, 16.7; \eta, 0. \]

Correlation of $\mu$ for XSnMe$_3$ (set PP5) and XSnMe$_3$ (set PP6) with the LD equation gave the regression equations 57 and 58:

\[ \mu_X = 7.16(\pm 1.57)\sigma_{c16.7} - 0.324(\pm 0.317) \]  
\[ 100r^2, 83.85; F, 20.77; S_{est}, 0.690, S^0, 0.492; N_{dp}, 6; P_D, 0; \eta, 0. \]

\[ \mu_X = 10.8(\pm 1.13)\sigma_{c16.7} - 3.72(\pm 0.941)\sigma_{dX} + 0.343(\pm 0.317) \]  
\[ 100R^2, 98.62; A 100R^2, 98.16; F, 71.62; S_{est}, 0.341; S^0, 0.186; N_{dp}, 5; P_D, 25.7(\pm 8.23), \eta, 0; r_{ld}, 0.544. \]

Correlation of $\mu$ for XSiH$_3$ (set PP7) with the CR equation and the $\sigma_{c14.3}$ and $\sigma_{c16.7}$ constants gave the regression equations 59 and 60:

\[ \mu_X = 4.85(\pm 0.441)\sigma_{c16.7} + 7.43(\pm 2.42)\sigma_{cX} - 0.610(\pm 0.144) \]  
\[ 100R^2, 93.47; A 100R^2, 92.82; F, 64.45; S_{est}, 0.310, S^0, 0.295; N_{dp}, 12; P_D, 16.7; \eta, -7.64(\pm 2.39); r_{ce}, 0.544. \]
\[ \mu_X = 4.78(\pm 0.435)\sigma_{c14.3,X} + 7.69(\pm 2.42)\sigma_{eX} - 0.634(\pm 0.146) \]  
(60)

\[ 100R^2, 93.45; A 100R^2, 92.79; F, 64.19; S_{est}, 0.311, S^0, 0.296; N_{dp}, 12; P_D, 14.3; \eta, -8.03(\pm 2.42); r_{ce}, 0.031. \]

However correlation of \( \mu \) for XGeH\(_3\) (set PP8) with the CR equation gave the regression equation 61:

\[ \mu_X = 6.42(\pm 0.685)\sigma_{c16.7,X} - 0.318(\pm 0.254) \]  
(61)

\[ 100r^2, 95.64; F, 87.75; S_{est}, 0.387, S^0, 0.256; N_{dp}, 6; P_D, 16.7; \eta, 0. \]

Because substituents are either overall electron donors or electron acceptors, they can in many cases cause the molecular dipole moment to have one direction for acceptors and the opposite direction for donors. In such cases, to account for this, it is necessary to assign a negative sign to the dipole moment when the substituent is an overall electron donor. This was done for alkyl groups in sets PP7 and PP8. In Table 6, when this has been done, the minus sign is in parentheses to show that it has been assigned.

Correlation of \( \mu \) for X\(_2\)SiMe\(_2\) (set PP9) with the LDR equation gave the regression equation 62:

\[ \mu_X = 4.14(\pm 0.507)\sigma_{lX} + 0.115(\pm 0.153) \]  
(62)

\[ 100r^2, 88.10; F, 66.60; S_{est}, 0.295, S^0, 0.381; N_{dp}, 11; P_D, 0; \eta, 0. \]

Correlation of \( \mu \) for X\(_2\)GeMe\(_2\) (set PP10) with the CR equation and the \( \sigma_{c14.3} \) and \( \sigma_{c16.7} \) constants gave results which show no significant difference in goodness of fit between the regression equations. They are equations 63 and 64, respectively:

\[ \mu_X = 5.71(\pm 0.974)\sigma_{c14.3,X} + 0.353(\pm 0.230) \]  
(63)

\[ 100r^2, 87.31; F, 34.41; S_{est}, 0.380, S^0, 0.421; N_{dp}, 7; P_D, 14.3; \eta, 0. \]

\[ \mu_X = 5.79(\pm 0.989)\sigma_{c16.7,X} + 0.413(\pm 0.222) \]  
(64)

\[ 100r^2, 87.25; F, 34.22; S_{est}, 0.380, S^0, 0.422; N_{dp}, 7; P_D, 16.7; \eta, 0. \]

Correlation of \( \mu \) for X\(_2\)SnMe\(_2\) (set PP11) with the LD equation gave the regression equation 65:

\[ \mu_X = 8.75(\pm 0.570)\sigma_{lX} - 0.0345(\pm 0.196) \]  
(65)

\[ 100r^2, 98.33; F, 235.5; S_{est}, 0.243, S^0, 0.158; N_{dp}, 6; P_D, 0; \eta, 0. \]

Correlation of \( \mu \) for X\(_3\)SnMe (set PP12) with the LD equation gave the regression equation 66:

\[ \mu_X = 6.81(\pm 0.657)\sigma_{lX} + 0.308(\pm 0.213) \]  
(66)

\[ 100r^2, 96.42; F, 107.6; S_{est}, 0.332, S^0, 0.232; N_{dp}, 6; P_D, 0; \eta, 0. \]

In discussing these results it is necessary to consider the relationship between the molecular dipole moment \( \mu \) and the individual bond moments \( \mu_b \) (equation 67):

\[ \mu = \sum \mu_b \]  
(67)
Then for $XMeZ_3$, equations 68 and 69 apply:

$$\mu = \mu_{b, MX} - 3 \cos 70.52^\circ \mu_{b, MZ}$$  \hspace{1cm} (68) \\
$$= \mu_{b, MX} - \mu_{b, MZ}$$  \hspace{1cm} (69) \\

for $X_2MZ_2$, equations 70 and 71 apply:

$$\mu = 2 \cos 54.76^\circ (\mu_{b, MX} - \mu_{b, MZ})$$  \hspace{1cm} (70) \\
$$= 1.154(\mu_{b, MX} - \mu_{b, MZ})$$  \hspace{1cm} (71) \\

and for $X_3MZ$, equations 72 and 73 apply:

$$\mu = 3 \cos 70.52^\circ \mu_{b, MX} - \mu_{b, MZ}$$  \hspace{1cm} (72) \\
$$= \mu_{b, MX} - \mu_{b, MZ}$$  \hspace{1cm} (73) \\

Assuming that $\mu_b$ is a function of $\Delta \chi$, the electronegativity difference between X and M or Z and M is given by equations 74a and 74b:

$$\mu_b = \chi_X - \chi_M$$  \hspace{1cm} (74a) \\
$$\mu_b = \chi_Z - \chi_M$$  \hspace{1cm} (74b) \\

and then equations 75 and 76 apply:

$$\mu = f[(\chi_X - \chi_M) - (\chi_Z - \chi_M)]$$  \hspace{1cm} (75) \\
$$= f(\chi_X - \chi_Z)$$  \hspace{1cm} (76) \\

As $Z$ is constant throughout a data set, it follows that within a data set $\mu$ should be a function of $\chi_X$.

$L$ and $C$ are equivalent to each other insofar as the magnitude of the localized electrical effect is concerned. The $L$ values obtained in the correlations are the same for a given M, as they are all less than two standard deviations from each other. The mean values of $L$ for Si, Ge and Sn are 4.46(±0.392), 5.90(±0.459) and 7.88(±0.846), respectively. Although only one $L$ value is available for Pb, it seems that $L$ increases with the atomic number for group 14 elements other than carbon.

There seems to be a linear relationship between the mean value of $L$ and the first ionization potential (IP) of MMe$_4$ when M is Si, Ge, Sn and probably Pb as well. As the IP of PbMe$_4$ is regarded as uncertain and only one data set for lead derivatives was available, making the $L$ value for lead uncertain, no definite conclusion regarding the fit of lead compounds in this relationship can be reached. The only $L$ value available for carbon at this time is reliable but does not fit the $L$–IP relationship.

The value of $PD$ for Si and Ge data sets is generally about 16, that for Sn is generally about 0. For the only carbon data set studied it is 28, but this is a large set with a wide range of substituent types and the value is reliable. For the only lead data set available, the range of substituent types is small as is the number of data points; we therefore regard the $PD$ value for this set as unreliable. We conclude that for the group 14 elements the order of $PD$ values is C > Si ≈ Ge > Sn. In view of this sequence we suspect that the correct $PD$ value for Pb is probably zero and that it follows Sn in the sequence. The value of $\eta$ generally obtained is 0.

Overall, the goodness of fit obtained for these correlations is about what can be expected for the quality of the data, particularly when we take into account the fact that in most
cases the dipole moments were determined in benzene, a Lewis base, while the compounds studied are all Lewis acids.

2. Ionization potentials

First ionization potentials of substituted ethylenes32 (set PP13, Table 6) were correlated with the LDRA equation (equation 38). The regression equation is equation 77:

$$ IP_X = 1.58(\pm 0.218)\sigma_f X - 2.45(\pm 0.123)\sigma_d X - 1.09(\pm 0.455)\alpha X $$
$$ + 10.11(\pm 0.0819) $$

(77)

100R², 96.24; A 100R², 95.85; F, 153.9; S_est, 0.140; S°, 0.214;
N_dp, 22; P_D, 60.7(±4.83), η, 0; r_id, 0.157; r_le, 0.394; r_dα, 0.058;
C_l, 37.3; C_d, 57.6; Cα, 5.11.

Correlation of first ionization potentials of substituted acetylenes33 (set PP14, Table 6) with the LDRA equation gave the regression equation 78:

$$ IP_X = 1.13(\pm 0.324)\sigma_f X - 2.63(\pm 0.472)\sigma_d X + 7.72(\pm 3.57)\sigma_e X $$
$$ - 4.67(\pm 0.752)\alpha + 11.36(\pm 0.166) $$

(78)

100R², 91.94; A 100R², 90.52; F, 45.65; S_est, 0.249; S°, 0.325; N_dp, 21;
P_D, 70.0(±16.4), η, 2.35(±1.23); r_id, 0.211; r_le, 0.276; r_dα, 0.634;
r_de, 0.748; r_dα, 0.142; r_eα, 0.370; C_l, 20.7; C_d, 48.1; C_e, 14.1; Cα, 17.1.

Correlation of vertical ionization potentials of the πS(π₃) orbital of substituted benzenes33,34 (set PP15, Table 6) gave, on exclusion of the values for N₃, SiBr₃, SiF₃ and CH₂SnMe₃, the regression equation 79:

$$ IP_X = 0.895(\pm 0.117)\sigma_f X - 1.61(\pm 0.0976)\sigma_d X + 4.12(\pm 0.480)\sigma_e X $$
$$ - 0.628(\pm 0.113)\alpha + 9.28(\pm 0.0515) $$

(79)

100R², 93.18; A 100R², 92.75; F, 157.2; S_est, 0.151; S°, 0.275; N_dp, 51;
P_D, 64.3(±5.52), η, 2.56(±0.254); r_id, 0.166; r_le, 0.037; r_dα, 0.464;
r_de, 0.346; r_dα, 0.497; r_eα, 0.470; C_l, 29.4; C_d, 52.1; C_e, 13.5; Cα, 4.13.

The lack of fit of the CH₂SnMe₃ group is certainly due to an error in the value of σ_d. The poor fit of the SiBr₃ and SiF₃ groups is probably also due to errors in their substituent constants. The cause for the lack of fit of the N₃ group is unknown.

The P_D values are in good agreement for all three data sets. The lack of dependence on σ_e for the substituted ethylenes is surprising; we are unable to account for it. The dependence on α is much smaller for the substituted benzenes and ethylenes than for the acetylenes. We are unable to account for this at the present time.

3. Infrared A values

Egorochkin and coworkers35 have reported A¹/² values for 1-substituted-2-trimethylgermylacetylenes (set PP16, Table 6), where A is the stretching frequency of the triple
bond. We have correlated the data set with the LDR equation (equation 1); the regression equation is given by equation 80:

$$A_X^{1/2} = 191(\pm 5.11)\sigma_d - 8.50(\pm 1.61)$$

(80)

100\(r^2\), 99.01; \(F\), 1398; \(S_{est}\), 5.94; \(S^0\), 0.106; \(N_{dp}\), 16; \(P_D\), 100; \(\eta\), 0.

Here, \(A^{1/2}\) is a function solely of \(\sigma_d\). This is surprising as it has been reported that \(A^{1/2}\) is a function solely of \(\sigma^R\), which is itself a composite parameter that is dependent on both \(\sigma_d\) and \(\sigma_e^{36}\). We have made use of equation 80 in the form of equation 81:

$$\sigma_{dX} = 0.00524A_X^{1/2} + 0.0445$$

(81)
to calculate new \(\sigma_d\) values for a number of substituents and regard these values as very reliable.

4. NMR chemical shifts

Correlation of \(^{13}\)C chemical shifts for 1-substituted-2-trimethylsilylacetylenes\(^{29}\) (set PP\(^{17}\), Table 6) with the LDRA equation (equation 41) gave the regression equation 82:

$$\delta_X = 12.3(\pm 8.43)\sigma_{1X} - 62.4(\pm 9.81)\sigma_{dX} - 201(\pm 44.4)\sigma_{eX} - 29.1(\pm 14.3)\alpha + 87.0(\pm 3.23)$$

(82)

100\(R^2\), 89.30; \(A\) 100\(R^2\), 87.16; \(F\), 29.20; \(S_{est}\), 5.07; \(S^0\), 0.381; \(N_{dp}\), 19;

\(P_D\), 83.2(\pm 16.4), \(\eta\), 3.22(\pm 0.501); \(r_{ld}\), 0.667; \(r_{le}\), 0.144; \(r_{la}\), 0.596;

\(r_{de}\), 0.266; \(r_{da}\), 0.558; \(r_{ea}\), 0.242; \(C_1\), 12.5; \(C_d\), 61.8; \(C_e\), 19.9; \(C_\alpha\), 5.78.

The term in \(\sigma_{1}\) was retained because of the highly significant collinearity between \(\sigma_{1}\) and \(\sigma_d\). Correlation of chemical shifts for \(^{29}\)Si (set PP\(^{18}\), Table 6) with the LDRA equation gave the regression equation 83:

$$\delta_X = 8.45(\pm 1.00)\sigma_{1X} - 4.37(\pm 1.09)\sigma_{dX} - 3.94(\pm 1.51)\alpha + 18.2(\pm 0.392)$$

(83)

100\(R^2\), 89.64; \(A\) 100\(R^2\), 88.26; \(F\), 40.40; \(S_{est}\), 0.609; \(S^0\), 0.365; \(N_{dp}\), 18;

\(P_D\), 34.1(\pm 9.34), \(\eta\), 0; \(r_{ld}\), 0.641; \(r_{le}\), 0.129; \(r_{la}\), 0.557; \(r_{de}\), 0.261;

\(r_{da}\), 0.504; \(r_{ea}\), 0.280; \(C_1\), 62.1; \(C_d\), 32.1; \(C_\alpha\), 5.79.

However, correlation of \(^{119}\)Sn chemical shifts of 1-substituted-2-trimethylstannyl acetylenes (set PP\(^{19}\), Table 6) gave the regression equation 84:

$$\delta_X = 34.9(\pm 4.10)\sigma_{1X} - 9.42(\pm 4.43)\sigma_{dX} - 12.6(\pm 6.08)\alpha - 70.5(\pm 1.47)$$

(84)

100\(R^2\), 89.17; \(A\) 100\(R^2\), 87.81; \(F\), 41.15; \(S_{est}\), 2.49; \(S^0\), 0.370; \(N_{dp}\), 19;

\(P_D\), 21.3(\pm 10.4), \(\eta\), 0; \(r_{ld}\), 0.627; \(r_{le}\), 0.140; \(r_{la}\), 0.491; \(r_{de}\), 0.260;

\(r_{da}\), 0.483; \(r_{ea}\), 0.366; \(C_1\), 74.5; \(C_d\), 20.1; \(C_\alpha\), 5.38.

Structural effects on the silicon and tin chemical shifts are very similar. The \(P_D\) values do not differ significantly and \(\eta\) is zero in both data sets. These results are very different from those observed for \(^{13}\)C chemical shifts.
D. Bioactivities (QSAR)

Little in the way of data sets involving the effect of structural variation on bioactivity is available for compounds of germanium and lead. Some data are available for alkylstannanes although the data sets are very limited in both the number of data points and in the extent of variation in the alkyl group structure. The toxicity of trialkylstannanes to *Botrytis* and of dialkylstannanes to *B. subtilis* (sets BA1 and BA2, Table 7) were modeled using the simple branching equation (equation 4) in the form of equation 85:

\[ \text{BA}_{Ak} = a_1n_1 + a_cn_C + a_0 \]  

(85)

where \( n_C \) is the number of carbon atoms in the alkyl group and \( a_C \) is its coefficient, and in the form of equation 86:

\[ \text{BA}_{Ak} = a_1n_1 + a_2n_2 + a_0 \]  

(86)

Correlation of the data sets with equations 85 and 86 gave the regression equation 87:

\[
\log \text{BA}_{Ak} = -2.48(\pm 0.478)n_1 - 0.458(\pm 0.427) \\
100r^2, 84.97; F, 26.92; S_{est}, 0.427; S^0, 0.409; N_{dp}, 5.
\]  

(87)

With the exclusion of the data point for hexyl, it gave equation 88:

\[
\text{BA}_{Ak} = -0.653(\pm 0.0547)n_1 - 0.478(\pm 0.0446)n_2 - 0.458(\pm 0.0387) \\
100R^2, 99.70; A 100R^2, 99.60; F, 331.5; S_{est}, 0.0387; S^0, 0.0867; \\
N_{dp}, 5; r_{12}, 0.612; C_{n1}, 57.7; C_{n2}, 42.3; B_1/B_2, 1.37.
\]  

(88)

**LD**\(_{50}\)s for the toxicity of trialkylstannanes (set BA3, Table 7) to the rat were correlated with equation 89:

\[
LD_{50,Ak} = Sv + A\alpha + B^o
\]  

(89)

**TABLE 7.** QSAR data sets

<table>
<thead>
<tr>
<th>BA1</th>
<th>Toxicities of trialkylstannanes to <em>Botrytis</em> (mM). Ak, BA: Me, 0.9; Et, 0.004; Pr, 0.002; Bu, 0.001; Pe, 0.01.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA2</td>
<td>Toxicities of dialkylstannanes to <em>B. subtilis</em> (mM). Ak, BA: Me, 0.9; Et, 0.2; Pr, 0.07; Bu, 0.07; Pe, 0.06; Hx, 0.14.</td>
</tr>
<tr>
<td>BA3</td>
<td>Toxicities of trialkylstannanes to the rat (mM). Ak, BA: Me, 0.07; Et, 0.04; Pr, 0.3; Bu, 0.7; Hx, 2; c-Hx, 1.</td>
</tr>
<tr>
<td>BA4</td>
<td>Toxicities of trialkylstannanes to crab larvae (mM). Ak, BA: Me, 0.56; Et, 0.39; Pr, 0.19; Bu, 0.055; c-Hx, 0.02.</td>
</tr>
<tr>
<td>BA5</td>
<td>Toxicities of dialkylstannanes to crab larvae (mM). Ak, BA: Me, 82; Et, 15; Pr, 2.8; c-Hx, 0.37.</td>
</tr>
</tbody>
</table>

| BA6 | LD\(_{50}\)’s (mM kg\(^{-1}\)) of substituted germatranes to white mice (ip). X, LD\(_{50}\): 2-Tp, 0.0546; 3-Tp, 0.295; H, 1.46; CH\(_2\)Br, 1.14; CH\(_2\)NEt\(_2\), 1.17; 3-Fr, 5.70; 2-Fr, 7.17; CH\(_2\)CH\(_2\)CO\(_2\)Et, 7.50; CH\(_2\)Cl, 11.0; OSiMe\(_3\), 11.7; CH\(_2\)CH\(_2\)CN, 15.8; Vi, 22.8; OH, 35.6; CH\(_2\)Tp-2, 1.03; CH\(_2\)Fr-2, 9.87; PnNET\(_2\)-4, 8.86; PnNM\(_2\)-2, 10.9; CH\(_2\)CHMeCO\(_2\)Me, 21.3; CH\(_2\)CH\(_2\)Py-4, 7.91; CH\(_2\)CH\(_2\)Py-2, 8.65. |

\(^a\)For abbreviations, see Section I.A.
The regression equation is equation 90:

\[ \text{LD}_{50,Ak} = 6.88(\pm 1.28)\alpha - 1.63(\pm 0.238) \]  
\[ 100r^2, 87.90; F, 29.06; S_{est}, 0.261; S^0, 0.426; N_{dp}, 6 : r_{nl,\alpha}, 0.890. \]

As \( \alpha \) and \( \nu \) are highly collinear, a possible dependence on the latter cannot be excluded.

LD_{50}s for the toxicity of di- and trialkylstannanes to crab larvae (sets BA4 and BA5, Table 7) were correlated with equation 91:

\[ \text{LD}_{50,Ak} = S\nu + B\alpha \]

giving the regression equations 92 and 93:

\[ \log \text{LD}_{50,Ak} = -6.20(\pm 1.07)\nu_{Ak} + 4.86(\pm 0.125) \]
\[ 100r^2, 94.34; F, 33.33; S_{est}, 0.292; S^0, 0.336; N_{dp}, 4. \]
\[ \log \text{LD}_{50,Ak} = -4.18(\pm 0.826)\nu_{Ak} + 1.90(\pm 0.556) \]
\[ 100r^2, 89.53; F, 25.65; S_{est}, 0.225; S^0, 0.418; N_{dp}, 5. \]

As expected, the bioactivities of alkylstannanes are a function only of steric effects and polarizability.

Lukevics and Ignatovich\(^{38}\) have reported intraperitoneal LD_{50} values (mg kg\(^{-1}\)) in white mice for substituted germatranes, XGe(OCH\(_2\)CH\(_2\))\(_3\)N. After conversion to mmol kg\(^{-1}\), these values (set BA6, Table 7) were correlated with the IMF equation in the form of equation 94:

\[ Q_X = C\sigma_{c50,X} + M\mu_X + A\alpha_X + H_1n_HX + H_2n_nX + S_1\nu_1X + S_2\nu_2X + B\alpha \]  
(94)

After excluding the values for 2- and 3-thienyl and for vinyl, regression equation 94 was obtained:

\[ \log \text{LD}_{50,X} = -1.91(\pm 0.954)\sigma_{c50,X} + 0.247(\pm 0.103)\mu_X + 0.298(\pm 0.194) \]
\[ 100R^2, 41.61; A 100R^2, 37.72; F, 4.989; S_{est}, 0.376; S^0, 0.842; N_{dp}, 17; \]
\[ P_D, 50 : r_{\sigma\mu}, 0.003; C_\sigma, 79.4; C_\mu, 20.6. \]

This equation is significant at the 97.5% confidence level, though it accounts for only about 40% of the variance of the data. There is a dependence on \( \mu \) and perhaps on \( \sigma \) as well. It is surprising to find no dependence on polarizability. The poor fit may be due to the existence of more than one mode of activity in the data set.

**VI. THE VALIDITY OF THE ESTIMATED SUBSTITUENT CONSTANTS**

The values of \( Q \) calculated for various Group 14 substituents from the applications reported in the previous section provide the only evidence for the validity of the parameter estimates in Reference 1. Table 8 presents values of \( Q_{obs}, Q_{calc} \) and \( \Delta Q \). The data set from which the calculated value was obtained, and the parameter types used in the calculation are also reported. The agreement between observed and calculated values is described in terms of the number of standard deviations, \( N_{SD} \), defined in equation 96:

\[ N_{SD} = \frac{\| \Delta Q \|}{S_{est}} \]  
(96)
## TABLE 8. Values of \( Q_{X,obs}, Q_{X,calc} \) and \( \Delta Q^a \)

<table>
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<tr>
<th>X</th>
<th>( Q ) type</th>
<th>( Q_{X,obs} )</th>
<th>( Q_{calc} )</th>
<th>( \Delta Q )</th>
<th>( N_{sd} )</th>
<th>Parameters</th>
<th>Set</th>
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<td>SiH₃</td>
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<td>10.32</td>
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<td>( \sigma_l, \sigma_d, \alpha )</td>
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<td>IP</td>
<td>10.73</td>
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<td>( \sigma_l, \sigma_d, \alpha )</td>
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<tr>
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<td>IP</td>
<td>9.18</td>
<td>9.27</td>
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<td>( \sigma_l, \sigma_d, \sigma_e, \alpha )</td>
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<tr>
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<td>( \Delta V_{OH} )</td>
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<td>-19.4</td>
<td>-0.656</td>
<td>-1.08</td>
<td>( \sigma_l, \sigma_d, \alpha )</td>
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<td>-75.5</td>
<td>-1.82</td>
<td>-0.730</td>
<td>( \sigma_l, \sigma_d, \alpha )</td>
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<td>GeEt₃</td>
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<td>( \Delta V_{OH} )</td>
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<td>173</td>
<td>9.42</td>
<td>0.745</td>
<td>( \sigma_l, \sigma_d, \alpha )</td>
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### TABLE 8. (continued)

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<th>X</th>
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<th>$\Delta Q$</th>
<th>$N_{sd}$</th>
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<td>114.35</td>
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<td>σ_l, σ_d, α</td>
<td>PP18</td>
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<td>81.46</td>
<td>2.41</td>
<td>0.475</td>
<td>σ_l, σ_d, σ_e, α</td>
<td>PP17</td>
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<td></td>
<td>$\delta^{29}Si$</td>
<td>−20.1</td>
<td>−21.0</td>
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<td>σ_l, σ_d, σ_e, α</td>
<td>PP18</td>
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<td>$\delta^{119}Sn$</td>
<td>−74.0</td>
<td>−75.1</td>
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<td>PP19</td>
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<tr>
<td>C(SiMe$_3$)$_3$</td>
<td>IP</td>
<td>8.10</td>
<td>8.27</td>
<td>−0.170</td>
<td>−1.13</td>
<td>σ_l, σ_d, σ_e, α</td>
<td>PP15</td>
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### TABLE 8. (continued)

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<th>ΔQ</th>
<th>N&lt;sub&gt;sd&lt;/sub&gt;</th>
<th>Parameters</th>
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</thead>
<tbody>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;GeMe&lt;sub&gt;3&lt;/sub&gt;</td>
<td>log&lt;sub&gt;k&lt;/sub&gt;&lt;sub&gt;rel&lt;/sub&gt;</td>
<td>−0.268</td>
<td>−0.306</td>
<td>0.038</td>
<td>0.271</td>
<td>σ&lt;sub&gt;l&lt;/sub&gt;</td>
<td>CR3</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;GeMe&lt;sub&gt;3&lt;/sub&gt;</td>
<td>log&lt;sub&gt;k&lt;/sub&gt;&lt;sub&gt;rel&lt;/sub&gt;</td>
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</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;GeMe&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Δν&lt;sub&gt;OH&lt;/sub&gt;</td>
<td>68</td>
<td>59.1</td>
<td>8.95</td>
<td>1.82</td>
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<td>CP5</td>
</tr>
<tr>
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<td>Δν&lt;sub&gt;OH&lt;/sub&gt;</td>
<td>59</td>
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<td>5.99</td>
<td>1.17</td>
<td>σ&lt;sub&gt;l&lt;/sub&gt;, σ&lt;sub&gt;d&lt;/sub&gt;</td>
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<td>IP</td>
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<td>9.02</td>
<td>−0.168</td>
<td>−1.20</td>
<td>σ&lt;sub&gt;l&lt;/sub&gt;, σ&lt;sub&gt;d&lt;/sub&gt;, α</td>
<td>PP13</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;SnMe&lt;sub&gt;3&lt;/sub&gt;</td>
<td>IP</td>
<td>8.21</td>
<td>8.66</td>
<td>−0.45</td>
<td>−2.98&lt;sup&gt;b&lt;/sup&gt;</td>
<td>σ&lt;sub&gt;l&lt;/sub&gt;, σ&lt;sub&gt;d&lt;/sub&gt;, σ&lt;sub&gt;e&lt;/sub&gt;, α</td>
<td>PP15</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Sn(Bu-t)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Δν&lt;sub&gt;OH&lt;/sub&gt;</td>
<td>55</td>
<td>51.8</td>
<td>3.2</td>
<td>0.623</td>
<td>σ&lt;sub&gt;l&lt;/sub&gt;, σ&lt;sub&gt;d&lt;/sub&gt;</td>
<td>CP6</td>
</tr>
</tbody>
</table>

<sup>a</sup>For abbreviations, see Section I. A.
<sup>b</sup>Using the σ<sub>d</sub> value given in Reference 1.
<sup>c</sup>Using the mean of the σ<sub>d</sub> values given in Table 1 for CH<sub>2</sub>SiMe<sub>3</sub> and CH<sub>2</sub>GeMe<sub>3</sub>.

When N<sub>SD</sub> ≤ 1 the agreement is considered excellent, for 1 < N<sub>SD</sub> ≤ 2 agreement is considered fair, for 2 < N<sub>SD</sub> ≤ 3 poor, and for N<sub>SD</sub> > 3 unacceptable. Values of N<sub>SD</sub> are also given in Table 8.

**MZ<sup>1</sup>Z<sup>2</sup>Z<sup>3</sup> groups.** The agreement between calculated and observed values for substituents in which Z groups are H, alkyl or aryl is good. For MEt<sub>3</sub> with M = Si, Ge and Sn, the electrical effect substituent constants were assumed equal to those for the MMe<sub>3</sub> groups. The same assumption was made for several SnAk<sub>3</sub> groups. The N<sub>SD</sub> values given in Table 8 show that the assumption is justified, in agreement with previous results for substituents of the type W Ak<sub>n</sub> in which W is an atom or group of atoms<sup>39</sup>. The electrical, steric and intermolecular force substituent constants for these substituents are probably reliable. The electrical effect substituent constants for groups in which Z is halogen gave poorer results, though the data available to test them are scanty. There continues to be a lack of data on M(OAk)<sub>3</sub> and M(SAk)<sub>3</sub> groups.

**C(MZ<sup>1</sup>Z<sup>2</sup>Z<sup>3</sup>)<sub>n</sub>H<sub>3</sub>–n groups.** We have calculated σ<sub>d</sub> values for the CH<sub>2</sub>SiMe<sub>3</sub> and CH<sub>2</sub>GeMe<sub>3</sub> groups directly from the A<sup>1/2</sup> values of set PP16. These values seem to be very reliable. Contrary to the statement in Reference 1, there appears to be a special capability for electron donation in these groups. Our results for the CH<sub>2</sub>SnMe<sub>3</sub> group are in agreement with this conclusion, as also are our results for the CH<sub>2</sub>Sn(Bu-t)<sub>3</sub> group.

There is still very little data available for Pb substituents. Much more experimental work is required before we can arrive at a reliable description of substituent effects of Group 14 elements other than carbon.

**VII. APPENDIX. SUPPLEMENTARY GLOSSARY**

**Electrical effect parameterization**

**CR equation:** A diparametric electrical effect model using the composite σ<sub>CK</sub>′ and pure σ<sub>e</sub> parameters. A value of P<sub>D</sub> is assumed and a value of η calculated.

**LD equation:** A diparametric electrical effect model using the pure σ<sub>l</sub> and composite σ<sub>D</sub> parameters. A value of P<sub>D</sub> is calculated and a value of η assumed.
8. Structural effects on germanium, tin and lead compounds

Steric effect parameterization

ν A steric effect parameter based on van der Waals radii that has been corrected for the difference in bond length between the X-G and Y-G bonds.

Other parameterization

τ A parameter that accounts for the effect of temperature on the reaction velocity. It is defined as $100 / T$ where $T$ is the absolute temperature.

ϕ A parameter that accounts for the effect of concentration of a component in a mixed solvent. It is the mole fraction of that component.

ζ A parameter used to combine two or more data sets into a single set. It is determined by choosing a substituent present in each of the data sets to be combined and defining $Q$ for that substituent as $\zeta$. Thus, if the substituent chosen is Z and there are sets 1, 2 and 3 to be combined, the $\zeta$ values are $Q_{Z1}$, $Q_{Z2}$ and $Q_{Z3}$ respectively.

The glossary to which this is a supplement will be found in Appendix I of Reference 1.

VIII. REFERENCES

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359–396.
CHAPTER 7

Recent advances in acidity, complexing, basicity and H-bonding of organo germanium, tin and lead compounds*

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I. ABBREVIATIONS
The following abbreviations are used in addition to the well-known abbreviations which are listed in each volume.

232tet 3,7-diazanonane-1,9-diamine
323tet 4,7-diazadecane-1,10-diamine

* In this chapter, full lines are used both for covalent chemical bonds as well as for partial bonds and for coordination.
II. OUTLINE

The aim of this review is to focus on the hydrogen bonding, the acidity and basicity and complexing chemistry concerning the organo-element chemistry of germanium, tin and lead. This chapter is not exhaustive in scope, but contains the most recent work of the last five to six years, since another review in this series was published\(^1\). This chapter emphasizes the synthesis, reactions and molecular structures of the class of compounds outlined above (less attention is paid to mechanism, spectroscopic properties and applications which can be found in other specialized chapters). Especially, the single-crystal X-ray diffraction technique has elucidated many novel and unusual structures of molecules.
and of the solid state in general. Not unexpectedly, certain organo-element compounds present problems concerning their classification as n-coordinated species, since it is sometimes difficult to distinguish between a weak long-range interaction in the solid state and the fact that two atoms can be forced a little bit closer together by crystal lattice effects.

Since organo-element chemistry is the discipline dealing with compounds containing at least one direct element–carbon bond, in this chapter we discuss germanium, tin and lead species in which at least one organic group is attached through a carbon, and as an extension also compounds where the organic group is connected through a nitrogen or an oxygen atom.

### III. INTRODUCTION

Considering the chemical reactivity and group trends of germanium, tin and lead, it can be stated that germanium is somewhat more reactive and more electropositive than silicon. Alkyl halides react with heated Ge (as with Si) to give the corresponding organogermainium halides. Tin, however, is notably more reactive and electropositive than Ge and Pb powder is pyrophoric whereas the reactivity of the metal is usually greatly diminished by the formation of a thin, coherent protective oxide layer. The steady trend towards increasing stability of \( \text{M}^{\text{II}} \) rather than \( \text{M}^{\text{IV}} \) compounds in general in the sequence Ge, Sn, Pb is an example for the ‘inert-pair effect’, which is well established for the heavier main group metals. Table 1 summarizes the physical properties of the group 14 elements Ge, Sn and Pb.

### IV. COMPLEXING, ACIDITY, BASICITY AND H-BONDING

#### A. Introduction

The concept of second- or outer-sphere coordination, originally introduced by Werner, has played a major role in the subsequent development of the theory of bonding in metal complexes and has recently re-emerged as a means of describing higher-order

---

**TABLE 1. Physical properties of Group 14 elements Ge, Sn and Pb**

<table>
<thead>
<tr>
<th></th>
<th>( ^{32}\text{Ge} )</th>
<th>( ^{70}\text{Sn} )</th>
<th>( ^{82}\text{Pb} )</th>
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<tbody>
<tr>
<td>Electron configuration</td>
<td>([\text{Ar}]3\text{d}^{10}4\text{s}^{2}4\text{p}^{2})</td>
<td>([\text{Kr}]4\text{d}^{10}5\text{s}^{2}5\text{p}^{2})</td>
<td>([\text{Xe}]4\text{f}^{14}5\text{d}^{10}6\text{s}^{2}6\text{p}^{2})</td>
</tr>
<tr>
<td>Atomic weight (g mol(^{-1}))</td>
<td>72.61</td>
<td>118.71</td>
<td>207.20</td>
</tr>
<tr>
<td>Electronegativity:</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Pauling</td>
<td>2.01</td>
<td>1.96</td>
<td>2.33</td>
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<tr>
<td>Allred–Rochow</td>
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<td>1.72</td>
<td>1.55</td>
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<td>Sanderson</td>
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<td>2.0</td>
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<tr>
<td>Ionization potential (eV)(^2)</td>
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</tr>
<tr>
<td>(1)</td>
<td>7.899</td>
<td>7.344</td>
<td>7.416</td>
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<tr>
<td>(2)</td>
<td>15.934</td>
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<tr>
<td>(3)</td>
<td>34.220</td>
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<td>(4)</td>
<td>45.710</td>
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<td>B.E.(E-C) (kcal mol(^{-1}))(^a)</td>
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<td>B.E.(E-H) (kcal mol(^{-1}))(^a)</td>
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<td>60</td>
<td>49</td>
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<td>B.E.(E-Cl) (kcal mol(^{-1}))(^a)</td>
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<td>(1.750)</td>
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<td>van der Waals radius (Å)</td>
<td>2.10</td>
<td>2.17</td>
<td>2.02</td>
</tr>
</tbody>
</table>

\(^a\)B.E. = Bond energy
bonding interactions in complexes with crown ether ligands and in systems involving supramolecular or host–guest interactions\textsuperscript{4}. In molecular compounds, the preference for inner-over outer-sphere coordination may be expected to be dependent primarily on (i) the size of the central atom, (ii) the symmetries and energies of the available unoccupied orbitals, (iii) the electronegativity differences and (iv) special structural features of the ligating groups. Accordingly, with certain metals and ligands, complexes with unusual coordination numbers and geometries were obtained, but because of the manifold nature of the metal–ligand interactions, predictions as to the behaviour of a given metal or ligand are not generally possible.

We divided Section IV into three parts according to the three elements of Group 14: germanium, tin, and lead. The main interest is the complexing chemistry of these elements.

**B. Reactions**

1. **Germanium**

Reports on the design, synthesis and modulation of the redox and photochemical function of germanium(IV) porphyrin-based, ‘axial-bonding’-type hybrid trimers are of interest, because photochemically active supramolecular arrays are investigated concerning their ability to transport charge, ions or energy\textsuperscript{5}. In Scheme 1 the synthesis of germanium compounds is shown.

Analysis of the UV-visible, ESR and redox potential data suggests the absence of any exciton coupling between the porphyrin rings and these trimers. Energies of the singlet and charge transfer states are shown in Figure 1. H\textsubscript{2} means H\textsubscript{2}L\textsubscript{2}, Ge means \(\text{[L}^\text{b}\text{Ge(OH)2]}\) and Zn means ML\textsuperscript{a}M\textsuperscript{A}Zn.

The compound \(\text{[L}^\text{b}\text{FeGeFeL}^\text{b}]\text{[PF}6\text{]}\)\textsubscript{2} (L\textsuperscript{b} = 1,4,7-(4-t-butyl-2-mercaptobenzyl)-1,4,7-triazacyclononane) (Figure 2) can be synthesized from GeI\textsubscript{2} in a reaction with \(\text{[L}^\text{1}\text{Fe}^\text{III}\text{]}\) and the addition of NaPF\textsubscript{6}. This complex can be one-electron oxidized by \(\text{[Ni}^\text{III}(\text{tacn})\text{]}\text{[ClO}4\text{]}\)\textsubscript{2} to form \(\text{[L}^\text{1}\text{FeGeFeL}^\text{1}]\text{[ClO}4\text{]}\)\textsubscript{2}.\textsuperscript{6} The oxidation state in the dication cannot be described as l.s.Fe\textsuperscript{III}Ge\textsuperscript{II}l.s.Fe\textsuperscript{III} species (l.s. = low-spin) but rather as a mixed valent species with a formal oxidation state distribution l.s.Fe\textsuperscript{2}Ge\textsuperscript{3}Fe\textsuperscript{2}.\textsuperscript{4} One-electron oxidation of the dication yields the trication and affects only the iron centres and not the respective central main group ion which possesses formally a +III oxidation state. An oxidation state distribution of l.s.Fe\textsuperscript{2}Ge\textsuperscript{3}Fe\textsuperscript{2}.\textsuperscript{9} can be envisaged in the trications yielding an \(S_z = \frac{S}{2}\) ground state.

Compounds which contain a Si–Ge bond and similar complexes are of interest for mass spectrometry because of their fragmentation. Experiments were carried out on the following compounds: Me\textsubscript{3}SiGeP\textsubscript{3}, Ph\textsubscript{3}SiGeMe\textsubscript{3}, FpSiMe\textsubscript{2}GeMe\textsubscript{3} (a), FpGeMe\textsubscript{2}SiMe\textsubscript{3} (b), (Fp = (\eta\textsuperscript{5} – C\textsubscript{5}H\textsubscript{5})Fe(CO)\textsubscript{2}), IFpSiMe\textsubscript{2}GeMe\textsubscript{3} (c), IFpGeMe\textsubscript{2}SiMe\textsubscript{3} (d), IFpSiMe\textsubscript{2}GePh\textsubscript{3} (e), IFpGeMe\textsubscript{2}SiPh\textsubscript{3} (f), (IFp = (\eta\textsuperscript{5} – C\textsubscript{9}H\textsubscript{7})Fe(CO)\textsubscript{2}) and fcSiMe\textsubscript{2}GeMe\textsubscript{2}fc (fc = ferrocenyl).\textsuperscript{7} For the non-iron-containing compounds R\textsubscript{3}SiGeR\textsubscript{3}, an exchange of R groups was observed, which is shown in the measured [R\textsubscript{3-n}R\textsubscript{n}Si\textsuperscript{+}] and [R\textsubscript{3-n}R\textsubscript{n}Ge\textsuperscript{+}] ions. For some of the above-mentioned compounds, Scheme 2 shows the suggested fragmentation patterns.

The products formed during a reaction of an allenic stannane with a Lewis acidic element halide have been less investigated. One example is the propargyltrichlorogermane (HC≡CH\textsubscript{2}GeCl\textsubscript{3}), which can be prepared from the starting material GeCl\textsubscript{4} and H\textsubscript{2}C≡C=CHSnBu\textsubscript{3} at 40°C. Even if the latter is absolutely pure, a mixture of products
SCHEME 1. Synthesis of a germanium ‘axial-bonding’-type hybrid trimer. Reprinted with permission from Reference 5. Copyright 1999 American Chemical Society

was obtained (HC≡CCH2GeCl3 48%, H2C≡C=CHGeCl3 1%). As the temperature of the reaction is substantially lower than the temperature of isomerization, it is possible to conclude that the formation of the propargylic compound occurs via an allenyl–propargyl transposition with more than 99% selectivity.

Heating up the propargyltrichlorogermane to 120°C for a few hours led only to very small amounts of allenyltrichlorogermane (H2C≡C=CHGeCl3), which can be synthesized from HC≡CCH2SnPh3 and GeCl4 at 50°C.

The calix[n]arenes are a class of ‘chalice-like’ macrocyclic molecules, which are useful ligands for divalent Ge. The divalent Ge complexes [t-Bu calix2(TMS)]Ge are observed by a reaction of [t-Bu calix2(TMS)]H2 with Ge[N(SiMe3)2]2 (Scheme 3). For this Ge system...
two isomers (exo: Figure 3 and endo: Figure 4) could be isolated, where the location of Ge with the respect to the calixarene cavity differs. This is the first pair of exo and endo isomers to be structurally characterized. For a schematic diagram clarifying the exo/endo coordination at Ge see Scheme 3.

The nature of multiple bonding between germanium and the heavier chalcogens in the complexes (η⁴-Me₈taa)GeE (E = Se, Te) is best described as an intermediate between the Ge⁺–E⁻ and Ge=E resonance structures. The preparation of these complexes involves the addition of the elemental chalcogen to (η⁴-Me₈taa)Ge, which is synthesized by the metathesis of GeCl₂(1,4-dioxane) and Li₂[Me₈taa] (Me₈taa = octamethyldibenzo[14]annulene dianion). The molecular structures of both complexes are shown in Figures 5 and 6.

In the reaction of lithiated 2-hydroxybiphenyl and 2'-hydroxy-m-terphenyl with germanium dichloride–dioxane complex and GeCl₄, respectively, spirocyclic germabiphenanthrene compounds (Scheme 4) and 1-oxa-10-germaphenanthrene (Scheme 5) were formed.

The first crystallographic evidence for a neutral and, according to the authors, hypervalent germanium(IV) complex (N.B. these complexes are definitely hypercoordinated) with sulphur-induced hexacoordination of germanium in a spirocyclic complex with two sterically hindered eight-membered 12H-dibenzo[d,g][1,2,3,6,2]dioxathiagermocin rings is shown in Figure 7. Scheme 6 presents the synthesis of the complex.

The apparent hypercoordination of the germanium atom in complexes is an interesting research field. A reaction between t-butyltrichlorgermane (t-BuGeCl₃) and mercaptoacetic acid (HSCH₂CO₂H) affords a novel type of pentacoordinate germanium compound via t-BuGe(SCH₂CO₂H)₃, which loses one mole of SCH₂CO₂H. Figure 8 shows the molecular structure of the formed product 2-(2-t-butyl-5-oxo-1,2,3-oxathiagermolan-2-ythio)acetic acid.
acid$^{13}$. For this compound some characteristic points could be observed: (a) The germanium atom is pentacoordinate with trigonal bipyramidal structure. (b) The Ge1−S1, Ge1−S2 and Ge1−C1 bonds are equatorial while the Ge1−O1 and Ge1−O3 bonds are apical with equal lengths (ca 2.04 Å, a little longer than the standard Ge−O covalent bond length (ca 1.7–1.8 Å). (c) Four atoms, Ge1, S1, S2 and C1, are coplanar with S1, S2 and C1 in a trigonal planar arrangement around Ge. (d) The O1−Ge1−O3 hypercoordinate bond is nearly perpendicular to the S1-S2-C1 plane, though the angle (166.7°) slightly deviates from the ideal trigonal bipyramidal structure.

The summary of all these characteristic points to a pentacoordinated organogermanium compound where no steric enforcement is involved to enhance the hypercoordination. The rotation about the S−CH$_2$ bond, which should be feasible, would move the CO$_2$H group far apart from germanium and should be noted. This in turn appears to suggest that the Ge−O interaction is strong enough to lead to hypercoordination.

FIGURE 2. Structure of [L$^1$FeGeFeL$^1$]$^{n+}$. Reprinted with permission from Reference 6. Copyright 1999 American Chemical Society
SCHEME 2. Suggested fragmentation patterns for some of the above-mentioned compounds. Reproduced by permission of Elsevier Science from Reference 7

SCHEME 3. Synthesis of $[t$-Bu calix$_2$(TMS)]Ge. Reproduced by permission of the Royal Society of Chemistry from Reference 9

Compounds of the type Ph$_3$GeCH$_2$SR were obtained by the reactions shown in equations 1–3.$^{14}$

$$\text{Ph}_3\text{GeBr} + \text{LiCH}_2\text{SMe} \longrightarrow \text{Ph}_3\text{GeCH}_2\text{SMe} \quad (1)$$

$$\text{(Ph}_3\text{GeBr + Li)} \longrightarrow \text{Ph}_3\text{GeLi} \quad \underset{\text{CICH}_2\text{SPh}}{\longrightarrow} \text{Ph}_3\text{GeCH}_2\text{SPh} \quad (2)$$
Recent advances in acidity, complexing, basicity and H-bonding

FIGURE 3. The molecular structure of \textit{exo}-[\textit{t}-\text{Bu calix}_{2}^{(TMS)}]\text{Ge}. Reproduced by permission of the Royal Society of Chemistry from Reference 9

FIGURE 4. The molecular structure of \textit{endo}-[\textit{t}-\text{Bu calix}_{2}^{(TMS)}]\text{Ge}. Reproduced by permission of the Royal Society of Chemistry from Reference 9

FIGURE 5. Molecular structure of (\eta^{4}-\text{Me}_{8}\text{taa})\text{GeSe}. Reproduced by permission of the Royal Society of Chemistry from Reference 10
FIGURE 6. Molecular structure of ($\eta^4$-Me$_8$taa)GeTe. Reproduced by permission of the Royal Society of Chemistry from Reference 10

SCHEME 4. Synthesis of spirocyclic germabiphenanthrene compounds from Reference 11. Permission granted by Gordon and Breach publishers, copyright OPA (Overseas Publishers Association)

A mild and effective reagent for the formation of alkyl- and arylsulphinylmethylgermanium compounds (R = Me, p-R\textsuperscript{1}C\textsubscript{6}H\textsubscript{4}, R\textsuperscript{1} = H, Me or t-Bu) from Ph\textsubscript{3}GeCH\textsubscript{2}SR is m-chloroperbenzoic acid (m-ClC\textsubscript{6}H\textsubscript{4}CO\textsubscript{3}H). No cleavage of the phenyl–germanium bonds occurred during these reactions. The structure of the sulfoxide is shown in
FIGURE 8. Molecular structure of product 2-(2-t-butyl-5-oxo-1,2,3-oxathiagermolan-2-ylthio)acetic acid. Reproduced by permission of the Royal Society of Chemistry from Reference 13

FIGURE 9. Molecular structure of Ph₃GeCH₂S(O)R, R = p-t-BuC₆H₄. Reproduced by permission of Elsevier Science from Reference 14

Figure 9. Further oxidation of the sulfoxides (Ph₃GeCH₂S(O)R) to the sulphones Ph₃GeCH₂S(O)₂R also occurs smoothly using m-chloroperbenzoic acid.

Compounds like 1,4,7-trimethyl-1,4,7-triazacyclononane (L2) and 1,3,5-trimethyl-1,3,5-triazacyclohexane (L3) are useful ligands in germanium chemistry. Reactions of L² with GeCl₄ and L³ with GeBr₄ both in the ratio 1 : 1 in acetonitrile solution form ionic compounds with GeX₃⁺ cations: [GeCl₃(L²)]Cl₃•MeCN and [GeBr₃(L³)]Br₃•MeCN. Acetonitrile is trapped in the lattice as solvate molecules¹⁵.
The ligand binding of $L^2$ and $L^3$ to Ge(IV) are for both compounds terdentate N-donor ($\eta^3$). The resulting GeX$_3^{+}$ cations are effectively stabilized by ($\eta^3$) azamacrocyclic chelation to give six-coordinate species that show the anticipated fac-octahedral metal geometry. The structures of the cations are given in Figures 10 and 11.

Interestingly, for these compounds simple halide ions constitute the counter anion in salt formation. The compactness of the ring, especially in the case of $L^3$, does impose a severe steric constriction at the metal centre. In the case of uncomplexed $L^2$ the preferred endodentate conformation identifies it as an (almost) ideal ligand for occupation of three metal coordination sites (fac-octahedral)$^{16–20}$. For free $L^3$ there are four chair conformers

![FIGURE 10. Molecular structure of the [GeCl$_3$(L$^2$)]$^+$ cation. Reproduced by permission of the Royal Society of Chemistry from Reference 15](image1)

![FIGURE 11. Molecular structure of the [GeBr$_3$(L$^3$)]$^+$ cation. Reproduced by permission of the Royal Society of Chemistry from Reference 15](image2)
possible, of which the aee arrangement with two methyl groups in equatorial positions and the remaining one in an axial location is preferred\textsuperscript{21–23}. Formation of an $\eta^3$ complex is associated with rearrangement of all three methyl groups to equatorial sites, thereby facilitating maximal lone pair interactions with a metal ion acceptor.

2. Tin

Cyanamides are pseudo-halide nitrogen ligands that are readily coordinated to metals. A novel compound is 2-cyanaminofluoren-9-one (HL\textsuperscript{4})\textsuperscript{24}. Its thallium salt Tl\textsuperscript{+}(L\textsuperscript{4})\textsuperscript{−} (Scheme 7) is useful as a transmetallating agent in a reaction with trimethyltin chloride to produce the corresponding tin cyanamide complex [SnMe\textsubscript{3}L\textsuperscript{4}] (Scheme 8).

$\text{M}^+ + \text{M}^+ = \text{Tl}^+(L^4)^-$

SCHEME 7. Tl\textsuperscript{+}(L\textsuperscript{4})\textsuperscript{−}. Reproduced by permission of the Royal Society of Chemistry from Reference 24

\[ \text{Cl} \rightarrow \text{SnMe}_3 \]

\[ \text{Tl}^+(L^4)^- \rightarrow \text{CH}_2\text{Cl}_2, \text{r.t.}, \text{overnight} \]

SCHEME 8. [SnMe\textsubscript{3}L\textsuperscript{4}]. Reproduced by permission of the Royal Society of Chemistry from Reference 24

The synthesis of [PtCl(SnMe\textsubscript{2}Cl)(dmphen)(E-MeO\textsubscript{2}CCH=CHCO\textsubscript{2}Me)] (dmphen = 2,9-Me\textsubscript{2}-1,10-phenanthroline) is given in equation 4. In this reaction a platinum(0) nucleophile [Pt(N,N\textsuperscript{0}-chelat)(olefin)] and an organometal electrophile R\textsubscript{m}SnX\textsubscript{n} (X = Cl, Br, I; R = hydroxycarbonyl group) are involved\textsuperscript{25}. It has been found that the adduct is stabilized by the presence of electron-donor olefins on the platinum and by electron-withdrawing groups on the electrophilic metal. It has also been found that the influence of the halide moving onto the platinum can be rationalized in terms of the relative softness of the two metals involved in the equilibrium. Figure 12 shows the structure of [PtCl(SnMe\textsubscript{2}Cl)(dmphen)(E-MeO\textsubscript{2}CCH=CHCO\textsubscript{2}Me)]. The coordination geometry is the expected one, i.e. the anionic ligands Cl and SnMe\textsubscript{2}Cl define the axial sites of the trigonal bipyramid [Cl–Pt–Sn angle 177.5(2)°], while the phenanthroline and the fumarate double
bond occupy the equatorial coordination sites. The phenanthroline plane is not coincident with the coordination plane [Pt, N(1), N(2)], and it is tilted by 13° towards the chloride ligand in order to optimize the contacts of the methyl groups with the axial ligands. The molecule is chiral because of the prochiral nature of the fumarate ligand and is asymmetric because the conformations of the CO₂Me and SnMe₂Cl groups do not conform to any regularity.

\[
\text{[Pt(dmphen)(E-MeO₂CCH=CHCO₂Me)] + Me₂SnCl₂} \rightleftharpoons \text{[PtCl(SnMe₂Cl)(dmphen)(E-MeO₂CCH=CHCO₂Me)]}
\]

The use of a polynuclear dimethylamido compound \([\text{[Sn(NMes)₂][Sn(μ-NMes₂)]₂}]\) as a reagent in reactions with \([\text{RNHLi}]\) allows the formation of imido Sn(II) anions. One example of this reaction type is the deprotonation reaction of primary amido and phosphido lithium complexes ([REHLi]; E = N, P) with the cubane \([\text{SnNBu-₄}])₄\), which give heterometalllic complexes containing Sn(II) imido and phosphinidene anions, e.g. \([\text{[Sn(μ-PCy)]₂[μ-PCy]}]_{\text{2}}\) (Li•THF)₄ containing a metallacyclic \([\text{[Sn(μ-PCy)]₂[μ-PCy]}]_{\text{4}}\) moiety. The reaction shown in Scheme 9 of the polynuclear dimethylamido Sn(II) reagent \([\text{[Sn(NMes)₂][Sn(μ-NMes₂)]₂}]\) with \([\text{LiN(H)ma]}\text{[ma = 2-MeOC₆H₄]}\) in a 1 : 2 ratio follows an unexpected pathway in which elimination of \([\text{Sn(NMes₂)]_2}\), rather than facial deprotonation, gives rise to the novel heterobimetallic ladder complex \([\text{[MesHNSn(μ-Nma)]_2(Li•THF)₄]}\) (the molecular structure is shown in Figure 13), containing the first example of a dinuclear Sn(II) imido dianion, \([\text{(MesNH)Sn(μ-Nma)]_2}^{2-}\).
3[Sn(NMe₂)₂] + 2[RNH₂] → 2[LiN(H)ma]/thf − [Sn(NMe₂)₂]

R = Mes, R’ = 2-MeOC₆H₄


FIGURE 13. Molecular structure of [[MesNHSn(µ-Nma)]₂(Li•THF)₄]. H atoms, except those attached to N which have been omitted for clarity. Copyright 1998 American Chemical Society
Covalent fitting of Lewis acidic centres such as tin in suitable organic molecular structures results in multidentate Lewis acidic host molecules, which were shown to be efficient in coordinating anions and neutral Lewis bases.\(^{27-40}\) The guest selectivity and stability of the host–guest complexes of these compounds strongly depend on the preorganization of the host molecule, i.e. the more rigid the host, the better the selectivity to be expected. Electrochemical studies show the potential ability of organotin(IV) halides to act as carriers in phosphate-selective electrodes\(^{41-44}\). Because of their potential use in electrochemical sensing, interest in the synthesis of redox-active host molecules with Lewis acidic centres is high\(^{45}\).

For this reason, tin containing ferrocenophanes are being investigated by Jurkschat and coworkers\(^{45}\). Their synthesis is given in Scheme 10\(^{45}\) and the structures of two of them are given in Figures 14 and 15.

Tin(IV) complexes are models for chemical investigations about biologically relevant ions in oxidation state four like vanadium, molybdenum and manganese. Examples are in Figure 16 and X-ray structure of one of them is given in Figure 17. Useful ligands are all diacidic tridentate chelate compounds. Tin(IV) chelates have a good solvolytic and redox stability, so it is easy to investigate their structural behaviour. The metal chelate compounds are made via a ligand exchange reaction with bis(acetylacetonato)dichlorotin(IV) as well as via the reaction between the ligands and tin(II) chloride. In this case air oxygen oxidizes tin(II) and the tin(IV) chelate compounds are formed\(^{48}\).

Compounds of the type [SnR\(_2\)X\(_2\)(L-L)], where L-L is a bidentate N,N'-donor ligand, have been extensively studied with regard to antitumour activity\(^{49}\). The mechanism of this activity is still under discussion. However, studies of the structure–activity relationship show that the Sn–N distance is important, the average Sn–N bond length being \(>2.39\) Å among the active complexes and \(<2.39\) Å among the inactive complexes. Sn–N distances which suggest possible antitumour activity are present in the eight-membered CS\(_2\)C\(_2\)N\(_2\)Sn rings of [SnEt\(_2\)Br\(_2\)(bmimt)] (Figure 18) and [SnBu\(_2\)Cl\(_2\)(bmimt)] (Figure 19), with bmimt = bis(1-methyl-2-imidazolylthio)methane (Figure 20\(^{50}\)).

Hydrolysis reactions of organotin(IV) halides have been established as viable sources of oligomeric tin clusters\(^{51}\). Given that tin–oxygen oligomers of predetermined size may have use in industrial applications\(^{52}\), the rational synthesis of such species remains an important synthetic target. Intramolecular donors may allow specific control over the geometry of tin sites from which additional linkages can form during hydrolysis. For this reason the polyfunctional ligand system L\(^5\)H, bis(2-methoxy-3-t-butyl-5-methylphenyl)methane and tin complexes with this ligand were synthesized (equations 5–8, Figures 21–24\(^{53}\)).

\[
\begin{align*}
L^5H + n-\text{BuLi} & \xrightarrow{\text{THF/–20°C}} L^5\text{Li} \xrightarrow{\text{THF/Ph}_3\text{SnCl}} L^5-\text{SnPh}_3 \\
L^5\text{SnPh}_3 + 2\text{HgCl}_2 & \xrightarrow{\text{acetone/0°C}} \text{PhCl}_2\text{SnL}^5 + 2\text{PhHgCl} \\
L^5\text{SnPh}_3 + 2\text{X}_2 & \xrightarrow{\text{CH}_2\text{Cl}_2 \text{or MeOH/25 or 0°C}} \text{PhX}_2\text{SnL}^5 + 2\text{PhX} \\
\text{X} = \text{Br, I} \\
\text{PhBr}_2\text{SnL}^5 & \xrightarrow{2\text{PhNa/MeOH}} \text{Ph(SPh)}_2\text{SnL}^5 + 2\text{NaBr}
\end{align*}
\]
SCHEME 10. Synthesis of different tin containing ferrocenophanes. Reprinted with permission from Reference 45. Copyright 2000 American Chemical Society.
The preparation of materials with high chemical reactivity, especially $\eta^6$-arene lability, is an interesting field of research. The lability of the arene ring facilitates its displacement by other ligands, which could be an initiative step in some catalytic reactions. For this reason, the synthesis of additional stannyl complexes like ($\eta^6$-arene)Cr(CO)$_2$(HSnR$_3$) and ($\eta^6$-arene)Cr(CO)$_2$(SnR$_3$)$_2$ were investigated\textsuperscript{54}. Figures 25 and 26 show the molecular structures of two stannyl complexes, where the arene is 1,4-C$_6$H$_4$(OCH$_3$)$_2$ and R = Ph. Both compounds are prepared in a reaction between ($\eta^6$-1,4-C$_6$H$_4$(OCH$_3$)$_2$Cr(CO)$_3$) and HSnPh$_3$ in a hexane/toluene mixture. The separation of the two products was done on a silica gel column with hexane/toluene as the eluting solvent. The bis-stannyl compound was eluted first.

The chemotherapeutic properties, especially the antitumour activities, of diorganotin compounds continue to be the focus of many reports\textsuperscript{55,56}. An interesting compound is

FIGURE 14. Molecular structure of [fc(SiMe$_2$CH$_2$SnPhICH$_2$SiMe$_2$)$_2$fc]. Reprinted with permission from Reference 45. Copyright 2000 American Chemical Society
[Ph2Sn(2-OC10H6CH=NCH2COO)]SnPh2Cl257, which is prepared in a reaction between diphenyltin dichloride and Ph2Sn(2-OC10H6CH=NCH2COO) in refluxing benzene. The crystal structure of the product shows a monomeric 1:1 donor–acceptor dinuclear tin complex. Each of the two tin atoms, Sn(1) and Sn(2), has a five-coordination geometry in a distorted trigonal bipyramidal arrangement (Figure 27).

Complexes that exhibit terminal multiple bonds to the heavier chalcogens are subjects of considerable attention. Terminal chalcogenido complexes (η4-Me8taa)SnE (E = S, Se; Me8taa = octamethylidibenzotetraaza[14]annulene dianion) react with MeI to give the corresponding methylchalcogenolate derivatives, [(η4-Me8taa)Sn(EMe)]58. The molecular structure of the methylseleno derivative is shown in Figure 28.

An interesting part of chemistry comprises the divalent complexes of the Group 14 elements, germanium, tin and lead, supported by tetradentate nitrogen and oxygen donor ligands. The [SalenR,R'] ligand system, obtained by condensation of a salicylaldehyde
FIGURE 16. Some tin(IV) chelate complexes, which are used as models for biologically relevant ions. Reproduced by permission of Verlag der Zeitschrift für Naturforschung from Reference 46
FIGURE 17. Molecular structure of bis[4-(2'-hydroxyphenylazo)-3-methyl-1-phenylpyrazol-5-onato(2-)]tin(IV). Reproduced by permission of Verlag der Zeitschrift für Naturforschung from Reference 46

FIGURE 18. Molecular structure of [SnEt₂Br₂(bmimt)]. Reproduced by permission of John Wiley & Sons, Inc. from Reference 50
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**FIGURE 19.** Molecular structure of [SnBu₂Cl₂(bmimt)]. Reproduced by permission of John Wiley & Sons, Inc. from Reference 50

**FIGURE 20.** bmimt = bis(1-methyl-2-imidazolylthio)methane. Reproduced by permission of John Wiley & Sons, Inc. from Reference 50

**FIGURE 21.** Tin complexes with the L₅H ligand. Reprinted with permission from Reference 53. Copyright 1997 American Chemical Society
derivative with 1,2-ethylenediamine, has proved to be very useful in coordination chemistry. The divalent tin complex, \([\text{Salen}^{+}\text{Bu},\text{Me}]\)Sn is readily prepared by the reaction of \([(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}\) with \([\text{Salen}^{+}\text{Bu},\text{Me}]\)H\(_2\) (Scheme 11). It could also be prepared by the reaction of SnCl\(_2\) with \([\text{Salen}^{+}\text{Bu},\text{Me}]\)H\(_2\) in the presence of Et\(_3\)N\(^{60}\). A notable feature of the structures of \([\text{Salen}^{+}\text{Bu},\text{Me}]\)Sn is that the \([\text{Salen}^{+}\text{Bu},\text{Me}]\) ligand is not flat.
but adopts a slightly twisted conformation, such that the four coordinating atoms of the [N₂O₂] core are not coplanar but deviate significantly from their mean plane (Figure 29).

Tin(II) compounds are known to have both acid and base properties; the metal centre can either react with electrophiles or act as a Lewis acid and thus be susceptible to
FIGURE 26. Molecular structure of $(\eta^6$-1,4-C$_6$H$_4$(OCH$_3$)$_2$Cr(CO)$_2$)(SnPh$_3$). Reproduced by permission of Elsevier Science from Reference 54.

FIGURE 27. Molecular structure of [Ph$_2$Sn(2-OC$_{10}$H$_6$CH=NCH$_2$COO)]SnPh$_2$Cl$_2$. Reproduced by permission of Elsevier Science from Reference 57.
nucleophilic attack. It has been shown that nucleophilic addition of organolithium reagents to organotin(II) compounds formed triorganostannate compounds. Alkylation using 1 equivalent of $[\text{LiR}^N(\text{TMEDA})]$ with $\text{SnCl}_2$ afforded the binuclear chlorotin(II) alkyl $[\text{R}^N\text{SnCl}]_2$ in 75% yield. In similar reactions using 3 equivalents of $[\text{LiR}^N(\text{TMEDA})]$ $[\{\text{SnR}^3_3\text{Li}(\mu^3-\text{Cl})\text{[Li(TMEDA)]}_2}(\mu^2-\text{Cl})\}]$ (for structure, see Figure 30) and with 3.5 equivalents of $[\text{LiR}^N(\text{TMEDA})]$, $[\{\text{SnR}^3_3\text{Li}(\mu^3-\text{Cl})\text{Li(TMEDA)]}_2}$ (for structure, see Figure 31) are formed$^{61}$ $[\text{R}^N = \text{CH}(\text{Si}(\text{t}-\text{Bu})\text{Me}_2)\text{C}_5\text{H}_4\text{N}-2, \text{TMEDA} = N,N,N',N'-\text{tetramethylethylene diamine}].$ $[\{\text{SnR}^3_3\text{Li}(\mu^3-\text{Cl})\text{[Li(TMEDA)]}_2}(\mu^2-\text{Cl})\}]$ is a binuclear molecule with $(\text{RN})_2$ acting as a bidentate C,N-bridging mode between two tin(II) atoms forming an eight-membered ring in a ‘boat’ conformation.

Triphenyltin chloride forms a dimeric hydrated complex with 1,10-phenanthroline in which the coordinated water molecule is linked by hydrogen bonds (O–O–N = 2.96 and 3.02 Å) to two 1,10-phenanthroline bases$^{62}$. Addition of four methyl substituents to the 1,10-phenanthroline ligand increases the basicity of its N atoms, enhancing the propensity for hydrogen bonding with water of aquachlorotriphenyltin molecules. In the complex shown in Figure 32 (1 : 1 adduct of aquachlorotriphenyltin with $3,4,7,8$-tetramethyl-1,10-phenanthroline$^{63}$) the ligand forms much shorter hydrogen bonds (2.661 and 2.767 Å) with aquachlorotriphenyltin than does 1,10-phenanthroline. In the adduct, $[\text{SnCl}(\text{C}_6\text{H}_5)_3(\text{H}_2\text{O})]\text{C}_{16}\text{H}_{16}\text{N}_2$, the aquaorganotin moiety is linked by hydrogen bonds through its axial bonded water molecule to the substituted 1,10-phenanthroline moiety. The Sn atom has trans-trigonal bipyramidal coordination, with aqua and chloro ligands in the axial positions.

The formation of $\text{SnR}_2[(\text{OPPh}_2)(\text{SPh}_2)\text{N}]_2$, with $R = \text{Me, Ph}$, is done by metathesis reactions between $\text{SnR}_2\text{Cl}_2$ and $\text{K[(OPPh}_2)(\text{SPh}_2)\text{N]}$ in toluene$^{64}$. The molecular structures of both compounds are shown in Figures 33 and 34. The central tin atom occupies a centre of inversion. The $\text{SnC}_2$ unit is linear (C–Sn–C 180°). The two asymmetric ligand moieties are monometallic biconnective, thus resulting in a distorted-octahedral
SCHEME 11. Synthesis route for [Salen$^{t-Bu, Me}$]Sn. Reproduced by permission of the Royal Society of Chemistry from Reference 59
7. Recent advances in acidity, complexing, basicity and H-bonding

FIGURE 29. Two views of the molecular structure of [Salen$^{+}$Bu,Me]Sn. Reproduced by permission of the Royal Society of Chemistry from Reference 59

FIGURE 30. Molecular structure of [(SnR$_3^+$)Li](μ$_3^-$Cl)[Li(TMEDA)$_2$](μ$_2^-$Cl)]. Reprinted with permission from Reference 61. Copyright 1999 American Chemical Society
FIGURE 31. Molecular structure of $\left[\left(\text{SnR}_3\right)\text{Li}\right]\left(\mu^3-\text{Cl}\right)\text{Li(TMEDA)}\right)_2$. Reprinted with permission from Reference 61. Copyright 1999 American Chemical Society
FIGURE 32. Molecular structure of [SnCl(C₆H₅)₃(H₂O)]•C₁₆H₁₆N₂. Reproduced by permission of the International Union of Crystallography, Nunskgaard International Publishers from Reference 63

FIGURE 33. Molecular structure of SnMe₂[(OPPh₂)(SPPh₂)N]₂. Reproduced by permission of the Royal Society of Chemistry from Reference 64
coordination around tin, with the carbon atoms of the organic groups in axial positions. The equatorial SnO$_2$S$_2$ system is planar, with the *trans* positions occupied by pairs of the same donor chalcogen atoms (O-Sn-O and S-Sn-S angles 180°). The bidentate nature of the monothio ligand units leads to an inorganic bicyclic system, NP$_2$SOSnOSP$_2$N, with the metal as spiro atom. Although some delocalization of the $\pi$ electrons over the OPNPS systems is suggested by the magnitude of the bonds, the SnOSP$_2$N rings are not planar but exhibit a twisted-boat conformation (Figure 35).

**FIGURE 34.** Molecular structure of SnPh$_2$[(OPPh$_2$)(SPPh$_2$)N]$_2$. Reproduced by permission of the Royal Society of Chemistry from Reference 64

**FIGURE 35.** Conformation of the inorganic SnOSP$_2$N chelate rings in SnMe$_2$[(OPPh$_2$)(SPPh$_2$)N]$_2$ (only *ipso*-carbon atoms of the phenyl groups are shown for clarity). Reproduced by permission of the Royal Society of Chemistry from Reference 64
Fluorine-doped tin oxide thin films deposited by chemical vapour deposition (CVD) techniques are used as transparent conductors in various applications. For this reason, the goal of this research field is to synthesize thin-film precursors that have the potential to deposit tin oxide or fluorine-doped tin oxide. The ligand hexafluoroisopropoxide, ORf with Rf = CH(CF3)2, is used because alkoxide complexes are known to be viable oxide film precursors and metal hexafluoroisopropoxide complexes are reported to decompose to metal fluorides under certain conditions. Sn(ORf)2 and the amine adducts Sn(ORf)L, L = HNMe2 or pyridine, are prepared in high yield from bis(amido)tin(II) compounds (Scheme 12). Sn(ORf)2 is proposed to be a dimer with bridged alkoxide ligands (Figure 36). The crystal structure of Sn(ORf)2(HNMe2) (Figure 37) shows it to have a trigonal pyramidal geometry. The compounds are volatile solids, an important attribute if they are used as conventional CVD tin oxide precursors.

A useful ligand in tin chemistry is thiophene-2-carboxaldehyde thiosemicarbazone, 2-C4H3S-CH=N-NH-C(S)NH2 (tctscH). It is formed during a reaction of thiophene-2-carboxaldehyde with thiosemicarbazide. The complex SnPh2Cl(tctsc) is obtained in a reaction of SnPh2Cl2 and this ligand in a ratio 1 : 1 and the compound SnCl2(tctsc)2 is the product of SnPhCl3 and the ligand in a ratio 1 : 2. In both complexes, the tctsc ligand functions as a bidentate anion, coordinates to the central Sn atom through the thiol-S

![FIGURE 36. Proposed structure of ‘Sn(ORf)2’. Reprinted with permission from Reference 74. Copyright 1996 American Chemical Society](image-url)
atom and the azomethine-N atom, yielding a five-membered chelate ring after the enolization and deprotonation of the thiol proton. The occurrence of the enolization process is supported by the shortening of the C(1)–N(2) bond (increase in bond order). During the formation of these complexes, a conformational change of the ligand from trans to cis configuration [refer to S(1) and N(3) atoms] occurs so as to enable it to coordinate in a bidentate manner\(^\text{76,77}\). SnPh\(_2\)Cl(tctsc) (Figure 38) exists in a distorted trigonal bipyramidal geometry about the tin atom, where the Cl and azomethine-N atoms, which are most electronegative, occupy the axial position. In the formation of the complex SnCl\(_2\)(tctsc)\(_2\) (Figure 39), dephenylation has taken place, where the phenyl group is released from the coordination to the tin atom, so that an idealized geometry in the product is achieved. Complex SnCl\(_2\)(tctsc)\(_2\) exists in a distorted octahedral geometry.

2-Alkoxycarbonylpropyltin trichlorides, ROCOCH(CH\(_3\))CH\(_2\)SnCl\(_3\), have attracted considerable attention\(^\text{78}\) ever since their syntheses were first reported because of the variety of coordination geometries about the tin atom and also due to their applicability as PVC stabilizers with low mammalian toxicities\(^\text{79–86}\). The ROCOCH(CH\(_3\))CH\(_2\) moiety acts as a C, O chelating ligand in the solid state and non-coordinating solvents\(^\text{80,81}\), but the intramolecular coordination by the carbonyl oxygen of the ester group can be broken by additional donor molecules\(^\text{81–84}\). In this research field some complexes of ROCOCH(CH\(_3\))CH\(_2\)SnCl\(_3\) with hexamethylphosphoramide (HMPA) and \(N\)-(2-hydroxyphenyl)-2-hydroxy-1-naphthylaldimine (H\(_2\)L\(_5\)) were prepared (equations 9–12). The structures of the complexes are displayed in Figure 40, and the X-ray diffraction of 1a is shown in Figure 41. These complexes are air-stable and soluble in benzene and common polar organic solvents, such as methanol, chloroform, acetone and nitrobenzene, but insoluble in saturated hydrocarbons such as hexane and petroleum ether.

\[
\text{ROCOCH(CH}_3\text{)CH}_2\text{SnCl}_3 + \text{HMPA} \rightarrow \text{ROCOCH(CH}_3\text{)CH}_2\text{SnCl}_3 \cdot \text{HMPA} \quad (9)
\]

(1a)–(1c)
7. Recent advances in acidity, complexing, basicity and H-bonding

FIGURE 38. Molecular structure of SnPh₂Cl(tctsc). Reproduced by permission of Elsevier Science from Reference 75

FIGURE 39. Molecular structure of SnCl₂(tctsc)₂. Reproduced by permission of Elsevier Science from Reference 75
Organotin complexes show a spectrum of biological effects\textsuperscript{87}. Their chemotherapeutic properties, including antitumor activity, have been extensively investigated. The chelation between the organotin(IV) and a Schiff-based ligand enhances the $\alpha$-CH acidity of the amino acid fragment in such complexes. The carbanions formed from the organotin(IV) complexes e.g., $5$–\textsuperscript{7} (Scheme 13) are stabilized by resonance. Since the $pK_a$ value of complex $5$ in DMSO is $17.43$\textsuperscript{88}, its $\alpha$-CH acidity is greater than that of fluorene ($pK_a = 22.6$)\textsuperscript{89} and the Ni\textsuperscript{2+} chelate with the Schiff base derived from glycine ($pK_a = 18.8$)\textsuperscript{90}, and it approaches that of mononitro compounds $\textit{RNO}_2$, $\textit{R} = \text{Me, Et}$ ($pK_a = 17$)\textsuperscript{89}. Because of the relatively high thermodynamic acidity and great kinetic stability, the carbanions formed from complexes $5$–\textsuperscript{7} are able to condense, not only under strongly basic conditions, such as the use of 1.5 N MeONa giving $8$–\textsuperscript{15} (Scheme 13), but also in the presence of the weak base $\text{Et}_3\text{N}$ (Scheme 14).
Hetero-atom-substituted stannylenes, which are electron-deficient compounds, are known in a larger number. This deficiency is compared with the interaction between the 5pπ orbital of the tin atom and the free electron pairs at the hetero atom. In contrast, alkyl- and aryl-substituted compounds are not very well investigated. The first-mentioned donor-free diarylstannylene is bis[(2,4,6-tris(tert-buty1)phenyl)tin]. In solution, this compound isomerized to a less bulky alkylarylstannylene (Scheme 15).
SCHEME 14. Reproduced by permission of John Wiley & Sons, Inc. from Reference 88

SCHEME 15. Reproduced by permission of Wiley-VCH from Reference 98

SCHEME 16. Reproduced by permission of Wiley-VCH from Reference 98

The rearrangement could be corroborated via addition and cycloaddition reactions and also by the synthesis of the [(OC)\textsubscript{5}W=SnRR’] complex\textsuperscript{97}. The analogous chromium complex is formed via a reaction of chromium hexacarbonyl in THF (Scheme 16)\textsuperscript{98}. The molecular structure is shown in Figure 42. The molybdenum complex is formed in the same way (Scheme 16, Figure 43)\textsuperscript{98}.

3. Lead

Among toxic metals, lead is one of the principal poisoning metals, the environmental occurrence of which is mainly due to inorganic industrial derivatives and organic compounds from antiknock agents in petroleum\textsuperscript{1,10}. Macrocyclic ligands can be used as effective sequestering agents for this toxic metal\textsuperscript{99}. Phenanthroline is a useful ligand for this purpose (Figure 44). It is rigid, and provides two aromatic nitrogens whose unshared electron pairs are beautifully placed to act cooperatively in binding cations\textsuperscript{100}. An interesting compound is the [(PbL\textsubscript{7}Br)\textsubscript{2}(\mu-Br)][PbL\textsubscript{7}Br\textsubscript{2}]Br\textsubscript{5}H\textsubscript{2}O complex (Figure 45)\textsuperscript{101}. It crystallizes in a triclinic crystal structure. The asymmetric unit contains two independent complexes, (a) [(PbL\textsubscript{7}Br)\textsubscript{2}(\mu-Br)]\textsuperscript{+} and (b) [PbL\textsubscript{7}Br\textsubscript{2}], a bromine as a counter ion and five water solvent molecules. Complex (a) consists of two PbL\textsubscript{7} units bridged by one bromine anion. The overall conformations of L\textsubscript{7} and coordination geometry for the metal atoms are very similar in the two PbL\textsubscript{7} units. Atom Pb(1) is coordinated by the five nitrogens N(1)–N(5) and two bromide anions, one of them weakly interacting. The resulting arrangement for the seven donor atoms around the lead ion is rather asymmetric.
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FIGURE 42. Molecular structure of [(OC)$_5$Cr=SnRR']. Reproduced by permission of Wiley-VCH from Reference 98

FIGURE 43. Molecular structure of [(OC)$_5$Mo=SnRR']. Reproduced by permission of Wiley-VCH from Reference 98
FIGURE 44. Ligands with a phenanthroline moiety. Reproduced by permission of the Royal Society of Chemistry from Reference 101

FIGURE 45. Molecular structures of (a) \([\text{PbL}^7\text{Br}_2(\mu-\text{Br})]^+\) and of (b) \([\text{PbL}^7\text{Br}_2]\). Labels of the carbon atoms are omitted for clarity. Reproduced by permission of the Royal Society of Chemistry from Reference 101
In the case of complex (b), \([\text{PbL}_7\text{Br}_2]\), the coordination geometry of the metal and the conformation of the macrocycle are almost equal to that found in complex (a).

Another interesting compound in this area is \([\text{PbL}_8][\text{ClO}_4][\text{BPh}_4]\) (Figure 46). It consists of the \([\text{PbL}_8]^{2+}\) cation and the two anions \([\text{ClO}_4]^-\) and \([\text{BPh}_4]^-\). The metal atom is seven-coordinated by the nitrogen atoms of the macrocycle. The resulting arrangement for the seven donor atoms around the lead ion is rather asymmetric, leaving a zone free from coordinated donor atoms, which is occupied by the lone pair of Pb\(^{2+}\).

The 1 : 1 adducts of different lead(II) (pseudo-)halides with 1,10-phenanthroline (phen), (phen)\(\text{PbX}_2\) (\(X = \text{Cl}, \text{Br}, \text{I}\)) and 2,2'-bipyridine (bpy), (bpy)\(\text{PbX}_2\) (\(X = \text{Cl}, \text{I}, \text{SCN}\)), take the form of a one-dimensional polymer disposed along the \(c\) axis of the assigned cell. In the halides, the lead atom is six-coordinate, the \(\text{N},\text{N}'\)-bidentate ligand being necessarily \(\text{cis}\) in the coordination sphere and the polymer being generated by a succession of \(\text{Pb}(\mu-X)_2\text{Pb}\) rhombus. In the thiocyanate, the environment, although derivative, is more complex by virtue of more elaborate bridging behaviour of the thiocyanate group\(^{102}\). The structure of (bpy)\(\text{PbI}_2\) is shown in Figures 47 and 48.

3,6-diformylpyridazine (Figure 49) is a building block for different macrocycles\(^{103}\). Interest in these macrocycles and their metal complexes is based on their potential relevance as structural models for metalloproteins\(^{104}\) and, in particular, on the ability of pyrazine to mediate magnetic exchange\(^{105–122}\), a property reminiscent of analogous phenol-bridged complexes\(^{123–125}\). When lead(II) ions are used as templates, two different macrocycle sizes can be isolated depending on the reaction conditions employed. Specifically, a 1 : 1 : 1 ratio of 3,6-diformylpyridazine:1,3-diaminopropane:lead(II) perchlorate resulted in the formation of \(\text{Pb}_2\text{L}^9(\text{ClO}_4)_4\) (for the structure of ligand \(\text{L}^9\), see Figure 50) whereas a 2 : 2 : 1 ratio gave \([\text{Pb}_2\text{L}^{10}]^4[\text{ClO}_4]_4\) (for the structure of ligand \(\text{L}^{10}\), see Figure 51). The \([\text{Pb}_2\text{L}^{10}]^{4+}\) cation is shown in Figure 52. The ability of the same metal to template two different macrocycle ring sizes efficiently, in this case lead(II) perchlorate and \(\text{L}^9\) vs. \(\text{L}^{10}\) macrocycles, simply by employing different reagent ratios, is first mentioned by Brooker and coworkers\(^{103}\). In previous studies, a given metal salt templated the formation of only one specific macrocycle ring size, so that to obtain a macrocycle of different size quite different reaction conditions had to be employed, for example a different template ion or a different anion.

Some other Lewis base adducts of lead(II) compounds are the 2 : 1 adducts of the \(\text{N},\text{N}'\)-bidentate aromatic base 1,10-phenanthroline (phen) with lead(II) nitrate and perchlorate\(^{126}\).
FIGURE 47. Unit cell projection of the (bpy)PbI$_2$ complex projected down monoclinic axis b. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 102.
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FIGURE 48. A strand of the (bpy)PbI₂ polymer projected normal to the plane containing the 2 axis and the polymer axis (i.e. down a*). Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 102

FIGURE 49. 3,6-diformylpyridazine. Reproduced by permission of the Royal Society of Chemistry from Reference 103

FIGURE 50. Structure of ligand L⁹. Reproduced by permission of the Royal Society of Chemistry from Reference 103
FIGURE 51. Structure of ligand L\textsuperscript{10}. Reproduced by permission of the Royal Society of Chemistry from Reference 103.

FIGURE 52. Perspective view of the cation of the complex [Pb\textsubscript{2}L\textsuperscript{10}][ClO\textsubscript{4}\textsubscript{4}]\textsuperscript{4}. Reproduced by permission of the Royal Society of Chemistry from Reference 103.
[(phen)$_2$Pb(NO$_3$)$_2$] is monoclinic whereas [(phen)$_2$Pb(ClO$_4$)$_2$] is triclinic. Both systems are mononuclear with eight-coordinate PbN$_4$O$_4$ coordination environments incorporating a pair of $O,O'$-bidentate anions. The complexes are essentially of the type ML$_2$L$_0$ where L, here phen, and L', here the oxoanion, both act as bidentate ligands. In projection normal to the quasi-2 axis (Figures 53 and 54) the two pairs of ligand type display the feature of being compressed towards each other from either pole, more so at the oxoanion end, so that if sterically active lone pairs are to be postulated, they are most likely to be found between the oxoanions and directed along the quasi-2 axis.

If 2,2'-bipyridine (bpy) is used instead of phen, the situation is different$^{127}$, [(bpy)$_2$Pb(NO$_3$)$_2$] (Figures 55 and 56) is triclinic and [(bpy)$_2$Pb(ClO$_4$)$_2$] (Figures 57 and 58) is monoclinic. The bpy systems are centrosymmetric dimers; in each case the
FIGURE 55. Projection of the asymmetric unit of the \( \text{(bpy)}_2\text{Pb(NO}_3\text{)}_2 \) down the Pb–Pb vector. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 127.

FIGURE 56. Projection of the asymmetric unit of the \( \text{(bpy)}_2\text{Pb(NO}_3\text{)}_2 \) down the quasi-2 axis. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 127.
FIGURE 57. Projection of the asymmetric unit of the \((\text{bpy})_2\text{Pb(ClO}_4)_2\) down the Pb…Pb vector. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 127.

FIGURE 58. Projection of the asymmetric unit of the \((\text{bpy})_2\text{Pb(ClO}_4)_2\) down the quasi-2 axis. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 127.
coordination environment incorporates a pair of $N,N'$-bidentate aromatic bases and an $O,O'$-bidentate anion, but the other anion is not only $O,O'$-bidentate, but also bridges by a third oxygen atom the other lead atom so that it is nine-coordinate PbN$_4$O$_5$. In another synthesis a mixture of lead(II) perchlorate and lead(II) acetate (ac) in 1 : 1 stoichiometry were used in a reaction with an overall 1 : 2 lead(II) salt/2,2'-bipyridine ratio. The crystalline product shows a discrete mononuclear complex of [(bpy)$_2$Pb(ClO$_4$)(ac)] (Figures 59 and 60).

The complexes (tpy)Pb(oxoanion)$_2$, oxoanion = ClO$_4^-$, NO$_3^-$, NO$_2^-$, tpy = 2,2' : 6',2''-terpyridine, all have a monoclinic structure$^{128}$. One-half of the [(tpy)Pb(oxyanion)$_2$] (H$_2$O) formula unit comprises the asymmetric unit of the structure, the lead atom lying on a crystallographic 2-axis which also passes through the axis of the central ring of the tpy ligand, defining its polarity and relating the two halves of that ligand, and also relating the associated anionic components of the coordination sphere, one anion only being crystallographically independent. The lead environment comprises the N$_3$-tridentate ligand at one pole of the symmetry element, a pair of symmetry-related $O,O'$-chelating anions lying more or less equatorial, and a final pair or monodentate oxygen or nitrogen atoms bridging from anions associated with adjacent lead atoms about the other pole of the symmetry axis (Figures 61–63).

In this series of complexes of lead(II) nitrate and nitrogen containing ligands in a ratio 1 : 1, many different ligands are used. Some examples are the multidentate aliphatic
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FIGURE 60. A projection of (bpy)$_2$Pb(ac)(ClO$_4$) normal to the twofold axis. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 127

FIGURE 61. Projection of the (tpy)Pb(ClO$_4$)$_2$ complex: a strand of each polymer, normal to the plane of $b$ and the $ac$ cell diagonal. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 128
FIGURE 62. Projection of the (tpy)Pb(NO$_3$)$_2$ complex: a strand of each polymer, normal to the plane of $b$ and the $ac$ cell diagonal. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 128

FIGURE 63. Projection of the (tpy)Pb(NO$_2$)$_2$ complex: a strand of each polymer, normal to the plane of $b$ and the $ac$ cell diagonal. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 128

nitrogen bases of increasing denticity (the number of active coordination sites a ligand has) and chain length; ethane-1,2-diamine = ethylenediamine = en, 3-azapentane-1, 5-diamine = diethylenetriamine = ‘22’ = dien, 3,6-diazaoctane-1,8-diamine = 222tet = trien, 3,7-diaza-nonane-1,9-diamine = 232tet, 4,7-diazadecane-1,10-diamine = 323tet.$^{129}$ (en)Pb(NO$_3$)$_2$ (Figure 64) has an interesting structure. It is a double-stranded one-dimensional polymer, lying parallel to axis $a$, with the axis of the polymer disposed across the $bc$ cell diagonal; the lead atoms of the two strands are linked by Pb$_2$(O(12))$_2$
centrosymmetric, necessarily planar rhombus, separated by the $a$ translation. The lead environment is nine-coordinate PbN$_2$O$_7$, with four of the oxygen atoms being bridging, and the array essentially being comprised of three bidentate and one tridentate ligands. (dien)Pb(NO$_3$)$_2$ (Figure 65), the principal motifs in the array, which is polymeric, are the lead atom and the saturated triamine; each ligand is associated with one metal atom,
and adopts a quasi-facial coordination mode with the fused chelate rings in mirror image conformations. The structure of (232tet)Pb(NO$_3$)$_2$ is shown in Figure 66, and that of (323tet)Pb(NO$_3$)$_2$ in Figure 67.

Adducts of lead(II) bromide with ethane-1,2-diamine (en) and propane-1,2-diamine (pn) are of 2 : 1 and 1 : 1 stoichiometry, respectively$^{130}$. [(en)$_2$PbBr$_2$]$_{\infty}$ (Figure 68) is a
single-stranded linear polymer parallel to \( c \); the lead atom, lying on a crystallographic twofold axis, is six-coordinate \( \text{PbN}_4\text{Br}_2 \), with the bromine atoms \( \text{cis} \) in the coordination sphere and lying opposite to a bidentate en ligand. The \( \text{trans} \) sites are linked into a chain by bridging en ligands, \( [(\text{pn})\text{PbBr}_2]_{\infty}^{\infty} \) (Figure 69) is a more complex two-dimensional polymer; the pn is bidentate, but the lead atoms are now eight-coordinate with doubly and quadruply bridging bromines linking them into a polymeric sheet. The adduct with 323tet (4,7-diazadecane-1,10-diamine) is of a \([(323\text{tet})_2\text{PbBr}_6]_3^{\infty} \) stoichiometry, best represented as \([\text{Pb}(323\text{tet})][\text{PbBr}_6]\) (Figure 70). About one lead atom type, the ligand is quadridentate, lying on one face of the coordination sphere; the region opposite is occupied by four triply bridging bromine atoms from \([\text{PbBr}_6]^{-} \) anionic units (which contain quasi-octahedral, centrosymmetric lead, with a pair of \( \text{trans} \)-bromine atoms terminal and the others bridging) linking the array into a two-dimensional polymer.

Adducts of 1,4,8,11-tetraazacyclotetradecane (cyclam) with lead(II) perchlorate and \( (7\text{R}^*,14\text{R}^*)^{-}\)5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet-b) with lead(II) nitrate, perchlorate and acetate (ac) have the ratio 1 : 1 \(^{131} \). \([(\text{cyclam})\text{Pb(ClO}_4\text{)}]^{\infty} \) is orthorhombic (Figure 71), \([(\text{tet-b})\text{Pb(NO}_3\text{)}_2]^{\infty} \) and \([(\text{tet-b})\text{Pb(ClO}_4\text{)}_2]^{\infty} \) \( \cdot \) \( \text{H}_2\text{O} \) are monoclinic (Figures 72 and 73) and \([(\text{tet-b})\text{Pb(ac)}_2]^{\infty} \) \( \cdot \) \( \text{H}_2\text{O} \) is triclinic (Figure 74). In all complexes, the macrocycle-N\(_4\) ligand occupies one side of the coordination sphere of the lead atom, with anionic oxygens opposed; the cyclam/perchlorate complex is, like the nitrate, mononuclear with seven-coordinate \((\text{N}_4)\text{PbO}_3 \) with a bidentate \( \text{O},\text{O}' \) and a unidentate \( \text{O}-\text{perchlorate} \). In the tet-b acetate, the anionic oxygen atoms are surprisingly sparse, comprising simply a bidentate acetate, in a mononuclear \((\text{N}_4)\text{PbO}_2 \) environment with the other (lattice) acetate bonded to the macrocycle axial NH hydrogens. The nitrate and perchlorate complexes involve bridging anions: in the nitrate, a central centrosymmetric \( \text{PbO}_2\text{Pb} \) array is found, the lead atoms being bridged by one oxygen of a bidentate nitrate, the other nitrate being unidentate and the coordination sphere \((\text{N}_4)\text{PbO}_4 \); in the perchlorate, again a centrosymmetric dimer is found, the lead atoms being linked by
FIGURE 69. Projection of a sheet of the polymer of (pn)PbBr₂ down a. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 130

FIGURE 70. Unit cell contents of (323tet)₂(PbBr₂)₃ down a, showing the polymeric sheet; note also the quasi-anti-square-prismatic environment of ‘cationic’ Pb(2). Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 130
FIGURE 71. Projection of the ‘molecule’ of (cyclam)Pb(ClO₄)₂ normal to the N₄ plane, with ellipsoids showing the large vibrational amplitudes. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 131.

FIGURE 72. Projection of the [(tet-b)Pb(ac)]⁺ cation in the tet-b/acetate adduct normal to the N₄ plane. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 131.
FIGURE 73. Projection of (tet-b)Pb(ClO$_4$)$_2$ showing the lead environment, normal to the ligand plane. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 131

FIGURE 74. Projection of the (tet-b)Pb(NO$_3$)$_2$ dimer normal to the Pb(O(21))$_2$Pb plane. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 131
$O, O'$-bridging perchlorates [again with (N$_4$)PbO$_2$ coordination environment], the complex being essentially \[\text{[(tet-b)Pb(OClO}_2\text{O)}_2\text{Pb(tet-b)}(\text{ClO}_4)})_2\cdot2\text{H}_2\text{O}.\]

Some other 1:1 adducts with tet-b are known. For example, \[\text{[(tet-b)PbCl}_2]\] (Figure 75) and \[\text{[(tet-b)PbI}_2]\] (Figure 76) are monoclinic, \[\text{[(tet-b)Pb(NCS)}_2]\] (Figure 77) is orthorhombic$^{132}$. All are discrete mononuclear \[\text{[(tet-b)PbX}_2]\] entities in which the macrocyclic N$_4$ ligand occupies one ‘face’ of the N$_4$PbX$_2$ coordination sphere. The thiocyanate ligands being N-bonded, interesting hydrogen-bonding interactions are found, columns of molecules being formed by way of hydrogen bonding between the coordinated (pseudo-)halides and the NH hydrogen atoms which project to the ‘rear’ face of the ligand of the next molecule, opposite the metal. The bromine analogue complex is monoclinic and is best formulated as \[\text{[(tet-b)PbBr)}\text{Br}\] (Figure 78), only one of the bromine entities being

**FIGURE 75.** Molecule of \[\text{[(tet-b)PbCl}_2]\] normal to the macrocycle axis. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 132

**FIGURE 76.** Molecule of \[\text{[(tet-b)PbI}_2]\] normal to the macrocycle axis. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 132
bound to the lead, the other being fully dissociated by hydrogen bonding/ion pairing to the ‘rear’ side of adjacent ligands, forming hydrogen-bonded sheets rather than columns.

The bpy (2,2'-bipyridine) and phen (1,10-phenanthroline) ligands are useful compounds in lead(II) complex chemistry. [(bpy)\(\text{Pb(NO}_3\text{)}_2\)]\(\cdot\)\(\text{H}_2\text{O}\) (Figure 79) and [(phen)\(\text{Pb(NO}_3\text{)}_2\)]\(\cdot\)\(\text{H}_2\text{O}\) are monoclinic, [(phen)\(\text{Pb(ac)}_2\)]\(\cdot\)\(4\text{H}_2\text{O}\) is triclinic (Figure 80). The nitrates are one-dimensional polymers along \(b\), successive lead atoms being linked by one oxygen of one of the nitrate groups, each of the other oxygen atoms completing a chelate to either side; the lead environment is completed as \(\text{N}_2\text{PbO}_7\) by the other nitrate (as a chelate), the bidentate base and the water molecule. In the acetate which is a centrosymmetric dimer (manifested in two distinct independent dimers), the two lead atoms are linked by bridging oxygen atoms derived from pairs of chelating acetate moieties about each lead atom. The coordination sphere of each lead atom is completed by the bidentate aromatic base.
Another ligand is dpa (bis(2-pyridyl)amine). It also forms an adduct with lead(II) salts, for example [(dpa)PbBr₂]_{\infty} (Figure 81) and [(dpa)PbI₂]_{\infty} are both monoclinic\textsuperscript{134}. These two complexes are linear polymers with six-coordinate (cis-N\textsubscript{2})Pb(µ-X)₄ environments linked in infinite \(\cdots (\mu-\text{X})_{2}\text{Pb}(\mu-\text{X})_{2} \cdots\) one-dimensional chains, and with dpa being bidentate. A 2 : 1 adduct of dpa is [(dpa)₂Pb(ac)₂]_{\infty} (Figure 82), which is monoclinic\textsuperscript{134}. The complex is a linear polymer along \(c\); the lead atom lies on a crystallographic twofold axis with a coordination environment comprising a pair of symmetry-related dpa ligands, and a pair of symmetry-related bidentate acetate ligands with the first oxygen atom performing an additional bridging function to adjacent symmetry-related lead atoms.

2 : 1 adducts of 2-aminomethylpyridine (amp) with lead(II) nitrate and thiocyanate are [(amp)₂Pb(NO₃)₂]₂ (Figure 83) and [(amp)₂Pb(SCN)₂]₂ (Figure 84)\textsuperscript{135}. Both complexes are centrosymmetric dimers; the coordination environment is made up in each case of a pair of \(N, N'\)-bidentate bases, one terminally bound anion (\(O, O'\)-chelating nitrate or S-bonded thiocyanate) and bridging anions. In the case of the thiocyanates these bridge end-on, so that the lead(II) environment is seven-coordinate PbN₅S₂; in the nitrate, the anion chelates through two of its oxygen atoms, bridging via the third, so that the lead(II) environment is nine-coordinate PbN₄O₅.

The abbreviation trz denotes 2,4,6-tris(2-pyridyl)-1,3,5-triazine. In a reaction with lead(II) nitrate in 1 : 1 and 1 : 2 stoichiometry two complexes are formed, [(trz)Pb(NO₃)₂]_{\infty} (Figure 85) and [(trz)₂Pb(NO₃)₂] (Figure 86), respectively\textsuperscript{136}. [(trz)Pb(NO₃)₂]_{\infty} is an infinite polymer; the plane of the tridentate trz ligand lies normal to the polymer axis with unsymmetrically bidentate nitrate groups to either side. The third oxygen of each nitrate group bridges to the next lead atom in the polymer chain. [(trz)₂Pb(NO₃)₂] is a methanol monosolvate. The complex species is mononuclear, with the lead atom located on a crystallographic 2-\(\alpha\)-axis and 10-coordinated by pairs of symmetric-related tridentate trz and bidentate nitrate ligands. From this complex a hexahydrate compound is also known.

![Figure 79](image_url) View of a single strand of the polymer of [(bpy)Pb(NO₃)₂]_{\infty}·H₂O down \(a\). Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 133

[133] Another ligand is dpa (bis(2-pyridyl)amine). It also forms an adduct with lead(II) salts, for example [(dpa)PbBr₂]_{\infty} (Figure 81) and [(dpa)PbI₂]_{\infty} are both monoclinic\textsuperscript{134}. These two complexes are linear polymers with six-coordinate (cis-N\textsubscript{2})Pb(µ-X)₄ environments linked in infinite \(\cdots (\mu-\text{X})_{2}\text{Pb}(\mu-\text{X})_{2} \cdots\) one-dimensional chains, and with dpa being bidentate. A 2 : 1 adduct of dpa is [(dpa)₂Pb(ac)₂]_{\infty} (Figure 82), which is monoclinic\textsuperscript{134}. The complex is a linear polymer along \(c\); the lead atom lies on a crystallographic twofold axis with a coordination environment comprising a pair of symmetry-related dpa ligands, and a pair of symmetry-related bidentate acetate ligands with the first oxygen atom performing an additional bridging function to adjacent symmetry-related lead atoms.

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FIGURE 80. Unit cell contents of (phen)Pb(ac)$_2$$\cdot$2H$_2$O. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 133.
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FIGURE 81. The polymer strand of (dpa)PbBr$_2$, normal to its axis. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 134

FIGURE 82. The polymer (dpa)$_2$Pb(ac)$_2$ as shown in projection down $a^*$ (i.e. onto the $bc$ plane). Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 134
trz forms also 1 : 1 adducts with lead(II) chloride, bromide, iodide and thiocyanate, the chloride and bromide being methanol monosolvates\(^{137}\). \([\text{(trz)}\text{PbCl}_2]_{(\infty)}\cdot\text{MeOH}\) is monoclinic (Figure 87); the bromide is related (Figure 88), having a derivative triclinic cell. \([\text{(trz)}\text{PbI}_2]_{(\infty)}\) (Figure 89), also solvated, is triclinic. In all three compounds an infinite PbX\(_2\)PbX\(_2\)Pb polymer is found with the plane of tidentate trz lying quasi-normal to the polymer axis. The thiocyanate (monoclinic) (Figure 90) is a column of dimeric units stacked up \(b\), successive lead atoms being bridged by thiocyanate sulphur atoms packed in between them and quasi-parallel to \(a\), and by thiocyanates parallel to \(b\) which link pairs of lead atoms in each dimer with the same \(b\) coordinate by pairs of bridging nitrogens and bridging sulphurs from the adjacent pair.

One of the smallest and simple ligands is pyridine (py). In a reaction with lead(II) thiocyanate it forms a 1 : 1 adduct\(^{138}\) \([(\text{py})\text{Pb(SCN)}_2]_{(\infty)}\) is triclinic (Figure 91). The structure is a two-dimensional polymer in the \(bc\) plane with eight-coordination \((\text{py-N})\text{PbN}_3\) linked by the familiar four-membered Pb\(_2\)S\(_2\) and eight-membered Pb\(_2\)(SCN)\(_2\) motifs by way of bridging thiocyanate groups; one of the latter, unusually, has a bifurcating bridging nitrogen atom leading to the introduction of Pb\(_2\)N\(_2\) motifs.

The chemistry of tetraimino macrocyclic complexes is of considerable interest because of their applications for modeling bioinorganic systems, catalysis and analytical practice\(^{139}\). The lead(II) complex \([\text{Pb(L}\text{I}_{11})_2]\text{(BPh}_4\text{)}_2\cdot2\text{CH}_3\text{CN} \left(L_{11} = 3,10,17,24\text{-tetraaza-29,30-dioxapentacyclo[24.2.1.1^{12.15}0^{4.9}0^{18.23}]triaconta-1(28),2,4,6,8,10,12,14,16,18,20,22,24,26-tetradecaene, Figure 92; see Figures 93 and 94}\right)\) is prepared by a metathesis reaction of \([\text{Pb(L}\text{I}_{11})]\text{(ClO}_4\text{)}_2\cdot\text{H}_2\text{O}\) complex in methanol solution with
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FIGURE 84. The dimer of (amp)$_2$Pb(SCN)$_2$, projected normal to the Pb···Pb line. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 135

FIGURE 85. A polymer strand of (trz)Pb(NO$_3$)$_2$ is projected down the quasi-2-axis. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 136
FIGURE 86. A molecule of the methanol-solvated \((\text{trz})_2\text{Pb(NO}_3\text{)}_2\) adduct projected normal to the 2-axis. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 136.

FIGURE 87. Structure of \((\text{trz})\text{PbCl}_2\) projected normal to the ligand ‘plane’, showing the lead coordination environment. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 137.
FIGURE 88. Structure of \((\text{trz})\text{PbBr}_2\) projected normal to the ligand ‘plane’, showing the lead coordination environment. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 137.

FIGURE 89. Structure of \((\text{trz})\text{PbI}_2\) projected normal to the ligand ‘plane’, showing the lead coordination environment. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 137.
FIGURE 90. The (trz)Pb(SCN)$_2$ polymer projected normal to $b$. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 137

FIGURE 91. The unit cell of (py)Pb(SCN)$_2$ projected down $a$, normal to the polymer plane. Reproduced by permission of the Australian Academy of Science and CSIRO from Reference 138
7. Recent advances in acidity, complexing, basicity and H-bonding

FIGURE 92. Structure of $L^{11}$ = 3,10,17,24-tetraaza-29,30-dioxapentacyclo[24,2,1,1$^{12,15}$,0$^{4,9}$0$^{18,23}$]-triaconta-1(28),2,4,6,8,10,12,14,16,18,20,22,24,26-tetradecaene. Reproduced by permission of Elsevier Science from Reference 140

FIGURE 93. ORTEP drawings of the lead(II) complex [Pb($L^{11}$)$_2$](BPh$_4$)$_2$, showing the Pb atom and one of the two macrocycles. Reproduced by permission of Elsevier Science from Reference 140

NaBPh$_4$\textsuperscript{140}. This complex has a sandwich-type structure and the macrocycles show a folded conformation, in which two oxygen atoms lie on the opposite side of the ‘$N_4$’ plane from the lead atom (Figure 93). The perchlorate complex has a perchlorate anion as a ligand. If the perchlorate anions are replaced by non-coordinating tetraphenylborate anions, the coordination sphere of the Pb(II) ion becomes unsaturated; thus the Pb$^{2+}$ ion may prefer to coordinate two macrocyclic molecules.
The interest in mixed-metal complexes may be attributed to increased recognition of the importance of polynuclear centres in biological catalytic processes and the potential application of expected metal–metal interactions to synthetic systems possessing useful magnetic and electrochemical properties\textsuperscript{141,142}. For this reason two mixed-metal complexes of copper(II) and lead(II) with the ligand HL\textsubscript{12} (2-dimethylaminoethanol) are investigated, [CuPbCl\textsubscript{2}(L\textsubscript{12})\textsubscript{2}]\textsubscript{n} \cdot n/2 \text{H}_2\text{O} (Figure 95) and [CuPbI\textsubscript{2}(L\textsubscript{12})\textsubscript{2}] (Figure 96)\textsuperscript{143}. 

FIGURE 94. A side view of a cation of the sandwich-type [Pb(L\textsubscript{11})\textsubscript{2}]\textsuperscript{2+} complex. Reproduced by permission of Elsevier Science from Reference 140

FIGURE 95. Fragment of the polymeric chain present in the crystal structure of [CuPbCl\textsubscript{2}(L\textsubscript{12})\textsubscript{2}]\textsubscript{n} \cdot n/2 \text{H}_2\text{O}. Reproduced by permission of Elsevier Science from Reference 143
The metal complex motif of both compounds is a centrosymmetric tetranuclear dimer with square-pyramidal coordination geometry around the Cu atom and highly distorted octahedral coordination to the Pb atom. The Cu and Pb atoms are bridged by alkoxide oxygens from L₁₂ to form a Pb₂Cu₂O₄ core which displays a flattened chair conformation. In the chloride complex tetranuclear units are connected successively via \( \mu \)-chloro bridging between two Pb sites forming polymeric chains. The Pb atom is six-coordinate, being surrounded by three oxygen atoms from the three L₁₂ groups and three chloride atoms with substantial departure from an ideal octahedral geometry. In the iodide complex the I atom bonded to the Pb atom bridges to Cu and Pb atoms of adjacent complex molecules to produce a layer parallel to the \( bc \) plane. The one-pot synthesis of these complexes (reaction of copper powder with lead salt in non-aqueous solution of 2-dimethylaminoethanol, \( \text{HL}_{12} \)) has the merit of mild reaction conditions and short reaction time, good yield and its versatility. It is possible to produce predictable mixed-metal complexes by reacting different metal powders and metal salts in solutions of different aminoalcohols or other complexing agents.

The mesityl group (Mes = 2,4,6-(CH₃)₃C₆H₂), being a relatively bulky substituent, has been widely used in the chemistry of silicon and germanium in order to stabilize and isolate new types of compounds, such as disilenes and digermenes.\(^{144-150}\) In contrast, there are a few reports of mesityl derivatives of lead, such as \( \text{Mes}_4\text{Pb}^{151}, \text{Mes}_3\text{PbCl} \) and \( \text{Mes}_3\text{Pbl}^{152,153} \). The reaction of mesityllithium (prepared from mesityl bromide) with lead(II) chloride in THF results in the unexpected formation of trimesityllead bromide and dimesityllead dibromide as a side product.\(^{154}\) Their structures are given in Figures 97 and 98. The desired product mesityllead(II) chloride was not detected. It is believed...
FIGURE 97. ORTEP view of Mes$_3$PbBr (25% probability, H atoms are omitted for clarity). Reproduced by permission of Elsevier Science from Reference 154

FIGURE 98. ORTEP view of Mes$_2$PbBr$_2$ (25% probability). Reproduced by permission of Elsevier Science from Reference 154
that the lead–bromine bond was formed via exchange of the Cl for Br (arising from the precursor mesityl bromide). Initially formed plumblyenes, Mes$_2$Pb, MesPbCl or MesPbBr, which can be postulated as being intermediates, could then react with mesityl bromide to produce Mes$_3$PbBr and Mes$_2$PbBr$_2$. The $^{207}$Pb-$^1$H NMR spectrum of Mes$_3$PbBr in CDCl$_3$ (Figure 99) shows the $^{13}$C satellites. For C-1, the $^1J$ coupling is visible; the smaller couplings, $^2J$ and $^3J$, consisting of the satellites C-2, C-3 and 2,6-CH$_3$, are also present but cannot be resolved.
V. ACKNOWLEDGEMENTS

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VI. REFERENCES

7. Recent advances in acidity, complexing, basicity and H-bonding

7. Recent advances in acidity, complexing, basicity and H-bonding


CHAPTER 6

Further advances in germanium, tin and lead NMR

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I. INTRODUCTION

Despite their environmental problems organic tin and lead containing compounds are still in the focus of interest of both academic as well as industrial research. One of the most powerful tools for the characterization of derivatives in this field of chemistry is the application of NMR experiments. The properties of the isotopes of group 14 elements used for NMR experiments are shown in Table 1.

Therefore, it is no surprise that the group 14 elements, with the exception of germanium, are well investigated by NMR spectroscopy. This survey covers the development of NMR observations for $^{73}$Ge, $^{119}$Sn and $^{207}$Pb between 1995 and 2000 for organometallic compounds. In these years Chemical Abstracts lists more than 500 entries for $^{119}$Sn NMR results and nearly 50 entries for $^{207}$Pb NMR. In contrast, only a limited number of germanium resonances is found in the literature. Consequently, it will not be possible to give tin all the attention it deserves. However, there are data collections giving a much more detailed view of results obtained so far.

II. GERMANIUM NMR

A. History and Technical Details

In comparison with the homologous elements of germanium, for example silicon and tin, only little is known about germanium NMR. Germanium NMR had a ‘boom’ during the 1980s but research is proceeding relatively leisurely in recent years. The limitations in the observations of germanium resonance are mainly due to the nature of the element. Germanium has only one NMR active isotope, $^{73}$Ge, with a low gyromagnetic

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Natural abundance (%)</th>
<th>Nuclear spin</th>
<th>Magnetic moment $\mu^a$</th>
<th>Sensitivity rel.$^b$</th>
<th>Sensitivity abs.$^c$</th>
<th>Receptivity relative to $^{13}$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{13}$C</td>
<td>1.108</td>
<td>$\frac{1}{2}$</td>
<td>0.7022</td>
<td>$1.59 \times 10^{-2}$</td>
<td>$1.76 \times 10^{-4}$</td>
<td>1</td>
</tr>
<tr>
<td>$^{29}$Si</td>
<td>4.7</td>
<td>$\frac{1}{2}$</td>
<td>$-0.5548$</td>
<td>$7.84 \times 10^{-3}$</td>
<td>$3.69 \times 10^{-4}$</td>
<td>2.1</td>
</tr>
<tr>
<td>$^{73}$Ge</td>
<td>7.76</td>
<td>$\frac{9}{2}$</td>
<td>$-0.8768$</td>
<td>$1.4 \times 10^{-3}$</td>
<td>$1.08 \times 10^{-4}$</td>
<td>0.61</td>
</tr>
<tr>
<td>$^{115}$Sn</td>
<td>0.35</td>
<td>$\frac{1}{2}$</td>
<td>$-0.9132$</td>
<td>$3.5 \times 10^{-2}$</td>
<td>$1.22 \times 10^{-4}$</td>
<td>0.69</td>
</tr>
<tr>
<td>$^{117}$Sn</td>
<td>7.61</td>
<td>$\frac{1}{2}$</td>
<td>$-0.9949$</td>
<td>$4.52 \times 10^{-2}$</td>
<td>$3.44 \times 10^{-3}$</td>
<td>19.5</td>
</tr>
<tr>
<td>$^{119}$Sn</td>
<td>8.58</td>
<td>$\frac{1}{2}$</td>
<td>$-1.0409$</td>
<td>$5.18 \times 10^{-3}$</td>
<td>$4.44 \times 10^{-3}$</td>
<td>25.2</td>
</tr>
<tr>
<td>$^{207}$Pb</td>
<td>22.6</td>
<td>$\frac{1}{2}$</td>
<td>0.5843</td>
<td>$9.16 \times 10^{-3}$</td>
<td>$2.07 \times 10^{-3}$</td>
<td>11.8</td>
</tr>
</tbody>
</table>

$^a$In multiples of the nuclear magneton.$^1$.

$^b$For equal number of nuclei at constant field.

$^c$Product of the relative sensitivity and the natural abundance.

$^d$Quadrupole moment, $-0.18 \times 10^{-28}$ m.
6. Further advances in germanium, tin and lead NMR

ratio \((-0.9332 \text{ rad s}^{-1} \text{T}^{-1} \times 10^7\), a large nuclear spin \(\hbar^2\) and is observed at low resonance frequencies. Most of the \(^{73}\text{Ge}\) chemical shifts, known from the literature, were measured with respect to tetramethylgermane (Me4Ge: \(\delta = 0\) ppm) or GeCl4 [converted to Me4Ge: \(\delta(\text{Me}_4\text{Ge}) = \delta(\text{GeCl}_4) - 30.9\)]. Cited negative values mean that the resonance is at a lower frequency than Me4Ge. Absolute frequencies, relative to the \(^1\text{H}\) signal of Me4Si = 100 MHz, were 3.488423 MHz \(\pm 10\) Hz for GeCl4 and 3.488418 \(\pm 10\) Hz for Me4Ge2.

The first pioneering work of high resolution \(^{73}\text{Ge}\) nuclear magnetic resonance\(^3,4\) was undertaken by the groups of Kaufmann and Spinney at the beginning of the 1970s. More far-reaching progress is linked with the research groups of Lukevics\(^5\), Mackay\(^6\) and Takeuchi\(^7\) in the early 1980s.

B. Problems in \(^{73}\text{Ge}\) NMR Spectroscopy

In recent years a number of \(^{73}\text{Ge}\) chemical shifts were published. However, the method has still a vast number of limitations and therefore only a few hundred compounds are characterized by \(^{73}\text{Ge}\) NMR. Earlier reviews concerning \(^{73}\text{Ge}\) NMR chemical shifts are given in the literature\(^8–12\).

Especially, organometallic chemists might encounter a number of difficulties in attempting to use \(^{73}\text{Ge}\) NMR for the characterization of samples. Although a wide variety of classes of germanium containing compounds has been observed, including germanium hydrides, alkyl- and polyalkylgermanes, alkyl derivatives, tetra-alkoxides, tetraarylgermanes and mixed tetrahalides, as far as we are aware no chemical shifts have been given in the literature for mixed alkyl/aryl halides of germanium\(^13\). For example, in the \(^{73}\text{Ge}\) NMR spectra of 1-chloro-1,1-dimethyldigermane (H3Ge–GeMe2Cl) only the signal for the GeH3 unit was observed\(^13\). Similarly, the homoleptic Ge(OR)4 species were observable but mixed compounds of type RnGe(OR)4 were not, with one exception. This exception, i.e. Me3GeONMe2, is remarkable from another point of view as well. The \(^{73}\text{Ge}\) chemical shift has a value of +522 ppm\(^14\), which is the only known chemical shift in this low field region. All other described germanium resonances are in a range between +100 and −1200 ppm.

The germanium NMR data fit very well the linear relationships found between the chemical shifts of the group 14 elements\(^15\). There are linear \(^{73}\text{Ge}/^{29}\text{Si}\) and \(^{73}\text{Ge}/^{119}\text{Sn}\) chemical shift correlations between derivatives of silicon, germanium and tin\(^13\).

C. Current Progress in \(^{73}\text{Ge}\) NMR

One of the major problems of working with \(^{73}\text{Ge}\) is the baseline roll as a result of the acoustic ringing, which creates difficulties with the expected broader lines for many germanium derivatives. A solution to this problem might be the use of pulse techniques such as RIDE, PHASE or EXSPECT\(^13,16\). The first example for the application of such techniques was in solving the behavior of several exchange processes\(^13\).

The use of such pulse techniques and higher processing capacities of computers should allow some progress in this field in the near future, for example in getting a better understanding of the effects of substituents of the field gradients and therefore on the line widths in the germanium spectra.

D. \(^{73}\text{Ge}\) Chemical Shifts of Organometallic Compounds

\(^{73}\text{Ge}\) chemical shifts of selected organometallic compounds are given in Table 2.
### TABLE 2. $^{73}$Ge Chemical Shifts of Organometallic Compounds

<table>
<thead>
<tr>
<th>Structural formula</th>
<th>Chemical shift (ppm)</th>
<th>Linewidth (Hz) (solvent)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>R−X H X−R</td>
<td>85.4</td>
<td>350 (CDCl$_3$)</td>
<td>17</td>
</tr>
<tr>
<td>R = Me; X = O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R = Et; X = O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R = t-Bu; X = O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R = Me; X = S</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R = Me; X = NMe</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ (\text{C}_6\text{H}_5)_3\text{GeH} \]

\[ -(57.0) \quad 20 \quad (\text{CDCl}_3) \]

\[ -(55.4^a) \quad -(-\text{C}_6\text{D}_6) \]

\[ -(84.0) \quad 20 \quad (\text{CDCl}_3) \]

\[ -(33.2) \quad 80 \quad (\text{CDCl}_3) \]

\[ -(515.2) \quad -(-\text{C}_6\text{D}_6) \]

\[ -(169.0) \quad -(-\text{C}_6\text{D}_6) \]

\[ -(133.2) \quad -(-\text{C}_6\text{D}_6) \]

\[ (\text{Me}_3\text{Sn})_4\text{Ge} \]

\[ -(13.3) \quad -(-\text{C}_6\text{D}_6) \]

\[ (\text{Me}_3\text{Sn})_2\text{GeMe}_2 \]

\[ -(64.6) \quad -(-\text{C}_6\text{D}_6) \]

\[ -(169.0) \quad -(-\text{C}_6\text{D}_6) \]

\[ -(133.2) \quad -(-\text{C}_6\text{D}_6) \]

\[ \text{Me}_3\text{Sn}−\text{GeMe}_2−\text{GeMe}_2−\text{SnMe}_3 \]

\[ -(32.9) \quad -(-\text{C}_6\text{D}_6) \]

\[ \text{Ph}_4\text{Ge} \]

\[ -(32.9) \quad -(-\text{C}_6\text{D}_6) \]

\[ [\text{Me}_2N(\text{CH}_2)_3]_3\text{GePh}•\text{HCl} \]

\[ -(25.1) \quad -(-\text{C}_6\text{D}_6) \]

\[ (\text{Me}_3\text{C}_6\text{H}_4)\text{GePh}_3 \]

\[ -(32.5) \quad -(-\text{C}_6\text{D}_6) \]

\[ (\text{Me}_3\text{C}_6\text{H}_4)\text{GePh}_2 \]

\[ -(31.7) \quad -(-\text{C}_6\text{D}_6) \]

\[ (\text{Me}_3\text{C}_6\text{H}_4)\text{GePh} \]

\[ -(30.8) \quad -(-\text{C}_6\text{D}_6) \]

\[ (\text{Me}_3\text{C}_6\text{H}_4)\text{GePh} \]

\[ -(31.2) \quad -(-\text{C}_6\text{D}_6) \]

\[ \text{Me}_3\text{GeONMe}_2 \]

\[ 522.0 \quad -(-\text{C}_6\text{D}_6) \]

\[ 4\text{-MeOC}_6\text{H}_4\text{GeH}_3 \]

\[ -(189.9^b) \quad -(-\text{C}_6\text{D}_6) \]
III. TIN NMR

A. Introduction

As mentioned above, this review can not discuss all the $^{119}\text{Sn}$ NMR results published in the recent 5 years$^{23-389}$. A large number of them are compiled in other data collections$^{23-25}$. Elemental tin consist of ten stable isotopes. Three of them have a spin of $\frac{1}{2}$ and therefore a magnetic moment (see Table 1). Because of its high abundance and its higher magnetic moment leading to a sensitivity of 25.2 compared to that of carbon-13, tin-119 is mostly used for NMR purposes, although in some studies the isotopes $^{115}\text{Sn}$ or $^{117}\text{Sn}$ are used instead. Referencing is always done directly or indirectly to SnMe$_4$. Positive shifts mean shifts to a higher frequency or to a lower field.

B. Technical Details

The sensitivity of the $^{119}\text{Sn}$ experiment makes tin NMR spectroscopy a standard procedure for every tin containing compound. Most techniques of observing tin NMR were developed prior to the period covered in this review, but a few examples are presented here. Single resonance experiments and simple proton–tin decoupling do not present too many challenges except for the negative sign of the magnetic moments of the active tin isotopes, which could lead to a decrease in signal strength or even to a null signal, if an unfavorable mix of relaxation paths occurs. Reverse gated decoupling is then the best choice if quantitative results are required. If coupling constants to protons are known, pulse sequences such as $^{1}\text{H}-^{119}\text{Sn}$ INEPT$^{136}$ are used frequently. For special purposes such as the determination of coupling constants, variations of this method such as HEED INEPT$^{27,136,146}$ are of advantage because the central line, which can be rather broad and sometimes masking the satellites is suppressed. One cause of this could be the relaxation by chemical shift anisotropy$^{25}$.

For the determination of the sign of coupling constants involving tin, 2D correlation spectra in the form of $^{1}\text{H}-^{119}\text{Sn}$ HETCOR$^{27-29,136}$, HMOC$^{30,31}$ or HMBC$^{43,265}$ are employed. Due to the good sensitivity, Sn–Sn COSY experiments can be conducted in a reasonable time$^{32}$.
Solid state NMR can be performed for crystalline or amorphous samples. Tetracyclohexyltin, \((c-C_6H_{11})_4Sn\) \((\delta = -97.0 \text{ ppm})\), is often used as a secondary standard. The spinning side bands are very extensive due to the often sizeable chemical shift anisotropy which is especially pronounced for higher coordination numbers. The line representing the isotropic shift is not found easily. Very often it is one of smaller signals. Careful analysis is then needed to obtain the chemical shift tensors around the tin atom and the central line giving the isotropic shift. Extreme care should also be exercised in interpreting MAS chemical shift data without knowing the crystal structure of the compounds. A recent example is provided by Clayden and Pugh. To overcome the often high chemical shift anisotropies, high rotation frequencies must be used. To diminish the problem of unstable cross-polarization behavior at high spinning speeds, variable-amplitude cross-polarization pulse programs (VACP) have been used. High rotational speeds lead to high sample temperatures because of the friction between the rotor and the bearing gas. Use of the \(^{119}\text{Sn}\) chemical shift of \(\text{Sm}_2\text{Sn}_2\text{O}_7\) to determine the sample temperature has been proposed.

Besides the opportunity to measure chemical shift anisotropies, MAS NMR also offers the possibility to measure the scalar couplings to other isotopes with magnetic moments. Examples to determine the spatial components of these couplings can be found in the literature. Even couplings to quadrupolar nuclei not observable in solution can be deduced from the MAS spectra. 2D techniques such as HETCOR are also applicable for solids.

The \(^3J\((^{119}\text{Sn}–X)\) coupling constants of tin derivatives were discussed recently in a number of reviews and need not be repeated in this chapter.

C. Chemical Shifts

1. General remarks

Tin has a rather complicated chemistry. First, it must be distinguished between its two valency states Sn(II) and Sn(IV). Second, in both valency states tin may act as a Lewis acid connecting the tin with one or more donor atoms such as oxygen, nitrogen and other donors. Consequently, besides the so-called 'normal' coordination numbers of two for Sn(II) and four for Sn(IV), higher numbers up to eight are frequently encountered. The number and kind of donor atoms attached to tin change very easily, e.g. by using different solvents or between the solid and the dissolved state, making the assignment of chemical shifts to different types of tin compounds far from straightforward. In some studies of the biological effects of tin, the samples have many donor groups in the organic part and the environment of the tin is not very well defined. A proposal to classify tin chemical shifts by statistical methods has been advanced by Bartel and John.

2. Tin(II) compounds

A selection of chemical shifts of tin(II) compounds with direct tin-group 14 element or tin-group 15 element bonds encountered at the time of the report are collected in Table 3. More organometallic tin(II) derivatives are found in the literature. The tin-119 chemical shifts for tin(II) compounds cover a range from nearly 4000 to \(-3000 \text{ ppm}\). Due to this wide range it is impossible to recognize simple correlations between the coordination number at the tin center or the substituents directly bonded to tin(II) and the chemical shift value. What one can suggest are predictions within only one class of compounds, e.g. for the derivatives shown below with a given substitution pattern when the \(R\) group is changed selectively (see also Table 3).
This difficulty arises also from another problem in those compounds: the fact that equilibria exist between stannylenes in their true state as $R_2Sn$ and their dimeric counterparts, the distannenes $R_2Sn^D$, for this reason, the separation of compounds belonging to Tables 3 and 4 is probably open to debate. Recent reviews about the chemical behavior of stannylenes, distannenes and their relatives in group 14 are available \^{123,125,127–130}.

A rough correlation also exists between the shift of tin in the oxidation state $^{2}\text{inn}$ transition metal complexes and the coordination number, so that additional ligands also cause additional shielding. Although this is not exactly the topic of this review, some Sn(II) compounds with a surrounding of three transition metal atoms constitute the low shielding limit of tin so far. The shift of 3924 ppm for Sn(II) in 1, being in the center of a triangle of Cr atoms, is thought to be the result of low-lying $\pi^*$-orbitals $^{70}$. If the triangle is formed by Mn atoms in 2, a still lower shielding of 3301 ppm is observed $^{71}$.

$$\text{[(CO)$_5$Cr)$_3$Sn$]^{2-}} \quad \text{[(Cp$^*$s(CO)$_2$Mn)$_3$Sn$]}$$

| R = CH(PPh$_2$)$_2$ | R = Cl  | 793.4 | R = Cl  |$^{−100}$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>R = Tip</td>
<td>R = $t$-Bu</td>
<td>1904.4</td>
<td>R = CH(SiMe$_3$)$_2$</td>
<td>258</td>
</tr>
<tr>
<td>R = Si(SiMe$_3$)$_3$</td>
<td>R = N(SiMe$_3$)$_2$</td>
<td>1196.8</td>
<td>R = SiPh$_3$</td>
<td>192</td>
</tr>
<tr>
<td>R = Sn$_B$(SiMe$_3$)$_3$</td>
<td>R = Sn$_B$Me$_2$R$^{''}$</td>
<td>2856.9</td>
<td>R = Sn$_B$Me$_3$</td>
<td>217</td>
</tr>
<tr>
<td>Tip = 2,4,6-($i$-Pr)$_3$C$_6$H$_2$</td>
<td>R$^{'}$ = Tip</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R$^{''}$ = 2,6-Tip$_2$C$_6$H$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The increase of the coordination number by exchanging one metal center by two oxygen or nitrogen donor atoms in compounds 3 leaves the shift range between 600 and 1500 ppm.

<table>
<thead>
<tr>
<th>TM</th>
<th>D</th>
<th>Sn</th>
<th>D</th>
<th>TM</th>
<th>D</th>
<th>Sn</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3)</td>
<td>(4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TM = transition metal fragment; D = halogen, organic amine or alkoxy group

One transition metal atom and three other donor atoms around the tin in 4 result in resonances of tin(II) between 170 and 344 ppm. For transition metal tin(II) compounds
with similar substituents, the $^{119}$Sn chemical shifts for the tin compounds are significantly lower (high field shifted) than for the chromium or molybdenum derivatives. The order of shifts below is in good agreement with the results for tin(IV) compounds.

$$\delta[[(Z)_{5}Cr]_{2}Sn \text{ (bipy)}] \approx \delta[[(Z)_{5}Mo]_{2}Sn \text{ (bipy)}] > \delta[[(Z)_{5}W]_{2}Sn \text{ (bipy)}]$$

$Z = CO$, cyclopentadienyl

The high coordination numbers typical for the cyclopentadienyl ligand lead to strong shielding as exemplified in Table 3. The low coordination of the central tin atom in the tristannaallene $(t$-Bu$_3$Si)$_2$Sn=Sn=Sn(Si(Bu-$t$)$_3$)$_2$ also results in a strong deshielding. The mesomeric structures of this compound lead to an interpretation in which the terminal tin is regarded as tin(II)

| TABLE 3. $^{119}$Sn NMR data of tin(II) compounds |
|---------------------------------|---------------|---------|---------|
| Compound                        | Chemical shift (ppm) | Solvent | Reference |
| $(t$-Bu$_3$Si)$_2$Sn=Sn=Sn(Si(Bu-$t$)$_3$)$_2$ | 2208           | C$_6$D$_5$CD$_3$ | 72 |
| $(t$-Bu$_3$Si)$_2$Sn=Sn=Sn(Si(Bu-$t$)$_3$)$_2$ | 1329           | C$_6$D$_5$CD$_3$ | 73 |
| $(t$-Bu$_3$Si)$_2$Sn=Sn=Sn(Si(Bu-$t$)$_3$)$_2$ | 1329           | C$_6$D$_5$CD$_3$ | 74 |
| $(t$-Bu$_3$Si)$_2$Sn=Sn=Sn(Si(Bu-$t$)$_3$)$_2$ | 1401           | C$_6$D$_5$CD$_3$ | 75 |
| $(t$-Bu$_3$Si)$_2$Sn=Sn=Sn(Si(Bu-$t$)$_3$)$_2$ | 1401           | C$_6$D$_5$CD$_3$ | 76 |
## TABLE 3. (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift (ppm)</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>R' = 2,4,6-(i-Pr)₃C₆H₂ (Tip); R'' = C₆H₃-2,6-Tip₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[PhMe₂Si]₃CSnCl₂</td>
<td>777</td>
<td>C₆D₆</td>
<td>87</td>
</tr>
<tr>
<td>[(MeOMeSi)(Me₂Si₂)CSnCl]₂</td>
<td>469</td>
<td>C₆D₆</td>
<td>87</td>
</tr>
</tbody>
</table>

(continued overleaf)
TABLE 3. (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift (ppm)</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = N(SiMe₃)₂ 2,6-(Me₂N)₂C₆H₃</td>
<td>620.94 412</td>
<td>C₆D₆</td>
<td>88</td>
</tr>
<tr>
<td>R = CH(PPh₂)₂ 2,4,6-(i-Pr)₃C₆H₂</td>
<td>397 474 876</td>
<td>C₆D₆</td>
<td>89 90</td>
</tr>
<tr>
<td>Si(SiMe₃)₃ SnB(SiMe₃)₃</td>
<td>897</td>
<td></td>
<td>NBP: −502</td>
</tr>
<tr>
<td>Me₃Si PhSnMe₃Si Me₃Si Ph</td>
<td>156.18</td>
<td>C₆D₆</td>
<td>91</td>
</tr>
<tr>
<td>Me₃Si SiMe₃Sn</td>
<td>141.73</td>
<td>C₆D₆</td>
<td>91</td>
</tr>
<tr>
<td>(i-Pr₅Cp)₂Sn</td>
<td>−2262</td>
<td></td>
<td>93</td>
</tr>
<tr>
<td>[(η⁵-C₅H₅)₂Sn(μ-C₅H₅)]</td>
<td>−2312</td>
<td></td>
<td>94</td>
</tr>
</tbody>
</table>
6. Further advances in germanium, tin and lead NMR

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift (ppm)</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{[(η}^{3}\text{C}_5\text{H}_5)_3\text{Sn}\text{]}^2^-)</td>
<td>-1730</td>
<td>C(_6)D(_6)</td>
<td>94</td>
</tr>
<tr>
<td>(\text{[(η}^5\text{Me}_4\text{(Me}_3\text{Si)}\text{Cp})_2\text{Sn}\text{]})</td>
<td>-2171</td>
<td>C(_6)D(_6)</td>
<td>121</td>
</tr>
<tr>
<td>(\text{[(η}^5\text{-Me}_4\text{(t-BuMe}_2\text{Si)}\text{Cp})_2\text{Sn}\text{]})</td>
<td>-2236</td>
<td>C(_6)D(_6)</td>
<td>121</td>
</tr>
<tr>
<td>(\text{[(η}^5\text{(PhC(=O))C}_5\text{H}_4)_2\text{Sn}\text{]})</td>
<td>-2137.4</td>
<td>THF-d(_8)</td>
<td>95</td>
</tr>
<tr>
<td>(\text{[(t-Bu}_3\text{Si)}_2\text{Sn}\text{]})</td>
<td>412.6</td>
<td>C(_6)D(_6)</td>
<td>95</td>
</tr>
<tr>
<td>((\text{t-Bu}_3\text{Si)}_2\text{Sn} = \text{Sn}_A = \text{Sn}_B(\text{Bu-t}_3\text{Si)}_2)</td>
<td>Sn(_A): 2233</td>
<td>C(_6)D(_5)CD(_3)</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>Sn(_B): 503</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Bu-t: 412
- M = Sn
- Pb
- Sn-
- N: 45.7
- Sn-
- O: 205.7
- \(\text{[(Me}_3\text{Si)}_3\text{Si})\text{Me}_3\text{SiN]}_2\text{Sn}\) | 549.61 | C\(_6\)D\(_6\) | 102 |

complex with:
- Ge\((\text{C}_6\text{H}_3(\text{NMe}_2)_2)_2\text{-2.6}\) | -58 |
- SnB\((\text{C}_6\text{H}_3(\text{NMe}_2)_2)_2\text{-2.6}\) | SnB: -30/275 |

(continued overleaf)
<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift (ppm)</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Cp}_2\text{Zr}_2\text{Cl}_7]$</td>
<td>734</td>
<td>CDCl$_3$</td>
<td>106</td>
</tr>
<tr>
<td>$[\text{PhMe}_2\text{Si}]_2\text{N}\text{Sn}$</td>
<td>501</td>
<td>C$_6$D$_6$</td>
<td>108</td>
</tr>
<tr>
<td>$[2,6-(i-\text{Pr})_2\text{C}_6\text{H}_3(\text{Me}_3\text{Si})\text{N}]_2\text{Sn}$</td>
<td>440</td>
<td>C$_6$D$_6$</td>
<td>108</td>
</tr>
<tr>
<td>$[(\text{Me}_3\text{Si})_2\text{NSn}(\mu-\text{Cl})]_2$</td>
<td>39</td>
<td>C$_6$D$_5$CD$_3$</td>
<td>109</td>
</tr>
<tr>
<td>$[(\text{Me}_3\text{Si})_2\text{NSn}(\mu-\text{OSO}_2\text{CF}_3)]_2$</td>
<td>-270</td>
<td>THF-d$_8$</td>
<td>109</td>
</tr>
<tr>
<td>$(\text{Me}_3\text{Si})_2\text{N}(\text{ArO})\text{Sn}$</td>
<td>-52</td>
<td>C$_6$D$_6$</td>
<td>109</td>
</tr>
</tbody>
</table>

$R = i$-Pr; $Me_3Si$
TABLE 3. (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift (ppm)</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et₃Si</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(OC)₄Fe</td>
<td>489/520</td>
<td>C₆D₆</td>
<td>382</td>
</tr>
<tr>
<td>[(Tip₂Si(F))₂P]₂Snᵇ</td>
<td>1551</td>
<td></td>
<td>261</td>
</tr>
<tr>
<td>[(Me₃Si)₂As]₂Sn₂</td>
<td>475 (cis)ᶜ, 671 (trans)ᶜ</td>
<td>C₆D₆</td>
<td>111</td>
</tr>
<tr>
<td>t-Bu₃Si</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₆D₆</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t-Bu₃Si</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NPr-i</td>
<td>−59.4</td>
<td>C₆D₆</td>
<td>112</td>
</tr>
<tr>
<td>NPr-i</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnCl₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Me₄N][Sn(SOCPh)₃]</td>
<td>−227</td>
<td>CH₃CN (0.03 M)</td>
<td>122</td>
</tr>
<tr>
<td>M = W(CO)₅</td>
<td>−74</td>
<td>C₆H₅CH₃/D₂O</td>
<td>86</td>
</tr>
<tr>
<td>M = Cr(CO)₅</td>
<td>131</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M = Fe(CO)₄</td>
<td>54</td>
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<td></td>
</tr>
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</table>

(continued overleaf)
TABLE 3. (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift (ppm)</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{OC})_n\text{M} = \text{SnRR}^\prime)</td>
<td>(\text{M} = \text{W(CO)}_5)</td>
<td>799</td>
<td>(\text{C}_6\text{D}_6)</td>
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<tr>
<td>(\text{Mo(CO)}_5)</td>
<td>928.5</td>
<td></td>
<td>116</td>
</tr>
<tr>
<td>(\text{Cr(CO)}_5)</td>
<td>1001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Fe(CO)}_3)</td>
<td>889</td>
<td></td>
<td>117</td>
</tr>
<tr>
<td>(\text{Ni(CO)}_3)</td>
<td>956</td>
<td></td>
<td></td>
</tr>
<tr>
<td>free stannylene</td>
<td>960</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{RR'}\text{Sn} = \text{Mn(CO)}_4 = \text{SnRR}^\prime)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{R} = 2,4,6-(\text{t-Bu})_3\text{C}_6\text{H}_3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{R}’ = 2,6-(\text{t-Bu})_2-4\text{-EtMe}_2\text{CC}_6\text{H}_2)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
\text{OC} \quad \text{Sn} \quad \text{P} \quad \text{N} \\
\text{R} \quad \text{R} \quad \text{Sn} \\
\text{TFO}^- \\
\text{R} = \text{Me} \\
\text{n-Bu} \\
\text{R} = \text{Me} \\
\text{R} = 4\text{-MeC}_6\text{H}_4 \\
\text{t-Bu} \quad \text{N} \quad \text{N} \quad \text{Bu-t} \\
\text{Si} \\
\text{Ph}_3\text{P} \quad \text{PPH}_2 \\
\text{R}_3\text{P} \quad \text{Pt} \quad \text{Fe(CO)}_3 \\
\text{R} = \text{Ph} \\
\text{R} = 4\text{-MeC}_6\text{H}_4 \\
\text{t-Bu} \quad \text{N} \quad \text{N} \quad \text{Bu-t} \\
\text{Si} \\
\text{Ph}_3\text{P} \quad \text{PPH}_2 \\
\text{Me}_3\text{P} \quad \text{Fe(CO)}_3 \\
\text{M} = \text{Pt} \\
\text{M} = \text{Pd} \\
\text{t-Bu} \quad \text{N} \quad \text{N} \quad \text{Me}_3\text{Si} \quad \text{O} \quad \text{OMe} \\
\text{Me}_2\text{Si} \quad \text{Sn} \quad \text{Si} \quad \text{OMe} \quad \text{OMe} \\
\text{t-Bu} \\
\text{a} \quad \text{At 253 K;} \\
\text{b} \quad \text{No signal observed in solution, MAS spectra only;} \\
\text{c} \quad \text{Broad signal;} \\
\text{d} \quad \text{AMM'X type.} \\

3. Tin(IV) compounds

\text{a. Tin with a coordination number of four}. Despite the importance of tin in a coordination sphere greater than four, a number of tin compounds are at least thought to be connected to four substituents only. The wealth of data is organized into 10 tables. Table 5 comprises trimethylstannyl derivatives. Other publications of stannanes with Me3Sn units are found in the literature. A number of vinyl-substituted stannanes with and without the trimethylstannyl moiety is summarized elsewhere. Table 6 is devoted to aliphatic triorganostannyl derivatives, while Table 7 contains an assortment of compounds with substituents, such as H, Si or the halogenes. Aryl-substituted tin compounds can be found in Tables 8–10. Table 11 lists compounds with at least one transition metal bond to tin. Compounds containing two tin–carbon bonds are found in Table 12 while Table 13 presents compounds with tin–tin bonds. The limited space of this review,
6. Further advances in germanium, tin and lead NMR

TABLE 4. \(^{119}\)Sn NMR data of stanna-alkenes, germanes and phosphenes

<table>
<thead>
<tr>
<th>Structural formula</th>
<th>Chemical Shift [ppm]</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tip(_2)Sn=GeMes(_2)(^a)</td>
<td>360(^b)</td>
<td>ether-toluene</td>
<td>124</td>
</tr>
<tr>
<td>(X_2)Sn</td>
<td>X = 2,4,6-(t-Bu)(_3)C(_6)H(_2)</td>
<td>710</td>
<td>114</td>
</tr>
<tr>
<td>(X_2)Sn</td>
<td>X = Cl</td>
<td>-59.4</td>
<td>112</td>
</tr>
<tr>
<td>Me(_3)Si</td>
<td>(R = 2)-(t-Bu)-4,5,6-Me(_3)C(_6)H</td>
<td>374</td>
<td>C(_6)D(_6)</td>
</tr>
<tr>
<td>(Me(_3)Si)(_2)CHP=SnTip(_2)(^a)</td>
<td>606.0</td>
<td>—</td>
<td>123</td>
</tr>
</tbody>
</table>

\(^a\)Tip = 2,4,6-(i-Pr)\(_3\)C\(_6\)H\(_2\);

\(^b\)at 253 K.

However, does not allow us to present all these compounds in this way; the remainder can be found elsewhere\(^{196-224}\).

Most tin NMR data are just used for characterizing the substances. There are some series of compounds measured to obtain a better understanding of tin chemical shifts. Examples are 3-X-bicyclo[1.1.1]pent-1-yltrimethylstannes (5), with different X substituents (cf. Table 5) which show that the tin chemical shifts are influenced by rear lobe interactions of the orbitals of the bridgehead carbons\(^{134}\).

For aryl-substituted stannanes, some relationships between the electronic properties of the aryl groups and the chemical shifts have been observed. For instance, there is a dependence of shifts and the resonance parameters \(\sigma_R\)\(^6\) and \(\sigma_R\)\(^{51}\). The effect is larger for the p-substituted aryl groups XCl\(_6\)H\(_4\) (X = Me, F, Cl, Br) than for the corresponding m-substituted derivatives and there are also linear correlations with the \(^{207}\)Pb chemical shifts of the corresponding lead compounds\(^{191}\). Dräger and coworkers describe the \(^{119}\)Sn chemical shifts of tetraarylstannanes to charge transfers between \(\pi\)- and \(\sigma^*\)-orbitals\(^{181}\). A collection of such data is found in Tables 9 and 10.

A wide variety of compounds are known which contain at least one transition metal–tin bond. These derivatives undergo different types of reactions, such as substitution of ligands at the tin or the metal center, photochemical reactions and so on. Selected tin derivatives of such transition metal complexes are shown in Table 11.

Compounds of the type R\(_2\)SnX\(_2\), where X = H, Si, N, P, O, S or a substituted carbon, are listed in Table 12. Cyclic compounds of this type are summarized in Table 13.

Selected derivatives with at least one tin-tin bond are given in Table 14.
TABLE 5. Selected $^{119}$Sn NMR data of trimethyltin substituted compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift (ppm)</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Me}_3\text{Sn}]_4\text{C}$</td>
<td>49.3</td>
<td>C$_6$D$_6$</td>
<td>131</td>
</tr>
<tr>
<td>$[\text{Me}_3\text{Sn}]_3\text{CMe}_2$</td>
<td>-30.2</td>
<td>C$_6$D$_6$</td>
<td>131</td>
</tr>
<tr>
<td>$[\text{Me}_3\text{Sn}−\text{C}≡\text{C}−\text{SiMe}_2]_2(\text{C}≡\text{C})$</td>
<td>-74.5</td>
<td>C$_6$D$_3$CD$_3$</td>
<td>132</td>
</tr>
<tr>
<td>$[\text{Me}_3\text{Sn}−\text{C}≡\text{C}−\text{SiMe}_2−\text{C}≡\text{C}]_2\text{SiMe}_2$</td>
<td>-70.9</td>
<td>CDCl$_3$</td>
<td>133</td>
</tr>
<tr>
<td>$\text{Me}_2\text{Sn}−(\text{C}≡\text{SiMe}_2)_3−\text{C}≡\text{C}−\text{SiMe}_3$</td>
<td>-74.2</td>
<td>C$_6$D$_3$CD$_3$</td>
<td>133</td>
</tr>
<tr>
<td>$\text{Me}_3\text{Sn}(\text{CH}(\text{R})\text{OH})_3$</td>
<td>R = H&lt;br&gt;1.0</td>
<td>12.6</td>
<td>CDCl$_3$</td>
</tr>
</tbody>
</table>
| &nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&n...
TABLE 5. (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift (ppm)</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₃SnSi₃SiEt₂SnMe₃</td>
<td>-50.0</td>
<td>C₆D₆</td>
<td>133</td>
</tr>
<tr>
<td>X = H</td>
<td>-46.9</td>
<td>CDCl₃</td>
<td>134</td>
</tr>
<tr>
<td>CN</td>
<td>-32.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF₃</td>
<td>-31.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>COOMe</td>
<td>-34.1</td>
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<td></td>
</tr>
<tr>
<td>CONMe₂</td>
<td>-35.4</td>
<td></td>
<td></td>
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<td>[(η⁵-Me₄(Me₃Sn)Cp)₂Fe]</td>
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<tr>
<td>R</td>
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<tr>
<td>Me(Et)</td>
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<th>Solvent</th>
<th>Reference</th>
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<td>$n = 1$</td>
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<td>-97.6</td>
<td>C$_6$D$_6$</td>
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<td>-104.7</td>
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<td>[Me$_3$Sn]$_4$Ge</td>
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<td>-25.1</td>
<td>C$_6$D$_6$</td>
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<tr>
<td></td>
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<td>-25.2</td>
<td>C$_6$D$_6$</td>
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<td>[Me$_3$Sn]$_2$GeMe$_2$</td>
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<td>-79.5</td>
<td>C$_6$D$_6$</td>
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<td>Me$_3$SnPbEt$_3$</td>
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<td>-36.2</td>
<td>C$_6$D$_6$</td>
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<td>Me$_3$SnPb(Pr-i)$_3$</td>
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<td>-7.5</td>
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<td>[Me$_3$Sn]$_3$N</td>
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<td>[Me$_3$Sn]$_2$NPh</td>
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<td>63.0</td>
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<td>Me$_3$SnSiMe$_3$</td>
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<td>48.6</td>
<td>C$_6$D$_5$CD$_3$</td>
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<tr>
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<td>35.6</td>
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<td>[Me$_3$Sn]$_4$Ge</td>
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<td>72.9</td>
<td>C$_6$D$_6$</td>
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<td>73.1</td>
<td>C$_6$D$_6$</td>
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<td></td>
<td></td>
<td>64.3</td>
<td>C$_6$D$_6$</td>
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<td>Me$_3$SnNH(2-C$_5$H$_4$N)</td>
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<td>69.0</td>
<td>C$_6$D$_6$</td>
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<tr>
<td>Me$_3$SnNHPh</td>
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<td>26.8</td>
<td>C$_6$D$_6$</td>
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<td>Me$_3$SnN(R)(C(=O))R'</td>
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<td>46.4</td>
<td>C$_6$D$_6$</td>
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<td>Me$_3$SnN(R)(C(=O))R'</td>
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### TABLE 5. (continued)

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<th>Reference</th>
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<tbody>
<tr>
<td>Et</td>
<td>R = t-Bu SiMe₃</td>
<td>-48.6</td>
<td>C₆D₅CD₃</td>
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<tr>
<td>Me₃Sn-</td>
<td>M R</td>
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<tr>
<td>Al</td>
<td>Pr</td>
<td>78.5</td>
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<tr>
<td>Al</td>
<td>i-Pr</td>
<td>54.0</td>
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<tr>
<td>Al</td>
<td>Bu</td>
<td>68.5</td>
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</tr>
<tr>
<td>Ga</td>
<td>Me</td>
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<td>Ga</td>
<td>Pr</td>
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<td>Ga</td>
<td>i-Pr</td>
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<td>Ga</td>
<td>i-Bu</td>
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<td>In</td>
<td>Me</td>
<td>102.9</td>
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<tr>
<td>In</td>
<td>Pr</td>
<td>103.9</td>
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</tr>
<tr>
<td>In</td>
<td>i-Pr</td>
<td>66.8</td>
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<tr>
<td>In</td>
<td>i-Bu</td>
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### TABLE 6. Triorganotin compounds R₃SnX (R = aliphatic substituents)

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<th>Compound</th>
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<th>Solvent</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>R = Ethyl</td>
<td>(CO)₃C₉</td>
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<tr>
<td>Et₃Sn</td>
<td>(CO)₃Co-Co(CO)₃</td>
<td>10.6</td>
<td>C₆D₆</td>
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<tr>
<td>Et₃SnC₆F₅</td>
<td></td>
<td>-6.8</td>
<td>CDCl₃</td>
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<tr>
<td>N-SnEt₃</td>
<td></td>
<td>-48.0</td>
<td>C₆D₆</td>
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<tr>
<td>N-SnEt₃</td>
<td></td>
<td>53.9</td>
<td>C₆D₆</td>
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<tr>
<td>Et₃Sn-SiCl₃</td>
<td></td>
<td>-59</td>
<td>C₆D₆</td>
</tr>
<tr>
<td>(Et₃Sn)₂Si(SiCl₃)₂</td>
<td></td>
<td>-45.0</td>
<td>C₆D₆</td>
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<tr>
<td>Et₃Sn-Pb(Bu-t)₃</td>
<td></td>
<td>31.9</td>
<td>C₆D₆</td>
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(continued overleaf)
**TABLE 6. (continued)**

<table>
<thead>
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<th>Compound</th>
<th>Chemical shift (ppm)</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
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<tr>
<td><strong>R = t-Butyl</strong></td>
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<td></td>
</tr>
<tr>
<td>(CO)₃Co – Co(CO)₃</td>
<td>23.6</td>
<td>C₆D₆</td>
<td>138</td>
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<tr>
<td>t-Bu₃Sn</td>
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<td></td>
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<tr>
<td>N – Sn(Bu-t)₃</td>
<td>-106.9</td>
<td>C₆D₆</td>
<td>146</td>
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<tr>
<td>N – Sn(Bu-t)₃</td>
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<td>146</td>
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<td>t-Bu₃Sn–Pb(Bu-t)₃</td>
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<td>C₆D₆</td>
<td>135</td>
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<tr>
<td><strong>R = n-Butyl</strong></td>
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<tr>
<td>(Bu₃Sn)₂CHCHMeCO₂Me</td>
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<td>CD₂Cl₂</td>
<td>169</td>
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<tr>
<td>(Bu₃Sn)₂CHCH(CH₂CH₂CH = CH₂)CO₂Me</td>
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<td>CD₂Cl₂</td>
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<tr>
<td>(Bu₃Sn)₂CHCH(CH₂Ph)CO₂Me</td>
<td>4.6</td>
<td>CD₂Cl₂</td>
<td>169</td>
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<tr>
<td>(Bu₃Sn)₂CHCH(CH₂NMe₂)CO₂Me</td>
<td>5.0</td>
<td>CD₂Cl₂</td>
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<td>Bu₃Sn-α-D-glucuronate</td>
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<td><strong>R = CO₂SnBu₃</strong></td>
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<tr>
<td>R = CO₂SnBu₃</td>
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<td>114.4</td>
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<tr>
<td>R’ = OH</td>
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<td></td>
<td>106.7</td>
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</tr>
<tr>
<td><strong>R = CO₂[H₂N(C₆H₁₁-c)]₂</strong></td>
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<tr>
<td>R’ = OH</td>
<td>H 105.6</td>
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</tr>
<tr>
<td><strong>R = CO₂[H₃NC₆H₁₁-c]</strong></td>
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<tr>
<td>R’ = OH</td>
<td>H 105.9</td>
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<tr>
<td><strong>R = CO₂[H₂N(CH₂)₅]</strong></td>
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<tr>
<td>R’ = OH</td>
<td>H 105.3</td>
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<td><strong>Z = H</strong></td>
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<tr>
<td>[H₂N(C₆H₁₁-c)]₂</td>
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<td>CDCl₃</td>
<td>171</td>
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6. Further advances in germanium, tin and lead NMR

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<th>Reference</th>
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<td>Bu₃Sn-ON</td>
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<tr>
<td>Bu₃Sn-SiCl₃</td>
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<td>C₆D₆</td>
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<tr>
<td>Bu₃Sn-Si(SiCl₃)₃</td>
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<td>C₆D₆</td>
<td>143</td>
</tr>
<tr>
<td>(Bu₃Sn)₂Si(SiCl₃)₂</td>
<td>-52.7</td>
<td>C₆D₆</td>
<td>143</td>
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<tr>
<td>Bu₃Sn-Pb(Bu-t)₃</td>
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<tr>
<td>Bu₃SnO-ON</td>
<td>116.9</td>
<td>CDCl₃</td>
<td>172</td>
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<td>Bu₃SnO-ON</td>
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<td>Bu₃Sn-SePh</td>
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<td>Bu₃Sn-Se(C₆H₄F-4)</td>
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<tr>
<td>Bu₃Sn-Te(C₆H₄F-4)</td>
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<td>R = various aliphatic substituents</td>
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<td>(Ph-C≡C)₃SnR</td>
<td>R = Me Bu i-Pr t-Bu (CH₂)₂CO₂Me</td>
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<tr>
<td>(PhCH₂)₃SnPh</td>
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<td>-63.2</td>
<td>CDCl₃</td>
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<tr>
<td>((−)-Menthyl)₃SnZ</td>
<td>Z = H Cl</td>
<td>-102.9 93.6</td>
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(continued overleaf)
TABLE 6. (continued)

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<th>Solvent</th>
<th>Reference</th>
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<tbody>
<tr>
<td>N—Sn(CH(_2)Ph)(_3)</td>
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![Chemical structure](image1)

TABLE 7. Compounds with X\(_3\)Sn moieties (X = H, Si, halogen)

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</thead>
<tbody>
<tr>
<td>H(_3)Sn—CH=CH(_2)</td>
<td>-361</td>
<td>C(_6)D(_6)</td>
<td>259</td>
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<td>H(_3)Sn—CH=C=CH(_2)</td>
<td>-338.4</td>
<td>C(_6)D(_6)</td>
<td>260</td>
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<tr>
<td>H(_3)Sn—C≡CH</td>
<td>-320.6</td>
<td>C(_6)D(_6)</td>
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<tr>
<td>((t)-BuNCH(_2))(_2)SiCl(_3)SnCl</td>
<td>-222.6</td>
<td>C(_6)D(_6)</td>
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<td>([\eta^5-(X_3Sn)C_5H_4]_2Fe)</td>
<td>X = H Cl</td>
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<td>C(_6)D(_6)</td>
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<td>-23.2</td>
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<td>Cl(_3)Sn—CHPh—CHMe—C(O)Ph</td>
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<td>-252</td>
<td>C(_6)D(_6)</td>
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<td>5</td>
<td>-179</td>
<td>(CD(_3))(_2)C=O</td>
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<td>4</td>
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<td>Br(_3)SnPh</td>
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<td>Br(_3)Sn—CH(_2)C≡CH</td>
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![Chemical structure](image2)
TABLE 8. Triaryltin compounds (R₃SnX)

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<th>Compound</th>
<th>Chemical shift (ppm)</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₃SnR' (R' = aliphatic substituent)</td>
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<tr>
<td>(CO)₃Co – Co(CO)₃</td>
<td>-114.6</td>
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<tr>
<td>Ph₃SnCH₂Br</td>
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<td>CD₂Cl₂</td>
<td>178</td>
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<tr>
<td>[Ph₃Sn*CH₂]₂SnPh₂</td>
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<td>178</td>
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<td>[Ph₃Sn*CH₂SnPh₂]₂</td>
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<td>[Ph₃Sn(CH₂)]₂</td>
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<td>179</td>
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<tr>
<td>Ph₃Sn(CH₂)₃NMe₂</td>
<td>-101.9</td>
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<td>174</td>
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<tr>
<td>Ph₃Sn(CH₂)₃NMe₂·HCl</td>
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<tr>
<td>Ph₃Sn–C≡C–C≡C–SnPh₃</td>
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<td></td>
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<td>R₃SnR' (R' = aromatic)</td>
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<tr>
<td>Ph₃Sn(C₆H₄Me-2)</td>
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<td></td>
<td>-123.1a</td>
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<td>Ph₃Sn(C₆H₄Me-3)</td>
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<td>-120.2a</td>
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<tr>
<td>R₃SnOR'</td>
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<tr>
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<tr>
<td></td>
<td>-117.1</td>
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<tr>
<td>Ph₃Sn(CH₂)₃OC(O)Me</td>
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(continued overleaf)
### TABLE 8. (continued)

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<th>Solvent</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>R&lt;sub&gt;3&lt;/sub&gt;SnO</td>
<td>R = Ph 4-MeC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>-106.4, -94.5</td>
<td>CDCl&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>3-(Ph&lt;sub&gt;3&lt;/sub&gt;Sn)propyl 2,3:5,6-di-O-isopropylidene-α-mannofuranoside</td>
<td></td>
<td>-100.1</td>
<td>CDCl&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>3-(Ph&lt;sub&gt;3&lt;/sub&gt;Sn)propyl 2,3:5,6-di-O-isopropylidene-β-mannofuranoside</td>
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<td>-99.5</td>
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<tr>
<td>3-(Ph&lt;sub&gt;3&lt;/sub&gt;Sn)propyl-α-D-mannopyranoside</td>
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<td>-100.1</td>
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<tr>
<td>1,2:5,6-di-O-isopropylidene-3-O-3-(Ph&lt;sub&gt;3&lt;/sub&gt;Sn)propyl-α-D-glucofuranose</td>
<td></td>
<td>-99.7</td>
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<td>1,2:3,4-di-O-isopropylidene-6-O-(Ph&lt;sub&gt;3&lt;/sub&gt;Sn)methyl-α-D-galactopyranose</td>
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<td>-146.2</td>
<td>CDCl&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>3-(Ph&lt;sub&gt;3&lt;/sub&gt;Sn)propyl hepta-O-acetyl-β-D-lactoside</td>
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<td>-99.6</td>
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<td>-106.2</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;D&lt;sub&gt;6&lt;/sub&gt;</td>
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<tr>
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<td>R&lt;sub&gt;3&lt;/sub&gt;SnB</td>
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<tr>
<td>R&lt;sub&gt;3&lt;/sub&gt;SnZ (Z = Si, Pb)</td>
<td>Ph&lt;sub&gt;3&lt;/sub&gt;Sn−(SiMe&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;n&lt;/sub&gt;−SnPh&lt;sub&gt;3&lt;/sub&gt;</td>
<td>n = 1</td>
<td>-155.5, 157.5, 155.0, 156.4, 156.6</td>
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<tr>
<td>Ph&lt;sub&gt;3&lt;/sub&gt;Sn−SiMe&lt;sub&gt;2&lt;/sub&gt;−CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;−PPh&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>-330</td>
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<sup>a</sup>Solid state NMR
6. Further advances in germanium, tin and lead NMR

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<th>Compound</th>
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<th>Reference</th>
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<td>(3,5-Me₂C₆H₃)₃SnCl</td>
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<td>(3-C₆F₅)₃SnBr</td>
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<td>(3-ClC₆H₄)₄Sn</td>
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<td>(3,5-Cl₂C₆H₃)₄Sn</td>
<td>-122.6</td>
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(continued overleaf)
### TABLE 10. (continued)

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<th>Reference</th>
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<tr>
<td>(3.5-FC₆H₃)₄Sn</td>
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<td>(4-F₃CC₆H₄)₄Sn</td>
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<td>126.3</td>
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*Solid state NMR*

### TABLE 11. Transition metal–tin complexes

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<th>Compound</th>
<th>Chemical shift (ppm)</th>
<th>Solvent</th>
<th>Reference</th>
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<td>([Ph₃P]₂Cl(CO)(Bu₃Sn)Ru]</td>
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<td>([Ph₃P]₂Cl(CO)(Me₃Sn)(4-MeC₆H₄CN)Os]</td>
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<td>CDCl₃</td>
<td>191</td>
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<td>([Ph₃P]₂Cl(CO)(Bu₃Sn)(η²-S₂CNMe₂)Ru]</td>
<td>6.6</td>
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<td>([Ph₃Sn]Me(CO)₂/i-Pr-DAB)Ru]²</td>
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<td>([Ph₃Sn]Mn(CO)₅)(i-Pr-DAB)Ru]²</td>
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<td>([Ph₃Sn]Co(CO)₅)(i-Pr-DAB)Ru]²</td>
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<td>THF-d₈</td>
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<td>[Cp(CO)₂W]₂Sn(OSiPh₂)₂O</td>
<td>114.8</td>
<td>C₆D₆</td>
<td>246</td>
</tr>
<tr>
<td>[Cp(CO)₂W]²-BuSn(OSiPh₂)₂O</td>
<td>71.5</td>
<td>CH₂Cl₂</td>
<td>246</td>
</tr>
<tr>
<td>[PtMe₂(Me₂SnZ)₂(Bu₂bipy)]</td>
<td>Z = S</td>
<td>138.1</td>
<td>CD₂Cl₂</td>
</tr>
<tr>
<td></td>
<td>Z = S</td>
<td>51.9</td>
<td>CD₂Cl₂</td>
</tr>
<tr>
<td></td>
<td>Se</td>
<td>-60.3</td>
<td>CD₂Cl₂</td>
</tr>
<tr>
<td></td>
<td>Te</td>
<td>-168.1</td>
<td>CD₂Cl₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-340.3</td>
<td>CD₂Cl₂</td>
</tr>
<tr>
<td>[PtMe₂((Me₂SnZ)(Ph₂SnZ))(Bu₂bipy)]</td>
<td>Z = S</td>
<td>-51.7</td>
<td>CD₂Cl₂</td>
</tr>
<tr>
<td></td>
<td>Z = Se</td>
<td>-32.7</td>
<td>CD₂Cl₂</td>
</tr>
<tr>
<td></td>
<td>Z = Te</td>
<td>-57.4</td>
<td>CD₂Cl₂</td>
</tr>
<tr>
<td></td>
<td>Te</td>
<td>-72.5</td>
<td>CD₂Cl₂</td>
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<td></td>
<td>-334.5</td>
<td>CD₂Cl₂</td>
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<tr>
<td></td>
<td></td>
<td>-160.5</td>
<td>CD₂Cl₂</td>
</tr>
<tr>
<td>[PtMe₂((Me₂SnZ)(Me₂SnZ'))(Bu₂bipy)]</td>
<td>Z = S</td>
<td>-41.3</td>
<td>CD₂Cl₂</td>
</tr>
<tr>
<td></td>
<td>Z' = Se</td>
<td>-51.6</td>
<td>CD₂Cl₂</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>-50.5</td>
<td>CD₂Cl₂</td>
</tr>
<tr>
<td></td>
<td>Se</td>
<td>-128.4</td>
<td>CD₂Cl₂</td>
</tr>
<tr>
<td></td>
<td>Te</td>
<td>-86.0</td>
<td>CD₂Cl₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-193.2</td>
<td>CD₂Cl₂</td>
</tr>
<tr>
<td>[PtMe₂((Ph₂SnS)(Ph₂SnSe))(Bu₂bipy)]</td>
<td>Z = Se</td>
<td>-173.1</td>
<td>CD₂Cl₂</td>
</tr>
<tr>
<td></td>
<td>Z = Te</td>
<td>-22.3</td>
<td>CD₂Cl₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-160.5</td>
<td>CD₂Cl₂</td>
</tr>
</tbody>
</table>
6. Further advances in germanium, tin and lead NMR

### TABLE 11. (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift (ppm)</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
</table>
| [PtMe₂((Me₂SnSe)(Ph₂SnS))(Bu₂bipy)] | -188.6  
23.6 | CD₂Cl₂ | 249 |
| [Cp(CO)₂W]Sn(Bu-τ)X₂ | X = Ph  
Cl | C₆D₆ | 246 |

* aDAB = N,N'-diisopropyl-1,4-diaza-1,3-butadiene;  
* bCOD = cyclooctadiene;  
* c99% ¹³CO enriched product, 20°C.

### TABLE 12. Compounds of the type R₂SnX₂

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift (ppm)</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
</table>
| [t-Bu₂SnO][Ph₂SiO]₂ | -167.1<sup>a</sup>  
-119.5<sup>b</sup> | CDCl₃ | 234 |
| [η⁵-C₅H₅]₃Sn₃[Cl₂] | 7.8 | C₆D₆ | 139 |
| [η⁵-C₅H₅]₃Sn₃[Cl₂] | 125.5 | C₆D₆ | 235 |
| [η⁵-C₅H₅]₃Sn₃[Cl₂] | -102.4 | C₆D₆ | 235 |
| R₂SnX₂ | X = O  
S  
Se  
Te | 64.6  
66.5  
28.1  
-70.7 | C₆D₆ | 235 |
| RP(Me₂Sn(η⁵-C₅H₅))Fe | R = Me  
t-Bu  
c-C₆H₁₁  
Ph | -47.6  
-5.3  
1.4  
1.3 | C₆D₆ | 248 |
| ZPhP(MeSn(η⁵-C₅H₅))Fe | Z = Cr(CO)₅  
Mo(CO)₅  
W(CO)₅ | 11.1  
11.6  
13.1 | C₆D₆ | 248 |
| [η⁵-C₅H₅]₃Sn₃[Cl₂] | X = Cl  
S-Naph-2 | 53.0  
126.1 | CDCl₃ | 148 |
| [η⁵-C₅H₅]₃Sn₃[Cl₂] | R = Me R' = Me | -6.0 | CDCl₃ | 138 |
| [η⁵-C₅H₅]₃Sn₃[Cl₂] | Me  
Et  
t-Bu  
Ph | -4.9  
-20.5  
-71.3  
-114.6 | C₆D₆ | 237 |

(continued overleaf)
TABLE 12. (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift (ppm)</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t$-Bu$_2$ClSnOSi(Bu-t)$_2$Cl</td>
<td>$-58.5$</td>
<td>CDCl$_3$</td>
<td>237</td>
</tr>
<tr>
<td>$t$-Bu$_2$ClSnOSi(Bu-t)$_2$OH</td>
<td>$-56.8$</td>
<td>CDCl$_3$</td>
<td>237</td>
</tr>
<tr>
<td>$t$-Bu$_2$Sn(OSiH(Bu-t)$_2$)$_2$</td>
<td>161.4</td>
<td>CDCl$_3$</td>
<td>237</td>
</tr>
<tr>
<td>$t$-Bu$_2$Sn(OSiF(Bu-t)$_2$)$_2$</td>
<td>164.7</td>
<td>CDCl$_3$</td>
<td>237</td>
</tr>
<tr>
<td>$t$-Bu$_2$ClSnOSiH(Bu-t)$_2$Cl</td>
<td>58.4</td>
<td>CDCl$_3$</td>
<td>237</td>
</tr>
<tr>
<td>$t$-Bu$_2$Sn(OSiF(Bu-t)$_2$)$_2$</td>
<td>161.9</td>
<td>CDCl$_3$</td>
<td>237</td>
</tr>
<tr>
<td>[(Me$_3$Si)$_2$CH]$_2$Sn(NCO)$_2$</td>
<td>4.7</td>
<td>C$_6$D$_5$CD$_3$</td>
<td>58</td>
</tr>
<tr>
<td>[(Me$_3$Si)$_2$CH]$_2$SnCl$_2$</td>
<td>21.8</td>
<td>C$_6$D$_5$CD$_3$</td>
<td>58</td>
</tr>
<tr>
<td>[Me$_2$N(CH$_2$)$_3$]$_2$SnPh$_2$</td>
<td>103.0</td>
<td>CDCl$_3$</td>
<td>174</td>
</tr>
<tr>
<td>[Me$_2$N(CH$_2$)$_3$]$_2$SnCl$_2$</td>
<td>50.0</td>
<td>CDCl$_3$</td>
<td>174</td>
</tr>
<tr>
<td>PrR$_2$Sn(H)</td>
<td>R = Bu, Ph, c-C$<em>6$H$</em>{11}$</td>
<td>$-89.0$, $-137$, $-87.9$</td>
<td>C$_6$D$_6$</td>
</tr>
<tr>
<td>$i$-Pr$_3$Si−Sn(H)(C$<em>6$H$</em>{14}$−c)$_2$</td>
<td>$-196.6$</td>
<td>C$_6$D$_6$</td>
<td>386</td>
</tr>
<tr>
<td>$t$-Bu$_2$Sn(H)−(SiMe$_2$)$_n$−Sn(H)(Bu-t)$_2$</td>
<td>n = 1</td>
<td>$-111.3$</td>
<td>C$_6$D$_6$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>$-123.6$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>$-120.4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>$-122.2$</td>
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<tr>
<td></td>
<td></td>
<td>5</td>
<td>$-120.1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>$-121.7$</td>
</tr>
<tr>
<td>$t$-Bu$_2$Sn(X)−(SiMe$_2$)$_n$−Sn(X)(Bu-t)$_2$</td>
<td>X = Cl, Br</td>
<td>n = 2</td>
<td>104.1, 100.8, 98.1, 101.8, 100.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3, 4, 5, 6</td>
<td>CDCl$_3$</td>
</tr>
<tr>
<td></td>
<td>X = Br</td>
<td>n = 2</td>
<td>97.4, 97.7, 93.1, 98.3</td>
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<tr>
<td></td>
<td></td>
<td>3, 4, 5, 6</td>
<td>CDCl$_3$</td>
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</table>
TABLE 12. (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift (ppm)</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = CH₂CH = CH₂</td>
<td>-101.6</td>
<td>CDCl₃</td>
<td>168</td>
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<tr>
<td>Cl</td>
<td>-88.9</td>
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<td></td>
</tr>
<tr>
<td>Br</td>
<td>-236.5</td>
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<td></td>
</tr>
<tr>
<td>CH₂Ph</td>
<td>-102.0</td>
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<tr>
<td>Ph</td>
<td>-158.2</td>
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<td></td>
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<tr>
<td>Et</td>
<td>-61.5</td>
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<td></td>
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<tr>
<td>(C₆F₅)₂SnR₂</td>
<td>-263.3</td>
<td>C₆D₆</td>
<td>259</td>
</tr>
<tr>
<td>(CH₂=CH)₂SnH₂</td>
<td>-88.9</td>
<td>C₆D₆</td>
<td>259</td>
</tr>
<tr>
<td>(CH₂=CH)₂Sn(H)Cl</td>
<td>-13.2</td>
<td>CDCl₃</td>
<td>177</td>
</tr>
<tr>
<td>H₂C≡C=CH₂Sn(Cl)₂CH=CH₂</td>
<td>-35.7</td>
<td>CDCl₃</td>
<td>177</td>
</tr>
<tr>
<td>X</td>
<td>Y</td>
<td>X</td>
<td>Y</td>
</tr>
<tr>
<td>Me</td>
<td>Cl</td>
<td>Me</td>
<td>Cl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Me</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>R = H; R' = H</td>
<td>-71.4</td>
<td>C₆D₆</td>
<td>244</td>
</tr>
<tr>
<td>Me</td>
<td>-73.4</td>
<td>-61.5</td>
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</tr>
<tr>
<td>Me₁²</td>
<td>-40.1</td>
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<tr>
<td>Pr</td>
<td>-72.7</td>
<td>-62.4</td>
<td></td>
</tr>
<tr>
<td>Bu</td>
<td>-72.5</td>
<td>-62.4</td>
<td></td>
</tr>
<tr>
<td>n-C₅H₁₁</td>
<td>-72.5</td>
<td>-62.5</td>
<td></td>
</tr>
<tr>
<td>Ph</td>
<td>-66.7</td>
<td>-56.6</td>
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<tr>
<td>CH(OH)Et</td>
<td>-66.1</td>
<td>-64.4</td>
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<tr>
<td>R' = R = MeOOC</td>
<td>-35.7</td>
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<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-)-MenSnMe₂(CHPh=CHPhCOOMe)⁶,⁷</td>
<td>1.7</td>
<td>CDCl₃</td>
<td>245</td>
</tr>
<tr>
<td>(-)-MenSnMe₂(CHPh=CHPhCOOMe)⁶</td>
<td>-1.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-)-MenSnMe₂(CHPh=CHPhCOO(-)-Men)⁶,⁷</td>
<td>4.9</td>
<td>CDCl₃</td>
<td>245</td>
</tr>
<tr>
<td>(-)-MenSnMe₂(CHPh=CHPhCOO(-)-Men)⁶,⁷</td>
<td>-2.8</td>
<td>CDCl₃</td>
<td>245</td>
</tr>
</tbody>
</table>

(continued overleaf)
<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift (ppm)</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(—)-MenSnMe(_2)(CHPh—CHPhCOO(—)-Men)(^e)</td>
<td>4.0</td>
<td>CDCl(_3)</td>
<td>245</td>
</tr>
<tr>
<td>(—)-MenSnMe(_2)(CHPh—CHPhCN)(^e)</td>
<td>0.5</td>
<td>CDCl(_3)</td>
<td>245</td>
</tr>
<tr>
<td>Me(_2)Sn(C≡C—SiMe(_2)—C≡CR)(_2)</td>
<td>R = H</td>
<td>−164.5</td>
<td>C(_6)D(_6)</td>
</tr>
<tr>
<td></td>
<td>Bu</td>
<td>−166.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>t-Bu</td>
<td>−165.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>i-Pent</td>
<td>−166.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ph</td>
<td>−164.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SiMe(_3)</td>
<td>−164.1</td>
<td></td>
</tr>
<tr>
<td>R = H</td>
<td>−103.4</td>
<td>C(_6)D(_6)</td>
<td>133</td>
</tr>
<tr>
<td>Bu</td>
<td>−105.0</td>
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<tr>
<td>t-Bu</td>
<td>−106.2</td>
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<tr>
<td>3-Me-Bu</td>
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<tr>
<td>Ph</td>
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<td></td>
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</tr>
<tr>
<td>SiMe(_3)</td>
<td>−102.6</td>
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<td></td>
</tr>
</tbody>
</table>

\(^{a}\)MAS spectra.

\(^{b}\)equilibrium between 6-membered ring (in solution) and polymer (solid state).

\(^{c}\)Measured in THF with a D\(_2\)O-capillary.

\(^{d}\)Me in a second isomer.

\(^{e}\)Men = Menthol.

\(^{f}\)Differs from the following compound in the conformation of the Ph group.

### TABLE 13. Ring systems containing tin in the ring skeleton

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift (ppm)</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = 2,4,6-(i-Pr)(_3)C(_6)H(_2)</td>
<td>R' = Me</td>
<td>40.5</td>
<td>CDCl(_3)</td>
</tr>
<tr>
<td></td>
<td>Ph</td>
<td>42.5</td>
<td></td>
</tr>
<tr>
<td>R = 2,4,6-(i-Pr)(_3)C(_6)H(_2)</td>
<td>R' = i-Pr</td>
<td>135.2</td>
<td>CDCl(_3)</td>
</tr>
<tr>
<td></td>
<td>t-Bu</td>
<td>121.9</td>
<td></td>
</tr>
<tr>
<td>R'—B—R</td>
<td>R = 2,4,6-(i-Pr)(_3)C(_6)H(_2)</td>
<td>−117.8</td>
<td>CDCl(_3)</td>
</tr>
</tbody>
</table>
### TABLE 13. (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift (ppm)</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>([t\text{-Bu}_2\text{SnO}]_3)</td>
<td>(-83.5)</td>
<td>CDCl(_3)</td>
<td>237</td>
</tr>
<tr>
<td>([t\text{-Bu}_2\text{SnO}]_2\text{Si(Bu-t)}_2)</td>
<td>(-107.2)</td>
<td>CDCl(_3)</td>
<td>237</td>
</tr>
<tr>
<td>([t\text{-Bu}_2\text{SnOSi(Bu-t)}_2]_2)</td>
<td>(-106.6^a), (-178.1^a)</td>
<td>CDCl(_3)</td>
<td>237</td>
</tr>
<tr>
<td>([t\text{-Bu}_2\text{SnOSiPh}_2]_2)</td>
<td>(-149.5)</td>
<td>CDCl(_3)</td>
<td>237</td>
</tr>
<tr>
<td>(t\text{-Bu}_2\text{Sn[OSi(Bu-t)}_2]_3)</td>
<td>(-145.6^a), (-153.1)</td>
<td>CDCl(_3)</td>
<td>237</td>
</tr>
<tr>
<td>(t\text{-Bu}_2\text{SnSi(But)}_2)</td>
<td>(-150.2^a)</td>
<td>CDCl(_3)</td>
<td>237</td>
</tr>
<tr>
<td>(t\text{-Bu}_2\text{SnSiF(But)}_2)</td>
<td>(-161.2^a), (-164.9^a)</td>
<td>CDCl(_3)</td>
<td>237</td>
</tr>
<tr>
<td>(t\text{-Bu}_2\text{Sn}[O\text{SiMe}_2\text{CH}_2]_2)</td>
<td>(-135.7)</td>
<td>CDCl(_3)</td>
<td>237</td>
</tr>
<tr>
<td>(t\text{-Bu}_2\text{Sn[SiMe}_3\text{CH}_2]_2)</td>
<td>(-169.2)</td>
<td>CDCl(_3)</td>
<td>237</td>
</tr>
<tr>
<td>(t\text{-Bu}_2\text{Sn[OSiMe}_2\text{CH}_2]_2)</td>
<td>(-124.1), (-131.8)</td>
<td>CDCl(_3)</td>
<td>237</td>
</tr>
<tr>
<td>(t\text{-Bu}_2\text{Sn[OSiMe}_2\text{CH}_2]_2)</td>
<td>(-125.7)</td>
<td>CDCl(_3)</td>
<td>237</td>
</tr>
<tr>
<td>(t\text{-Bu}_2\text{Sn[OSiMe}_2\text{CH}_2]_2)</td>
<td>(-123.0^a), (-132.3^a)</td>
<td>CDCl(_3)</td>
<td>237</td>
</tr>
<tr>
<td>(t\text{-Bu}_2\text{Sn[OSiMe}_2\text{CH}_2]_2)</td>
<td>(-135.7)</td>
<td>CDCl(_3)</td>
<td>237</td>
</tr>
<tr>
<td>(t\text{-Bu}_2\text{Sn[OSiMe}_2\text{CH}_2]_2)</td>
<td>(-169.2)</td>
<td>CDCl(_3)</td>
<td>237</td>
</tr>
<tr>
<td>(t\text{-Bu}_2\text{Sn[OSiMe}_2\text{CH}_2]_2)</td>
<td>(-124.1), (-131.8)</td>
<td>CDCl(_3)</td>
<td>237</td>
</tr>
<tr>
<td>(t\text{-Bu}_2\text{Sn[OSiMe}_2\text{CH}_2]_2)</td>
<td>(-125.7)</td>
<td>CDCl(_3)</td>
<td>237</td>
</tr>
<tr>
<td>(t\text{-Bu}_2\text{Sn[OSiMe}_2\text{CH}_2]_2)</td>
<td>(-123.0^a), (-132.3^a)</td>
<td>CDCl(_3)</td>
<td>237</td>
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\(t\text{-Bu}_2\text{Sn[OSiMe}_2\text{CH}_2]_2\) | \(-124.1\), \(-131.8\) | CDCl\(_3\) | 237 |
| \(t\text{-Bu}_2\text{Sn[OSiMe}_2\text{CH}_2]_2\) | \(-125.7\) | CDCl\(_3\) | 237 |
| \(t\text{-Bu}_2\text{Sn[OSiMe}_2\text{CH}_2]_2\) | \(-123.0^a\), \(-132.3^a\) | CDCl\(_3\) | 237 |
| \(t\text{-Bu}_2\text{Sn[OSiMe}_2\text{CH}_2]_2\) | \(-135.7\) | CDCl\(_3\) | 237 |
| \(t\text{-Bu}_2\text{Sn[OSiMe}_2\text{CH}_2]_2\) | \(-169.2\) | CDCl\(_3\) | 237 |

6. Further advances in germanium, tin and lead NMR

(continued overleaf)
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*MAS spectra;*
*higher-order spin systems.
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</table>
Compounds containing one or two silyl substituents at one tin atom display tin-119 chemical shifts which are similar to those of the corresponding tin hydrides ($\pm 30$ ppm) as summarized below.

$$\delta^{119}\text{Sn: } R_3\text{SnH} \approx R_3\text{Sn} - \text{Si}$$

$$\delta^{119}\text{Sn: } R_2\text{SnH}_2 \approx \text{Si} - R_2\text{Sn} - \text{Si}$$

Examples for such derivatives are given in Tables 5, 8, 12 and 13. Bulky substituents ($t$-Bu, $i$-Pr) at the tin and/or silicon atoms may cause slightly higher deviations. Exceptions are compounds with a relatively high ring strain and therefore smaller bond angles such as, for example, four-membered Si–Sn rings (Chart 1). The $^{119}\text{Sn}$ resonance is shifted significantly to lower field values and this effect is in good agreement with results shown for rings containing carbon instead of the silyl moieties.

CHART 1. $^{119}\text{Sn}$ NMR chemical shift of tin-modified cyclosilanes
In contrast to carbon–tin rings the differences between the $^{119}$Sn chemical shifts of five- and six-membered Si–Sn rings are much smaller, possibly due to the larger Si–Si and Si–Sn bond lengths, atomic radii and therefore to the larger bond angles.

b. Tin(IV) compounds with coordination number higher than four. In the presence of Lewis bases tin can act as a Lewis acid. Higher coordination numbers than four are then possible and are very common. Coordination numbers of five$^{299–314}$ or six$^{310–363}$ are common but arrangements of seven and eight atoms surrounding the tin are rare. Especially for octacoordinated tin atoms only a few examples are known and they are from pure inorganic chemistry (e.g. Sn(NO$_3$)$_4$). $^{119}$Sn chemical shifts for some selected compounds having tin surrounded by seven ligands are found in Table 15. The geometry around the tin atom can change easily. A good demonstration of this point are the carboxylato derivatives of the tetraorganodistannoxanes. The three structures proposed for this type of compound are sketched in Chart 2. The structures consist of a central four-membered ring with two endocyclic tin atoms connected via oxygen bridges to the two exocyclic tin atoms. The carboxylato ligands O$_2$C–R (R = Me, t-Bu, p-Tol, C$_6$F$_5$) bond with one (X) or two oxygen atoms (Y) with the tin atom. The solution spectra consist of two lines at $−140$ and $−220$ ppm. One of the two signals is broader than the other. Two groups tried to assign these resonances. The main tool for studying such compounds was 2D $^1$H–$^{119}$Sn correlation NMR spectroscopy$^{30,32}$. Both groups agree that in solution, the first structure of chart 1 is present, but disagree in the assignment of signals to the endo- and exocyclic tin atoms. The $^{119}$Sn CP-MAS spectra for their compounds give three signals of equal intensity for the dibutyl but four for the dimethyl derivative (X, Y = MeCOO). This is interpreted by Willem and coworkers by the presence of the second structure in Chart 2.

Extensive spinning side bands are found and analyzed for the dimethyl derivative whereas the dibutyldistannaoxane does not show any such bands.

Solid state NMR indicates the third type structure of Chart 2, when R = Me, X = Y = t-BuCOO.

Similar cluster compounds are described in References 225–228 and 265. Another interesting cluster is (BuSn)$_{12}$O$_{14}$(OH)$_6$$^{2+}$ displaying two resonances at ca $−282$ and ca $−460$ ppm due to penta- and hexacoordinated tin$^{344,348,353}$. 

![Chart 2](image-url)

**Chart 2.** Sketches of tetramer diorganostannanes X = OCOR’, Y = O$_2$CR’ (R’ = Me, t-Bu, p-Tol, C$_6$F$_5$, R = Me, Bu)
### TABLE 15. Selected heptacoordinated tin(IV) compounds

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*MAS spectra.*
Many $^{119}$Sn NMR data exist for tin complexes with ligands of biological importance and activity such as *in vitro* antitumor activity or antimicrobial activity.\(^{229-232,365-381}\). The exact nature of the coordination sphere around the tin is not always given.

Triorganotin hydrides are common reductants in a large number of organic and organometallic syntheses. In many cases these reductions proceed by a normal radical reaction pathway. However, ionic reductions using tin hydrides also occur, but they were only sparsely investigated. Studies of ionic reduction processes with tin hydrides by using $^{119}$Sn NMR are found elsewhere.\(^{298,310}\)

## IV. LEAD NMR

### A. History and Technical Details

Since the first investigations about lead NMR in the late 1950s\(^{390}\) $^{207}$Pb NMR was, among other methods such as X-ray crystallography, one of the major tools for the determination of lead containing compounds in solution and in the solid state. In line with our own experience, solution state $^{207}$Pb NMR measurements are relatively simple to generate. Lead-207 chemical shifts were measured with respect to Me$_4$Pb or 1 M Pb(NO$_3$)$_2$ in water [$\delta$(Me$_4$Pb) = $\delta$(Pb(NO$_3$)$_2$) + 2961 ppm]. Absolute frequencies, relative to the $^1$H signal of Me$_4$Si = 100 MHz, were 20.920597 MHz for Me$_4$Pb (80% in toluene)\(^{391}\).

A number of reviews dealing with $^{207}$Pb NMR, sometimes in addition to other nuclei, were published over the years\(^{392-395}\). A summary of most NMR parameters and also chemical shifts was given by Wrackmeyer and Horchler in 1989\(^{394}\).

The $^{207}$Pb chemical shifts cover a range from +11 000 ppm to nearly −6500 ppm for lead(II) cyclopentadienyl derivatives. Analogous to $^{29}$Si/$^{73}$Ge, $^{29}$Si/$^{119}$Sn or $^{73}$Ge/$^{119}$Sn a linear relationships between $^{119}$Sn and $^{207}$Pb were found\(^{394,396-398}\).

### B. Recent Progress in $^{207}$Pb NMR Shifts

Selected $^{207}$Pb NMR data of organometallic lead compounds are given in Table 16. In over 50 publications $^{207}$Pb NMR chemical shifts have been reported since 1995. One of the major topics in recent years was investigations dealing with high resolution solid state $^{207}$Pb NMR. Besides pure inorganic compounds and theoretical studies\(^{399-402}\) a wide variety of $^{207}$Pb NMR of organometallic derivatives with Pb–X (X = C, N, P) and Pb–O–C\(^{403-418}\) bonds were described both in solution and in the solid state.\(^{207}\) Lead NMR deals mainly with compounds containing lead in the oxidation state IV. Only a limited, but in recent years increasing number of lead(II) derivatives were determined by $^{207}$Pb NMR\(^{394,401,419-423}\). An overview of compounds with direct lead–carbon, lead–nitrogen or–phosphorus bonds published since 1995 is given in Table 16\(^{419-443}\).

Due to the wide range of $^{207}$Pb chemical shifts, especially for lead(II) compounds, it is (in analogy to the tin compounds discussed above) impossible to recognize simple correlations between the coordination number at the lead atoms or the substituents directly bonded to lead(II) and the chemical shift value. What one can only do is make predictions within one class of compounds.

Lead-207 NMR will never be such an important spectroscopic tool like tin-119 NMR; however, it is very useful for the solution of many new and old problems in lead chemistry and will attract the interest of both the preparative as well as analytical chemist in the years to come.
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Mes\(_3\)PbBr

\( \delta = -97 \), CDCl\(_3\), 401

Mes\(_2\)PbBr\(_2\)

\( \delta = -149 \), CDCl\(_3\), 401

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</tr>
<tr>
<td>$R = R' = R'' = 2$-$\text{MeC}_6\text{H}_4$</td>
<td>180.9–181.3</td>
<td>CDCl$_3$</td>
<td>432</td>
</tr>
<tr>
<td>$R = R' = R'' = 4$-$\text{MeC}_6\text{H}_4$</td>
<td>172.6–173.3</td>
<td>CDCl$_3$</td>
<td>432</td>
</tr>
</tbody>
</table>

37 compounds with different substituents $R$, $R'$ and $R''$ are also given.

$\text{Pb}(\text{N(SiMe}_3)_2)_2$ | 4916 | $\text{C}_6\text{D}_6$ | 419 |
$\text{Pb}(\text{CH(SiMe}_3)_2)_2$ | 10050 | $\text{C}_6\text{D}_6$ | 420 |
$2,4,6$-[$(\text{SiMe}_3)_2\text{CH}]_3\text{C}_6\text{H}_2\text{Pb[CH(SiMe}_3)_2]$ | 8884 | $\text{C}_6\text{D}_5\text{CD}_3$ | 420 |

$R = \text{CH(SiMe}_3)_2$ | 9751 | $\text{C}_6\text{D}_5\text{CD}_3$ | 433 |
$\text{CH}_2\text{SiMe}_3$ | 8873 | $\text{C}_6\text{D}_6$ | 423 |
$\text{CHMe}_2$ | 8888 | $\text{C}_6\text{D}_6$ | 423 |

$R = \text{Me}$ | 7420 | $\text{C}_6\text{D}_6$ | 423 |
$R = \text{i-Bu}$ | 7853 | $\text{C}_6\text{D}_6$ | 423 |
$R = \text{Pr}$ | 6657 | $\text{C}_6\text{D}_6$ | 423 |
(2,3,4-Me₃-6-t-BuC₆H)₂Pb

2,3,4-Me₃-6-t-BuC₆H–Pb–Si(SiMe)₃

2,4,6-(t-Bu)₃C₆H₂–Pb–CH₂C₆H₃(Bu-t)₂-3,5

(continued overleaf)
<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift (ppm) ((^1J_{Pb−X}, \text{ Hz}))</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
</table>
| \[
\begin{align*}
\text{B} & \quad \text{N} \\
\text{SiMe}_3 & \quad \text{Pb} \\
\text{N} & \quad (\text{SiMe}_3)_2
\end{align*}
\] | 4968 | \(\text{C}_6\text{D}_6\) | 419 |
| \[
\begin{align*}
\text{Ph}_2\text{P} & \quad \text{N} \\
\text{PPh}_2 & \quad \text{Pb}^+ \\
\text{Pb}^+ & \quad \text{Pb}^+
\end{align*}
\] | −608 | \(\text{C}_6\text{D}_6\) | 429 |
| \[
\begin{align*}
\text{Me}_3\text{Pb} & \quad \text{B} \\
\text{Me}_2\text{SO}^+ & \quad \text{B}^−\text{Et}_2 \\
\text{Me}_2\text{N} & \quad \text{Et}
\end{align*}
\] | −27.6 | \(\text{CDCl}_3\) | 435 |
$[\text{Me}_3\text{Pb}]_4[\text{Fe(CN)}_6]^+\text{H}_2\text{O}$

$[\text{Me}_3\text{Pb}]_4[\text{Ru(CN)}_6]^+\text{H}_2\text{O}$

$[\text{Me}_3\text{Pb}]_4[\text{Fe(CN)}_6]$  

$[\text{Me}_3\text{Pb}]_4[\text{Ru(CN)}_6]$  

![Diagram of a molecule with labels Tip, M = Cr, Mo, W, and C6D6](image)

<table>
<thead>
<tr>
<th>M</th>
<th>9563</th>
<th>C6D6</th>
<th>422</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>9659</td>
<td></td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>9374</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$In the solid state;
$^b$Tip = 2,4,6-(i-Pr)3C6H2;
$^c$\(1\) \(J\)\(^{207}\text{Pb}–^{29}\text{Si}\);
$^d$\(1\) \(J\)\(^{207}\text{Pb}–^{119}\text{Sn}\);
$^e$External D2O;
$^f$At 358 K;
$^g$At 198 K.
V. REFERENCES

Further advances in germanium, tin and lead NMR
6. Further advances in germanium, tin and lead NMR

6. Further advances in germanium, tin and lead NMR


241. F. Uhlig and U. Hermann, unpublished results.


246. F. Uhlig and U. Hermann, unpublished results.


Further advances in germanium, tin and lead NMR


456 Heinrich Chr. Marsmann and Frank Uhlig


6. Further advances in germanium, tin and lead NMR

Further advances in germanium, tin and lead NMR

CHAPTER 10

Free and complexed $R_3M^+$ cations
($M = \text{Ge, Sn, Pb}$)

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Fax: (303) 492 0799; e-mail: michl@eefus.colorado.edu

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I. INTRODUCTION

The heavier congeners of carbenium ions, $R_3E^+$ ($E = \text{Si, Ge, Sn, Pb}$), have been of long-standing interest. Their preparation and structure in condensed media have been

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a subject of extensive studies and controversy for decades because of a fundamental interest in understanding similarities and differences between carbon and heavier group 14 elements. The silyl cations, $R_3Si^+$, have received the most attention$^{1-6}$ and their heavier analogues relatively little. Several reasons could be suggested to explain this. For example, increased metallic character of these elements places their compounds into an inorganic category, and their toxicity makes them less attractive to deal with. The latest book on the chemistry of organic germanium, tin and lead compounds$^7$ does not contain a chapter discussing their cations. We are unaware of any other full review on the subject. It is only mentioned briefly when the related cyclotrigermanium cation is discussed in reviews by Belzner$^8$ and Schleyer$^9$. Therefore, we tried to include older literature relevant to the subject.

A few words about the use of the word ‘cation’ and the ‘$R_3M^+$’ notation in our review are in order. ‘Cation’ means a species with a positive charge of +1 and ‘$R_3M^+$’ might be understood as a three-coordinate metal cation free of any significant interactions. However, with a couple of possible exceptions, in the case of group 14 elements such free species are only known in the gas phase, and their structures have not been determined experimentally. In bulk, these ions generally are complexed to one or more solvent molecules or a counterion. In solution, group 14 cations would therefore be more accurately represented by ‘$[R_3ML_n]^+$’, where $n$ is typically 1 or 2 and $M$ is only partially positively charged. In our review we concentrated on cations in which the three $R$ groups are covalently bound to $M$ and interactions with $L$ are weak. Throughout the text we used the word ‘cation’ and the ‘$R_3M^+$’ notation for such complexed cations, both for simplicity and because in many cases neither $n$ nor the exact nature of $L$ (a solvent molecule or a counterion) are known. The existence of such complexation was not always recognized explicitly in the earlier literature.

II. PREPARATION

A. Gas Phase

The formation of triorganogermyl and triorganostannyl cations in the gas phase was first reported half a century ago$^{10-13}$. There are several reviews of older literature discussing the preparation of gaseous group 14 cations$^{14-16}$. In a comprehensive study Lappert and coworkers$^{17}$ studied the mass spectra and measured the ionization potentials of the species $Me_3M$/$MeMe_2$ and $Me_4M$ ($M, M' = C, Si, Ge, Sn, Pb$) and the appearance potentials of the $Me_3M^+$ cations (Table 1). They found that in all spectra the $Me_3M^+$ cations were the most abundant and that their abundance decreased with increasing atomic weight of $M$, while that of the $Me_2M^+$, $MeM^+$ and $M^+$ cations increased. Both the ionization potentials and the appearance potentials decreased with increasing atomic weight of $M$ as would be expected for weaker $M-M'$ and $M-C$ bonds. Using these measurements the authors also calculated enthalpies of formation for the $Me_3M^+$ cations (Table 2) which showed that the formation of $Me_3Si^+$ and $Me_3Ge^+$ cations is thermodynamically more favorable than that of the $Me_3C^+$ cation. The appearance potentials for $Me_3Sn^+$ and $Me_2RSn^+$ cations produced by electron impact from $Me_3SnR$ ($R = Me, Et, n-Pr, i-Pr, n-Bu, i-Bu, t-Bu$ and $Me_3Sn$) were also measured$^{18}$ and the results are listed in Table 3. Based on these measurements it was concluded that the $Me_3Sn^+$ cation is energetically favored over $Me_3C^+$ unless unusually strong bonds to the $Sn$ atom must be broken to form the former. There appeared to be no clear relationship between the length or branching of the alkyl substituent and appearance potentials.
10. Free and complexed $R_3M^+$ cations ($M = Ge, Sn, Pb$)

**TABLE 1.** Ionization (IP) and appearance (AP) potentials for $Me_3M-M'\text{Me}_3$ and $Me_3M-M\text{Me}$ compounds$^{17}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>IP (eV)</th>
<th>AP (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Me_3C-Ge\text{Me}_3$</td>
<td>8.98</td>
<td>10.19</td>
</tr>
<tr>
<td>$Me_3C-Sn\text{Me}_3$</td>
<td>8.34</td>
<td>10.03</td>
</tr>
<tr>
<td>$Me_3C-Pb\text{Me}_3$</td>
<td>7.99</td>
<td>9.45</td>
</tr>
<tr>
<td>$Me_3Si-Si\text{Me}_3$</td>
<td>8.35</td>
<td>10.22</td>
</tr>
<tr>
<td>$Me_3Ge-Ge\text{Me}_3$</td>
<td>8.18</td>
<td>9.96</td>
</tr>
<tr>
<td>$Me_3Sn-Sn\text{Me}_3$</td>
<td>8.02</td>
<td>9.51</td>
</tr>
<tr>
<td>$Me_3Pb-Pb\text{Me}_3$</td>
<td>7.41</td>
<td>9.02</td>
</tr>
<tr>
<td>$Me_3Si-Ge\text{Me}_3$</td>
<td>8.31</td>
<td>10.19</td>
</tr>
<tr>
<td>$Me_3Si-Sn\text{Me}_3$</td>
<td>8.18</td>
<td>10.18</td>
</tr>
<tr>
<td>$Me_3Ge-Sn\text{Me}_3$</td>
<td>8.20</td>
<td>10.01</td>
</tr>
<tr>
<td>$Me_3Si-\text{Me}$</td>
<td>9.85</td>
<td>10.53</td>
</tr>
<tr>
<td>$Me_3Ge-\text{Me}$</td>
<td>9.29</td>
<td>10.05</td>
</tr>
<tr>
<td>$Me_3Sn-\text{Me}$</td>
<td>8.76</td>
<td>9.58</td>
</tr>
<tr>
<td>$Me_3Pb-\text{Me}$</td>
<td>8.26</td>
<td>8.77</td>
</tr>
</tbody>
</table>

**TABLE 2.** Standard enthalpies of formation for $Me_3M^+$ cations$^{17}$

<table>
<thead>
<tr>
<th>Cation</th>
<th>$\Delta H_f^{0}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Me_3C^+$</td>
<td>178.2</td>
</tr>
<tr>
<td>$Me_3Si^+$</td>
<td>158.56</td>
</tr>
<tr>
<td>$Me_3Ge^+$</td>
<td>164.99</td>
</tr>
<tr>
<td>$Me_3Sn^+$</td>
<td>184.25</td>
</tr>
<tr>
<td>$Me_3Pb^+$</td>
<td>200.07</td>
</tr>
</tbody>
</table>

**TABLE 3.** Ionization (IP) and appearance (AP) potentials for $Me_3Sn-R$ compounds$^{18}$

<table>
<thead>
<tr>
<th>$R$</th>
<th>IP (eV)</th>
<th>AP (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CH_3$</td>
<td>8.76</td>
<td>9.72</td>
</tr>
<tr>
<td>$C_2H_5$</td>
<td>—</td>
<td>9.49</td>
</tr>
<tr>
<td>$H_2C=CH$</td>
<td>—</td>
<td>10.44</td>
</tr>
<tr>
<td>$n-C_3H_7$</td>
<td>8.54</td>
<td>9.50</td>
</tr>
<tr>
<td>$i-C_3H_7$</td>
<td>8.28</td>
<td>9.17</td>
</tr>
<tr>
<td>$H_2C=CHC_2$</td>
<td>—</td>
<td>8.68</td>
</tr>
<tr>
<td>$n-C_4H_9$</td>
<td>—</td>
<td>9.80</td>
</tr>
<tr>
<td>$s-C_4H_9$</td>
<td>8.27</td>
<td>9.20</td>
</tr>
<tr>
<td>$i-C_4H_9$</td>
<td>8.34</td>
<td>9.79</td>
</tr>
<tr>
<td>$t-C_4H_9$</td>
<td>—</td>
<td>9.50</td>
</tr>
<tr>
<td>$SnMe_3$</td>
<td>8.08</td>
<td>9.85</td>
</tr>
</tbody>
</table>

$^{a}Me_3Sn-SnMe_2^+$. 

B. Strongly Acidic Media

It was found early on that, unlike silyl or germyl cations, stannyl cations can be prepared in strong acids from both triorganotin halides and tetraorganotin compounds. For instance, Robinson and coworkers\textsuperscript{19,20} studied solutions of tetramethyltin in sulfuric acid using cryoscopy and conductometry and concluded that ‘Me\textsubscript{3}Sn\textsuperscript{+}’ HSO\textsubscript{4}\textsuperscript{−} is present. These authors also showed that in the case of Ph\textsubscript{4}Sn no organostannyl cation is formed. Cryoscopy and conductometry suggested that ‘R\textsubscript{3}Sn\textsuperscript{+}’ cations are formed from various R\textsubscript{4}Sn and R\textsubscript{3}SnCl precursors (R = Et, n-Pr, Me, but not n-Bu) dissolved in sulfuric acid\textsuperscript{21}. Cationic tin species are also formed from methyltin hydrides in fluorosulfuric acid\textsuperscript{22}. A downfield \textsuperscript{119}Sn NMR signal found in the reaction of Me\textsubscript{4}Sn with SbCl\textsubscript{5} was attributed to the ‘Me\textsubscript{3}Sn\textsuperscript{+}’ cation\textsuperscript{23}.

C. Aqueous Solutions

While germyl cations are not known in aqueous solutions, reports on the formation of stannyl cations appeared as early as 1923\textsuperscript{24}. Since then, numerous investigations\textsuperscript{25–27} established that ions of the type R\textsubscript{3}M(OH\textsubscript{2})\textsubscript{n}\textsuperscript{+} (M = Sn, Pb) can be prepared in aqueous solutions. The early literature on this subject was reviewed in 1966 by Tobias\textsuperscript{28}. Among earlier studies one should mention a series of publications by the group of Rabenstein\textsuperscript{29,30} who studied plumbyl cation complexes in aqueous solutions by \textsuperscript{1}H NMR.

Presently, this subject received a renewed interest in terms of environmental effects of these cations. Two recent comprehensive reports\textsuperscript{31,32} describe the hydrolysis of trimethyltin compounds in aqueous and salt media at various temperatures and ionic strengths and provide an overview of the relevant literature.

D. Organic Solvents

Perhaps the most popular method of generating group 14 ‘R\textsubscript{3}M\textsuperscript{+}’ cationic species in organic media is the hydride abstraction reaction\textsuperscript{33}. For instance, in one of the early works Lambert and Schilf\textsuperscript{34} prepared germyl cations using hydride abstraction from R\textsubscript{3}GeH (R = Me, Ph) by Ph\textsubscript{3}C\textsuperscript{+}ClO\textsubscript{4}\textsuperscript{−} in sulfolane and dichloromethane. Tri-n-butylstannyl cations with less coordinating anions were generated similarly by Lambert and Kuhlmann\textsuperscript{35} in benzene (Scheme 1) and by Kira and coworkers\textsuperscript{36} in dichloromethane (Scheme 2). Halogen (and hydride) abstraction was used in the preparation of acetonitrile complexed R\textsubscript{3}Sn\textsuperscript{+}SbF\textsubscript{6}\textsuperscript{−} salts (R = t-Bu, t-BuCH\textsubscript{2}, cyclohexyl) from the corresponding triorganotin bromides (or hydrides) and SbF\textsubscript{5}\textsuperscript{37}.

\[
\begin{align*}
\text{R}_3\text{SnH} + \text{Ph}_3\text{C}^+ \text{ClO}_4^- & \rightarrow \text{R}_3\text{Sn}^+ \text{ClO}_4^- + \text{Ph}_3\text{CH} \\
\text{R}_3\text{SnCl} + \text{Ag}^+ \text{ClO}_4^- & \rightarrow \text{R}_3\text{Sn}^+ \text{ClO}_4^- + \text{AgCl} \\
\text{R}_3\text{SnH} + \text{B(C}_6\text{F}_5)_3 & \rightarrow \text{R}_3\text{Sn}^+ \text{BH(C}_6\text{F}_5)_3^- \\
\text{Bu}_3\text{SnH} + \text{Ph}_3\text{C}^+ \text{B(3,5-(CF}_3)_2\text{C}_6\text{H}_3)_4^- & \rightarrow \text{Bu}_3\text{Sn}^+ \text{B(3,5-(CF}_3)_2\text{C}_6\text{H}_3)_4^- + \text{Ph}_3\text{CH}
\end{align*}
\]

SCHEME 1

SCHEME 2
An alternative allyl leaving group approach was used by Lambert and coworkers in the preparation of the sterically hindered trimesitylgermyl and trimesitylstannyl cations (Scheme 3), analogous to their earlier preparation of the trimesitylsilyl ion.

Several examples of oxidative generation of \( \text{R}_3\text{Sn}^{+} \) cations have been reported. One-electron oxidation of \( \text{Me}_6\text{Sn}_2, \text{Me}_3\text{SnGeMe}_3 \) and \( \text{Me}_3\text{SnSiMe}_3 \) by the 10-methacridinium cation in acetonitrile was shown to lead to the (presumably solvent-complexed) trimethylstannyl cation. Oxidation of \( \text{R}_4\text{Sn}, \text{Me}_3\text{SnR} \) and \( \text{R}_6\text{Sn}_2 \) (\( \text{R} = \text{Me, Et, n-Bu, Ph, Vi} \)) by the thianthrene cation radical in acetonitrile also resulted in the formation of the corresponding presumably solvent-complexed \( \text{R}_3\text{Sn}^{+} \) cations. Recently, a series of nitrile complexes of \( t\text{-Bu}_3\text{M}^{+} \) cations (\( \text{M} = \text{Si, Ge, Sn} \)) has been prepared by Sekiguchi and coworkers by oxidation of the corresponding \( t\text{-Bu}_6\text{M}_2 \) dimetallanes with \( \text{Ph}_3\text{C}^+ \cdot \text{B}(3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3)_4^- \) (Scheme 4). The solvent-complexed \( \text{Ph}_3\text{Pb}^+ \) cation was prepared by an oxidation of \( \text{Ph}_6\text{Pb}_2 \) with \( \text{AgNO}_3 \) in acetonitrile. A crystalline solvent-free \( \text{CB}_{11}\text{Me}_{12}^- \) salt of the \( \text{n-Bu}_3\text{Sn}^+ \) cation with significant anion–cation interaction was prepared by Michl and coworkers in hexane by oxidizing \( \text{n-Bu}_6\text{Sn}_2 \) with \( \text{CB}_{11}\text{Me}_{12}^+ \) (Scheme 5).

Numerous studies of the electrooxidation of various organotin and organolead compounds have been conducted in the group of Kochi who showed electron transfer...
to be the limiting step of the oxidation. These oxidations are believed to first produce the radical cations \([R_3M-MR_3]^+\), which then decompose to give \('R_3M'^+ and \(R_3M'^\), and the radical is oxidized further. A number of oxidation potentials determined for group 14 dimetallanes \(R_3M-M'R_3\) (\(M\) and \(M' = Si, Ge, Sn, R = Me, Et\)) in acetonitrile\(^{49}\) and for triphenylstannyl derivatives in THF and DMF\(^{50}\) are summarized in Table 4. The oxidation potentials decrease with increasing atomic weight of \(M\) as expected. Substitution of \(Me\) by \(Et\) appears to have little effect, except in the case of \(Me_6Ge_2\) and \(Et_6Ge_2\), where the reported oxidation potential is significantly lower for the ethyl derivative, perhaps due to a different electrode mechanism or to an experimental problem. Out of the three oxidation potentials observed for \(Ph_3SnH\), the two lower ones were attributed to (i) \(Ph_3SnH \rightarrow Ph_3Sn^+ + H^+ + 1e^-\) and (ii) \(Ph_3Sn^+ \rightarrow 'Ph_3Sn'^+ + 1e^-\), and the third higher potential to the oxidation of \(Ph_6Sn_2\) formed by the dimerization of the \(Ph_3Sn^+\) radical. Oxidations of \(Ph_3SnI\), \(Ph_3SnSPh\) and \(Ph_3SnOCHO\) led directly to the \('Ph_3Sn'^+\) cation, while the corresponding chloride and triflate were not oxidizable.

**TABLE 4. Oxidation potentials \((E_p)\) of group 14 derivatives**

<table>
<thead>
<tr>
<th>Compound</th>
<th>(E_p), (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In MeCN, against Ag/AgCl/MeCN(^{49})</td>
</tr>
<tr>
<td>(Me_3Si-SiMe_3)</td>
<td>1.76</td>
</tr>
<tr>
<td>(Me_3Ge-GeMe_3)</td>
<td>1.70</td>
</tr>
<tr>
<td>(Me_3Sn-SnMe_3)</td>
<td>1.28</td>
</tr>
<tr>
<td>(Me_3Si-SiMe_3)</td>
<td>1.76</td>
</tr>
<tr>
<td>(Me_3Ge-SnMe_3)</td>
<td>1.60</td>
</tr>
<tr>
<td>(Et_3Si-SiEt_3)</td>
<td>1.76</td>
</tr>
<tr>
<td>(Et_3Ge-GeEt_3)</td>
<td>1.48</td>
</tr>
<tr>
<td>(Et_3Sn-SnEt_3)</td>
<td>1.24</td>
</tr>
<tr>
<td>(Et_3Si-GeEt_3)</td>
<td>1.70</td>
</tr>
<tr>
<td>(Et_3Si-SnEt_3)</td>
<td>1.56</td>
</tr>
<tr>
<td>(Et_3Ge-SnEt_3)</td>
<td>1.40</td>
</tr>
</tbody>
</table>
III. STRUCTURE AND PROPERTIES

A. Gas Phase

The structure of isolated $R_3M^+$ cations in the gas phase was the subject of several computational studies. Significant difficulties are associated with calculations for molecules containing the heavier elements, particularly Sn and Pb. NMR chemical shift calculations require consideration of relativistic effects (spin–orbit coupling). A discussion of these difficulties and of effective core potentials developed for these calculations is beyond the scope of this review.

Earliest studies concentrated on the $H_3M^+$ cations ($M = C, Si, Ge, Sn, Pb$) with planar $D_{3h}$ symmetry\textsuperscript{51}. However, CASSCF and MRSDCI calculations\textsuperscript{52} of the ground state geometries and energies of various germanium hydrides and hydride cations found a pyramidal $C_{3v}$ ground state structure for the $H_3Ge^+$ cation 4.6 kcal mol$^{-1}$ (CASSCF) or 6 kcal mol$^{-1}$ (MRSDCI) below the planar $D_{3h}$ structure, and predicted a rapid umbrella inversion at room temperature.

More recently, Schleyer and coworkers\textsuperscript{53} compared $H_3C^+$ with its heavier congeners using the B3LYP/6-311++G(2d,2p) method for C, Si, Ge and the B3LYP/TZ+ZP method with quasirelativistic effective core potentials for Sn and Pb, and found that at this level of calculation the $D_{3h}$ structures are favored for C, Si and Ge. For Sn and Pb the $D_{3h}$ cations were predicted to be metastable due to reductive elimination to HM$^+$–$H_2$, which are energetically favored. Another investigation of bonding in the $D_{3h}$ $H_3Ge^+$ cation showed that the HOMO($H_2$) and NLUMO($HGe^+$) orbitals are indeed appreciably populated and that this cation has a HGe$^+$–$H_2$ complex character\textsuperscript{54}. However, recently Schwarz and coworkers\textsuperscript{55} found using the B3LYP/6-311++G(2d,2p) method that the classical $D_{3h}$ $H_3Ge^+$ cation is by \textit{ca} 10 kcal mol$^{-1}$ more stable than the dihydrogen complex HGe($H_2$)$^+$. According to MP2/VDZ+P calculations\textsuperscript{56}, the $\pi$-donor ability of halogen substituents in Hal$_3M^+$ and HalH$_2M^+$ cations (Hal = F, Cl, Br, I; $M = C, Si, Ge, Sn, Pb$) increases from F to I for all of these cations, the thermodynamic stabilization of the cations by halogen substituents increases in the same order, and for the heavier congeners this stabilization is diminished compared to that in the carbocations.

B. Solution

1. Strong acids as solvents

Several important contributions to the understanding of the nature of ‘$R_3Sn^+$’ cations in superacids were made by Birchall and coworkers. They reported $^1H$ NMR and Mössbauer spectra for ‘Me$_3Sn^+$’ cations in sulfuric and fluorosulfuric acids\textsuperscript{57} and showed that cationic tin species formed under these conditions have coordination numbers of 5 or 6. The ‘Me$_3Sn^+$’ cation was not very stable in these solutions and was oxidized to ‘Me$_2Sn^2+$. The $^{119}Sn$ NMR chemical shift (Table 5) for ‘Me$_3Sn^+$’ in 92% sulfuric acid at 0°C is 194 ppm and, for ‘Et$_3Sn^+$’ in fluorosulfuric acid at −20°C, it is 288 ppm\textsuperscript{58}. Methyltin hydrides Me$_n$SnH$_{4-n}$ ($n = 1–3$) also gave cationic species in fluorosulfuric acid\textsuperscript{22}. Based on $^{119}Sn$ NMR and Mössbauer spectroscopy, it was concluded that the ‘Me$_2SnH_{3-n}$’ cations have two fluorosulfates occupying the positions above and below the plane of three covalently attached substituents, producing a trigonal–bipyramidal arrangement around the tin atom. A $^{119}Sn$ NMR chemical shift for Me$_3Sn^+$ in fluorosulfuric acid at −60°C was 322 ppm\textsuperscript{22}.


TABLE 5. $^{119}$Sn NMR chemical shifts for cationic tin species

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Chemical shift vs. Me$_4$Sn</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me$_4$Sn</td>
<td>92% H$_2$SO$_4$</td>
<td>194</td>
<td>58</td>
</tr>
<tr>
<td>Et$_3$Sn</td>
<td>HSO$_3$F</td>
<td>288</td>
<td>58</td>
</tr>
<tr>
<td>Me$_3$SnH</td>
<td>HSO$_3$F</td>
<td>322</td>
<td>22</td>
</tr>
<tr>
<td>Me$_2$SnH$_2$</td>
<td>HSO$_3$F</td>
<td>156</td>
<td>22</td>
</tr>
<tr>
<td>MeSnH$_3$</td>
<td>HSO$_3$F</td>
<td>−29</td>
<td>22</td>
</tr>
<tr>
<td>SnH$_4$</td>
<td>HSO$_3$F</td>
<td>−194</td>
<td>22</td>
</tr>
<tr>
<td>Me$_4$Sn</td>
<td>SbCl$_5$</td>
<td>208</td>
<td>23</td>
</tr>
<tr>
<td>Bu$_3$SnB(C$_6$F$_5$)$_3$H</td>
<td>C$_6$D$_6$</td>
<td>360</td>
<td>35</td>
</tr>
<tr>
<td>Bu$_3$SnClO$_4$</td>
<td>CD$_2$Cl$_2$</td>
<td>245</td>
<td>35</td>
</tr>
<tr>
<td>Bu$_3$SnClO$_4$</td>
<td>C$_6$D$_6$</td>
<td>231</td>
<td>35</td>
</tr>
<tr>
<td>Bu$_3$SnClO$_4$</td>
<td>sulfolane</td>
<td>150</td>
<td>35</td>
</tr>
<tr>
<td>Me$_3$SnClO$_4$</td>
<td>CD$_2$Cl$_2$</td>
<td>249</td>
<td>35</td>
</tr>
<tr>
<td>Me$_3$SnClO$_4$</td>
<td>C$_6$D$_6$</td>
<td>234</td>
<td>35</td>
</tr>
<tr>
<td>Bu$_3$SnB(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$</td>
<td>CD$_2$Cl$_2$</td>
<td>336</td>
<td>36</td>
</tr>
<tr>
<td>Bu$_3$SnOEt$_2$B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$</td>
<td>CD$_2$Cl$_2$</td>
<td>165</td>
<td>36</td>
</tr>
<tr>
<td>Bu$<em>3$SnClB$</em>{11}$Me$_{12}$</td>
<td>C$<em>6$D$</em>{12}$</td>
<td>454</td>
<td>44</td>
</tr>
<tr>
<td>Bu$<em>3$SnCB$</em>{11}$Me$_{12}$</td>
<td>solid</td>
<td>461</td>
<td>44</td>
</tr>
<tr>
<td>Bu$<em>3$SnOEt$<em>2$CB$</em>{11}$Me$</em>{12}$</td>
<td>C$<em>6$D$</em>{12}$</td>
<td>168</td>
<td>44</td>
</tr>
<tr>
<td>Mes$_3$SnB(C$_6$F$_5$)$_4$</td>
<td>C$_6$D$_6$</td>
<td>806</td>
<td>38</td>
</tr>
</tbody>
</table>

Also known are the deuterium-induced isotope effect on the $^{119}$Sn shielding of −0.05 ppm/D and the primary isotope effect of $-11.6 \pm 7$ Hz for Sn−H spin−spin coupling for the ‘SnD$_n$H$_{3-n}$’ cations generated in fluorosulfuric acid at low temperature from SnD$_n$H$_4$−$n$.$^{59}$ The chemical shift of 208 ppm found$^{23}$ in the $^{119}$Sn NMR of the reaction mixture of Me$_4$Sn and SbCl$_5$ was attributed to the ‘Me$_3$Sn$^+$’ cation.

A $^{209}$Pb NMR chemical shift of 980 ppm has been reported$^{60}$ for the ‘Me$_3$Pb$^+$’ cation in fluorosulfuric acid at low temperature.

2. Organic solvents

The nature of ‘Me$_3$M$^+$’ cations in organic solvents has been a subject of controversy similar to that for silyl cations$^1$, albeit not such a heated one.

Various monohalides of triorganotin derivatives have been shown by NMR spectroscopy to ionize in polar solvents, providing the corresponding coordinated cations$^{61}$. Solutions of tributyltin or triphenyltin chloride, perchlorate and tetrafluoroborate have been studied by Edlund and coworkers$^{62}$ in dichloromethane, sulfolane, acetonitrile, pyridine, DMPU, DMSO and HMPA (Table 6). They reported the most downfield $^{119}$Sn NMR chemical shift of 220 ppm for ‘n-Bu$_3$Sn$^+$’ ClO$_4^−$ in dichloromethane and showed that the $^{119}$Sn NMR

TABLE 6. $^{119}$Sn NMR chemical shifts vs. Me$_4$Sn for n-Bu$_3$Sn and Ph$_3$Sn derivatives$^{64}$

<table>
<thead>
<tr>
<th></th>
<th>CH$_2$Cl$_2$</th>
<th>Sulfolane</th>
<th>MeCN</th>
<th>Pyridine</th>
<th>DMPU</th>
<th>DMSO</th>
<th>HMPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bu$_3$SnCl</td>
<td>156</td>
<td>130</td>
<td>119</td>
<td>14</td>
<td>18</td>
<td>2</td>
<td>−47</td>
</tr>
<tr>
<td>Bu$_3$SnClO$_4$</td>
<td>220</td>
<td>139</td>
<td>54</td>
<td>−24</td>
<td>0</td>
<td>12</td>
<td>−43</td>
</tr>
<tr>
<td>Bu$_3$SnBF$_4$</td>
<td>160</td>
<td>168</td>
<td>44</td>
<td>1</td>
<td>4</td>
<td>11</td>
<td>−44</td>
</tr>
<tr>
<td>Ph$_3$SnCl</td>
<td>−44</td>
<td>−93</td>
<td>−98</td>
<td>−213</td>
<td>−223</td>
<td>−227</td>
<td>−242</td>
</tr>
<tr>
<td>Ph$_3$SnClO$_4$</td>
<td>−157</td>
<td>−211</td>
<td>−232</td>
<td>−263</td>
<td>−236</td>
<td>−275</td>
<td>−275</td>
</tr>
<tr>
<td>Ph$_3$SnBF$_4$</td>
<td>−152</td>
<td>−216</td>
<td>−229</td>
<td>−261</td>
<td>−236</td>
<td>−276</td>
<td>−276</td>
</tr>
</tbody>
</table>
10. Free and complexed $R_3M^+$ cations ($M = \text{Ge, Sn, Pb}$)

chemical shift moves upfield as the solvation power is increased from dichloromethane to HMPT for both series [a similar observation was made in the cases of $'\text{Bu}_3\text{Sn}^+$, B(3,5-$(\text{CF}_3)_2\text{C}_6\text{H}_3)_4$ and $'\text{Bu}_3\text{Sn}^+$, CB$_{11}\text{Me}_{12}^-$ whose upfield $^{119}\text{Sn}$ NMR chemical shifts of 165 ppm in CD$_2\text{Cl}_2$ and 168 ppm in C$_6\text{D}_{12}$, respectively, in the presence of ether, were attributed to the formation of the solvated $\text{Bu}_3\text{SnOEt}_2^+$ cations]. Based on their observation and on the $^{35}\text{Cl}$ NMR line width, Sn–C scalar coupling and $^{119}\text{Sn}$–$^{31}\text{P}$ coupling measurements, Edlund and coworkers concluded that in these solutions neutral tetrahedral and cationic trigonal bipyramidal species are in equilibrium, with bipyramidal coordination favored in solvents of higher donicity. ESI/MS of aqueous acetonitrile solutions of $R_3\text{SnHal}$ ($R = \text{Me, } n-\text{Bu, Ph, Hal} = \text{Cl, Br}$) showed $R_3\text{Sn}^+$ cations together with solvated cations such as $[(R_3\text{Sn})_n(\text{OH}_2)_x]^+$ and $[R_3\text{Sn}($NCMe$)_x]^+$ or $[R_3\text{Sn}($Py$)]^+$ in the presence of pyridine.

In another early report, Lambert and Schlif claimed germyl cations in sulfolane and dichloromethane to be free based on conductivity, cryoscopic measurements and $^{35}\text{Cl}$ NMR spectroscopy ($^{35}\text{Cl}$ line widths and chemical shifts). Later, Lambert and Kuhlmann reported a $^{119}\text{Sn}$ NMR chemical shift of ca 360 ppm for $'n-\text{Bu}_3\text{Sn}^+$, BH(C$_6\text{F}_5)_3^-$ in benzene at room temperature (but in a later paper a $^{119}\text{Sn}$ NMR chemical shift for the similar $'\text{Et}_3\text{Sn}^+$, B(C$_6\text{F}_5)_4^-$ salt in toluene was reported to be 251 ppm), while Kira and coworkers reported a $^{119}\text{Sn}$ NMR chemical shift of 356 ppm for $'n-\text{Bu}_3\text{Sn}^+$, B(3,5-$(\text{CF}_3)_2\text{C}_6\text{H}_3)_4^-$ in dichloromethane at $-20^\circ\text{C}$ and also showed that there is no interaction with the anion, based on the $^{19}\text{F}$ NMR measurements. Both groups claimed that they prepared tricoordinate stannyl cations with no significant coordination to the solvent, based on the downfield $^{119}\text{Sn}$ NMR chemical shifts.

This conclusion was disputed later by Edlund and coworkers who suggested that a solvent molecule occupies the fourth coordination site in both cases. Indeed, the $^{119}\text{Sn}$ NMR chemical shifts observed by Lambert and collaborators and Kira and coworkers are similar to that reported by Birchall and Manivannan for $'\text{Me}_3\text{Sn}^+$ in fluorosulfuric acid (322 ppm), where there is little doubt about the coordinated nature of the cationic tin species. Since an accurate computational prediction of $^{119}\text{Sn}$ NMR chemical shifts is hard, Edlund and coworkers used empirical correlations to show that the $^{119}\text{Sn}$ NMR chemical shifts observed lie in the range corresponding to covalent arene complexes of stannyl cations and predicted a $^{119}\text{Sn}$ NMR chemical shift of 1500–2000 ppm for a truly free stannyl cation. They also used scalar Sn–C coupling to support their conclusion about coordination and pyramidalization in the cationic species reported by Lambert and collaborators and Kira and coworkers. Another proof of the pyramidalization of triorganostannyl cations even by weak nucleophiles was obtained recently by Michl and coworkers who found a $^{119}\text{Sn}$ NMR chemical shift of 454 ppm for $'n-\text{Bu}_3\text{Sn}^+$, CB$_{11}\text{Me}_{12}^-$ in cyclohexane. The single crystal structure of this salt (whose solid sample had a CP-MAS $^{119}\text{Sn}$ NMR chemical shift of 461 ppm) showed no solvent coordination, but a significant interaction of the methyl groups of two carboranyl anions with the distinctly pyramidalized stannyl cation. The $^{119}\text{Sn}$ NMR signal of $n-\text{Bu}_3\text{Sn}^+$, CB$_{11}\text{Me}_{12}^-$ lies downfield relative to the signals reported by Lambert and collaborators and Kira and coworkers, but it is far from the value predicted for a free stannyl cation.

Optimized structures of $\text{Me}_n\text{SnH}_{4-n}$, $\text{H}_3\text{SnX}$ ($X = \text{OH}_2$, Cl), $\text{H}_3\text{Sn}^+$ solvated by one and two water molecules, and $\text{H}_3\text{SnOH}$ solvated by one molecule of water have been calculated by Cremer and coworkers at the HF/DZ+P and MP2/DZ+P level. They calculated $^{119}\text{Sn}$ chemical shifts using the IGLO/DZ and IGLO/DZ+P methods and showed that only strongly coordinated pyramidal and trigonal bipyramidal stannyl cations exist in solution. They predicted a $^{119}\text{Sn}$ NMR chemical shift of ca 1000 ppm for a free triorganostannyl cation.
The degree of cationic character of Mes$_3$Ge$^+$ in aromatic solvents could be only roughly estimated$^{38}$ from the $^{13}$C NMR data due to the lack of a suitable germanium nuclide for direct NMR observations. The conclusion was reached that the positive charge on germanium in Mes$_3$Ge$^+$ is comparable to that on silicon in the Mes$_3$Si$^+$ cation$^{39}$, which is believed to be the first free silyl cation in condensed media. The trimesitylstannyl cation prepared by Lambert and coworkers$^{38}$ has a record high $^{119}$Sn NMR chemical shift of 806 ppm, which still falls somewhat short of the 1000 ppm chemical shift predicted by Cremer and coworkers$^{65}$ and considerably short of the 1500–2000 ppm value estimated by Edlund and coworkers$^{60}$ for a free stannyl cation. The fact that no solvent dependence was found for the Mes$_3$Sn$^+$ cation led to the conclusion that in this case an interaction with the B(C$_6$F$_5$)$_4^-$ counterion is significant$^{38}$. Attempts to increase the steric hindrance around the cationic tin atom sufficiently have failed$^{38}$.

The interaction between R$_3$M$^+$ cations (R = H, Me, Cl, M = C, Si, Ge, Sn, Pb) and toluene was examined computationally by Basch$^{66}$ using MP2/CEP and MP2/RCEP methods. He found that the R$_3$M group in R$_3$M$^+$-toluene complexes for M = Si, Ge, Sn and Pb lies almost directly above the ipso carbon atom with the hydrogen atom almost in the plane of the aromatic ring, and also that the binding energy increases from Si to Pb, which he attributes to an additional non-bonding stabilizing interaction between one of the M/NUL C bonds in the R$_3$M$^+$ cation and the aromatic π system, which is especially strong when M = Pb.

C. Solid State

Several single crystal structures have been determined for solvated stannyl cations. Thus, a hydrated tributyltin cation n-Bu$_3$Sn(OH$_2$)$_2$$^+$ has a symmetry close to $D_{3h}$, with two water molecules occupying the axial positions$^{67}$. In [(c-C$_6$H$_{11}$)$_3$Sn(NCMe)$_2$]$^+$SbF$_6^-$ the cationic tin atom is trigonal bipyramidal, with two acetonitrile ligands occupying the axial sites$^{37}$. The structure of the pivalonitrile complexes of the t-Bu$_3$Ge$^+$ and t-Bu$_3$Si$^+$ cations has also been established by X-ray crystallography$^{42}$.

A single crystal structure was determined recently$^{44}$ for solvent-free n-Bu$_3$Sn$^+$ CB$_{11}$Me$_{12}^-$, crystallized from hexane (Figure 1). The methyl groups of two carboranyl anions interact with the somewhat pyramidalized stannyl cation in an approximately trigonal bipyramidal geometry (the average Sn—C distance is 2.81 Å and the sum of valence angles around the tin atom is 353°). As noted above, the $^{119}$Sn NMR chemical shift values of 454 ppm in cyclohexane and of 461 ppm in the solid are closer to those reported for solvated stannyl cations than to the chemical shift of the presumably largely free Mes$_3$Sn$^+$ cation. The authors used the B3LYP/SSD method to calculate the ion-pairing energies for four optimized isomers of an isolated Me$_3$Sn$^+$ CB$_{11}$Me$_{12}^-$ ion pair, with Me$_3$Sn$^+$ next to a methyl in position 1, 2, 7 or 12 of the CB$_{11}$ cluster. The 12-isomer was found to be the most stable and to have the shortest Sn—CH$_3$ and the longest B—CH$_3$ bond length, the flattest coordinated CH$_3$ group, the most pyramidalized Me$_3$Sn$^+$ cation and the largest degree of inter-ion charge transfer. The calculated stability of the ion pairs decreases in the order 12 > 7 > 2, with the Sn atom always located almost exactly on the B—CH$_3$ bond axis, and the stabilizing interaction not merely electrostatic but also of the donor–acceptor type. Me$_3$Sn$^+$ interacts much less with the carbon-attached 1-methyl group and the Sn atom is then tilted by 36° off the axial position toward the 2-methyl group.
FIGURE 1. Structure of \( n\)-Bu\(_3\)Sn\(^+\) CB\(_{11}\)Me\(_{12}\)\(^-\): segment of an infinite column of alternating cations and anions. Thermal ellipsoids are at 50% (not shown on two of the butyl groups in each cation). Hydrogen atoms and one component of the disordered butyl groups are omitted, Sn atoms are dark grey, C atoms are black and B atoms are light grey. Within each cage, one of the vertices is a carbon atom (disordered, not shown). Reprinted with permission from Reference 44. Copyright 2000 American Chemical Society
D. Intramolecular Stabilization

Many compounds are known in which a cationic Ge, Sn or Pb atom is intramolecularly stabilized by a strong interaction with lone pairs on donor atoms such as N or O. For instance, a series of germyl cations 1 stabilized by an intramolecular nitrogen–germanium bond have been prepared recently in the group of Jutzi. In these compounds there is no cation–anion interaction but the GeC₃ group is somewhat pyramidal (the sum of valence angles around Ge is ca. 352°). Several germyl cations of type 2 stabilized by an intramolecular bond to oxygen have been reported by the group of Rivière. In this case the germanium atom has a trigonal pyramidal geometry and a partially cationic character.

\[
\begin{align*}
\text{Ge} & \quad \text{N} & \quad \text{R}^2 \\
\text{R}^1 & \quad \text{I}^-
\end{align*}
\]

Protonated digermyl and distannyl ethers 3 were prepared by hydrolysis of the corresponding \( \text{R}_3\text{M}^+\text{B(C}_6\text{F}_5)_4^- \) salts. Their germanium and tin atoms possess a partial cationic character judging by the flattened tetrahedra around the metal atoms and elongated bonds to oxygen atoms. In stannyl cations 4 the cationic pentacoordinate trigonal bipyramidal tin atom is stabilized by two intramolecular tin–nitrogen bonds.

Tetrastannylammonium and -phosphonium cations 5 were prepared by the reaction of \( \text{Me}_3\text{Sn}_3\text{E(EN, P)} \) with \( \text{Me}_3\text{SnOTf or Me}_3\text{SnF/NaBPh}_4 \) in toluene. These cations dissociate slightly in THF and can be viewed as base-stabilized stannyl cations.

Wrackmeyer and coworkers characterized by NMR spectroscopy intermediate stannyl cations 6 and 7, in which cationic tin is stabilized by interactions with amino and alkynyl groups. In both cases the \( ^{119}\text{Sn} \) chemical shifts (ca. -35 ppm for 6 and ca. 110 ppm for 7) indicate a strong coordination of the cationic tin atom. A stannyl cation 8 (M = Sn) stabilized only by \( \pi \) coordination to a carbon–carbon triple bond was also prepared. Its crystal structure revealed a somewhat pyramidalized cationic tin atom with a sum of valence angles equal to 351°. The \( ^{119}\text{Sn} \) NMR chemical shift of 215 ppm also suggests a quite strong coordination of the cationic Sn atom. \( ^{119}\text{Sn} \) and \( ^{119}\text{B} \) NMR analysis of 8, M = Sn, showed that there is an equilibrium between two structures in which the alkynyl group is attached to either the tin or the boron atom. In its lead analogue 9, M = Pb, the cationic lead atom is less pyramidalized (a sum of valence angles is 356°), but the \( ^{209}\text{Pb} \) NMR chemical shift of 723 ppm suggests a strong coordination of the cationic lead atom (cf. the \( ^{209}\text{Pb} \) NMR chemical shift of 980 ppm reported for the ‘Me₃Pb⁺’ cation in fluorosulfuric acid).
IV. REACTIONS

A. Gas Phase

$\text{Me}_3\text{M}^+$ cations ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) produced by electron impact ionization of $\text{Me}_4\text{M}$ ($\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) have the highest intensity in the spectra and their fragmentation to give $\text{MeM}^+$ cations under higher electron impact energy increases for metals with a higher atomic number$^{79}$. Unimolecular and collision-induced fragmentations of $\text{Me}_3\text{Ge}^+$, $\text{Me}_3\text{Sn}^+$, and $\text{Me}_3\text{Pb}^+$ cations show the following results$^{80,81}$: $\text{Me}_3\text{Ge}^+$ loses ethylene,
methyl and ethane; Me$_3$Sn$^+$ loses one, two and three methyl groups, but no ethylene; Me$_3$Pb$^+$ loses methyl groups and ethane. The differences were explained in terms of the decreasing element–carbon bond strength and the increasing preference for the +2 oxidation state in the order Ge, Sn, Pb. Gas-phase fragmentation of a labeled trineopentyl-stannyl cation under electrospray ionization conditions proceeds via $\beta$-methide transfer to yield labeled isobutene and the dineopentylmethystannyl cation (Scheme 6)$^{82}$. 

\[
\text{Me}_3	ext{C} + \text{Sn(CH}_2\text{Bu}-t)_2 \rightarrow \left[\text{Me}_3\text{C} \right] + \left[\text{Sn(CH}_2\text{Bu}-t)_2 \right] + \left[t\text{-BuCH}_2\right]_2\text{MeSn}^+ \\
\rightarrow \text{Me}_2\text{CD}_2 \\
\rightarrow (t\text{-BuCH}_2)_2\text{MeSn}^+ \\
+ \text{Me}_2\text{CD}_2 
\]

\text{SCHEME 6}

The $n$-Bu$_3$Ge$^+$ cation produced from $n$-Bu$_4$Ge by electron impact, as well as Me$_3$Sn$^+$ and $i$-Pr$_3$Sn$^+$ cations, was found$^{83}$ to be more reactive than the corresponding carbocation. Adducts of Me$_3$Ge$^+$ to various N, O and S containing bases (such as alcohols, amines and esters) under ion cyclotron resonance conditions were found to be stable while the analogous Me$_3$Si$^+$ adducts were not$^{84}$. The binding energy of R$_3$M$^+$ cations (R = Me, Et, $n$-Pr, $n$-Bu) to water, studied by high pressure mass spectrometry$^{85}$, decreases in the series R$_3$Si$^+$, R$_3$Ge$^+$, R$_3$Sn$^+$, in contrast to the earlier observations$^{84}$. $\Delta H^\circ$ decreases with the increasing size of R, and $\Delta S^\circ$ is nearly constant.

The reaction of H$_3$Ge$^+$ cation with ethylene was found$^{86}$ by tandem mass spectrometry to yield stable adduct ions [C$_2$H$_7$Ge]$^+$ which first decompose to the ions [C$_2$H$_5$Ge]$^+$ with the proposed structure of a protonated germacyclopropane and then are proposed to rearrange to the ethylgermyl cation, which loses a hydrogen molecule and forms the vinylgermyl cation (Scheme 7).

\[
\text{H}_3\text{Ge}^+ + \text{C}_2\text{H}_4 \rightarrow [\text{C}_2\text{H}_7\text{Ge}]^+ \rightarrow [\text{CH}_2\text{CH}_2\text{GeH}_2]^+ \rightarrow [\text{CH}_2 \equiv \text{CHGeH}_2]^+ 
\]

\text{SCHEME 7}

Ion–molecule reactions in H$_4$Ge/hydrocarbons$^{87,88}$, H$_5$GeMe/hydrocarbons$^{89}$, H$_4$Ge/H$_4$Si$^{90,91}$ and H$_3$GeMe/H$_4$Si$^{92–94}$ mixtures have been studied by the group of Vaglio using ion trap mass spectrometry. They observed a variety of cations, such as H$_3$M$^+$, H$_2$M$^+$, HM$^+$, M$^+$, H$_5$M$_2^+$, H$_3$M$_2^+$, H$_7$M$_3^+$, H$_6$M$_3^+$, H$_5$M$_3^+$, H$_4$M$_3^+$ and H$_7$M$_4^+$, and described their interconversions. Recently, Schwarz and coworkers reported a study of fragmentation patterns for the H$_3$Ge$^+$ cation (dominated by the loss of one and two hydrogens) and the H$_2$Ge$^+$ cation$^{55}$. 
Gas-phase reactions of the methyl cation with Me₄M (M = Si, Ge, Sn) were studied using a radiochemically generated T₃C⁺ (Scheme 8). In this case the methide anion is readily abstracted from all three tetramethyl derivatives, tetramethyltin being the most reactive. An analogous reaction of methyl cations with Et₄M (M = C, Si, Ge, Sn) resulted mostly in abstraction of the ethyl anion when M was silicon, germanium or tin. As shown in Scheme 8, the authors assumed that the abstraction occurs by electrophilic substitution on the M–C bond, with front-side attack on the methyl group.

(SCHEME 8)

The following thermodynamic data have been reported for a methide anion transfer in the gas-phase equilibria Me₃M⁺ + Me₄M ⇌ Me₄M + Me₃M⁺ (M = Si, Ge, Sn): for Me₃Si⁺ + Me₄Ge ⇌ Me₄Si + Me₃Ge⁺, ΔH₀ = −10.2 ± 1.2 kcal mol⁻¹, ΔS₀ = −3.7 ± 2.4 cal K⁻¹ mol⁻¹; for Me₃Ge⁺ + Me₄Sn ⇌ Me₄Ge + Me₃Sn⁺, ΔH₀ = −8.1 ± 0.9 kcal mol⁻¹, ΔS₀ = −0.9 ± 1.6 cal K⁻¹ mol⁻¹.

Me₃M⁺ cations (M = C, Si, Ge, Sn) were used as a stereochemical probe in gas-phase reactions with 1,2-cyclopentanediol isomers. The decomposition pattern of the [1,2-cyclopentanediol·Me₃M]⁺ adducts depended on the stereochemistry of the diol. For cis-diol the decomposition led readily to hydrated [Me₃M(OH₂)]⁺ cations, while for trans-diol the adduct was significantly more stable; the Me₃Ge⁺ cation was a more sensitive and selective reactant than other group 14 cations.

B. Solution

Little is known about the reactivity of the group 14 cations in solution. Clearly, one would expect these strong electrophiles to react with common nucleophiles, but such trivial reactions were not documented except for the reaction of Bu₃Sn⁺·CB₁₁Me₁₂⁻ with PhLi which produced Bu₃SnPh⁺, [(c-C₆H₁₁)_₃Sn(NCMe)₂]⁺·SbF₆⁻ and compounds of this series have been shown to be effective promoters of Diels–Alder additions to furan.

V. RELATED SPECIES

Sekiguchi and coworkers reported the preparation and the crystal structure of a free cyclotrigermenium cation (9) as a tetraphenylborate salt. The stability of this cation stems from its aromatic 2π-electron system, and from the steric bulk of tri-tert-butylsilyl groups. They later expanded this work to similar cyclotrigermenium cations with various substituents and counterions.

Two transition metal stabilized germyl cations, 10 and 11, have been reported. In the first one the strongly pyramidalized cationic germanium center is bonded to two iron atoms and one t-Bu group, and is stabilized by the coordination to DMAP. The second one has a planar cationic germanium bonded to two tungsten atoms and one methyl group.
Several related cations have also been studied computationally. In the case of C2GeH7+ cations four local minima were found, with the planar Me2HGe+ cation representing the global one. For the cyclic cations Si3H3+ and Ge3H3+ the planar D3h structure was found to be the global minimum. Another study of the cyclic H3M3+ cations (M = C, Si, Ge, Sn, Pb) found non-planar C3v hydrogen-bridged structures for Ge, Sn and Pb to be more stable than the planar D3h structures. Kudo and Nagase published a short review discussing calculational results for the cations of strained polycyclic Si, Ge, Sn and Pb compounds.

1,3-Migrations of a methyl group in compounds of the type (Me3Si)2C(SiMe2X)(MMe3) between silicon and a heavier group 14 element, germanium or tin, were postulated by Eaborn and coworkers to proceed via a bridged cationic intermediate. Intermediacy of stannyl cations has also been postulated in aromatic electrophilic substitution reactions.

Pentamethylcyclopentadienylgermyl and pentamethylcyclopentadienylstannyl cations have been prepared by Jutzi and coworkers as tetrafluoroborate salts in ether. These cations, of course, are of the RM+ rather than the ‘R3M+’ kind. The structure of the tin derivative has been established by X-ray crystallography. It revealed an almost C5v symmetrical molecule with the average tin to ring carbon atom distance of 2.46 Å and with a somewhat short Sn–F distance of 2.97 Å. The reactivity of the pentamethylcyclopentadienylermnyl cation and its complexes with nitrogen nucleophiles has also been studied by Jutzi and coworkers. Recently, the reaction of Sn(C5Me5)2 with Ga(C6F5)3 was reported to produce the first group 14 triple-decker cation [(C5Me5)Sn(C5Me5)Sn(C5Me5)]+[Ga(C6F5)4]− (14). Its structure was determined by X-ray crystallography.
The structure of and bonding in the CpGe\(^+\) cation have been analyzed computationally\(^\text{117}\). The calculated Ge-to-ring distance was 1.99 Å for the \(C_5\) cation, in which the Ge atom is surrounded by eight valence electrons and its lone pair occupies an sp hybrid pointing away from the Cp ring.

VI. CONCLUSIONS

Several major advances have been made in the field of ‘R\(_3\)M\(^+\) cations (M = Ge, Sn, Pb) in recent years, including the preparation of free cyclotrimerium cations and possibly close to free trimetisylgermyl and trimesitylstannyl cations. However, many challenges remain, for example, a structural characterization of free R\(_3\)M\(^+\) cations (M = Ge, Sn, Pb). In many respects these cations appear to be even more challenging than the silyl cations, due to their weaker and longer bonds to carbon. Presently inadequate tools which need to be improved are computational methods for the NMR chemical shifts of the Sn and Pb nuclei.

VII. REFERENCES

10. Free and complexed $\text{R}_3\text{M}^+$ cations ($\text{M} = \text{Ge, Sn, Pb}$)

CHAPTER 11

Alkaline and alkaline earth metal-14 compounds: Preparation, spectroscopy, structure and reactivity

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I. LIST OF ABBREVIATIONS

CIDEP chemically induced dynamic electron polarization
CIP contact ion pair
CVD chemical vapor deposition
DBU 1,8-diazabicyclo[5.4.0]undec-7-ene
DCPH dicyclohexylphosphine
DME 1,2-dimethoxyethane
DMF N,N-dimethylformamide
DMPU dimethylpropyleneurea
DMSO dimethyl sulfoxide
ERF electron rich olefin
ESR electron spin resonance
HME halogen metal exchange
HMPT hexamethylphosphorous triamide
LDA lithium diisopropylamide
Men mentyl
Mes mesityl (2,4,6-trimethylphenyl)
MIMIRC Michael–Michael ring closure
Np = Naph Naphthyl
Nph Neophyl: PhMe2CCH2
PMDETA pentamethyldiethylenetriamine
SET single electron transfer
SSIP solvent separated ion pair
Tbt 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl
TFPB tetrakis[3,5-bis(trifluoromethyl)phenyl]borate
THF tetrahydrofuran
Tip 2,4,6-trisopropylphenyl
TMEDA tetramethylethylenediamine
TMS trimethylsilyl or tetramethylsilane
Tol tolyl: MeC6H4
II. INTRODUCTION

This chapter will concentrate on the chemistry of metal-14-centered anions (Ge, Sn, Pb). These compounds and their silyl analogues are ionic or polarized alkaline and alkaline earth metal-14 compounds, as well as delocalized molecules such as metalloles. Ammonium metallates $\text{M}_{14}^-\text{R}_4\text{N}^+$ or metal-14-centered anion radicals are also considered. The subject was explored during the 1960s and 1970s \cite{1,2} and thoroughly reviewed in 1982 and 1995 in Comprehensive Organometallic Chemistry, Vols. I and II \cite{3,4}, and for silicon species in a previous volume of this series \cite{5}. By that time the main routes to metal-14 anions were known. Since then, the subject has been developed in the topics of particular syntheses, stabilization using steric hindrance, electronic effects and complexation, spectroscopic and structural analyses \cite{6-10}.

This chapter will emphasize the synthesis, stabilization, spectroscopic and structural aspects, reactivity and synthetic use of these compounds. For completeness, a summary of the subject previously reviewed \cite{3-10} will be included together with recent examples from the literature. The material will be divided into three sections: preparations, spectroscopic and structural studies (with some characteristic spectroscopic and structural data) and reactivity (with some applications in organic synthesis). Each part will be organized into sections dealing with a particular element in the order: germanium, tin and then lead.

In the next section dealing with preparations we shall begin with mono-anions, and continue with gem and vicinal metal-centered di-anions, including the metalloles and polymetallated mono- and poly-anions.

III. PREPARATIONS

A. $\text{M}_{14}$—Alkali Metal Compounds

1. From $\text{M}_{14}^-$—$\text{H}$ compounds

Because of their use in Chemical Vapor Deposition (CVD), monometallated germanes and polygermanes were synthesized directly by the reaction of the germane itself with alkali metals (equation 1) \cite{3a}.

$$\text{GeH}_4 + \text{M} \rightarrow \text{H}_3\text{GeM} \quad (1)$$

where $\text{M} = \text{Li, Na, K}$

Similarly, when $\text{GeH}_4$ was added to freshly prepared solutions of sodium silylsilanides $[\text{NaSiH}_n(\text{SiH}_3)]_{3-n}$, $n = 0-3$ in diglyme at $100^\circ \text{C}$, a vigorous evolution of hydrogen and a loss of $\text{SiH}_4$ was observed \cite{11}. The reaction led to sodium silylgermanides $[\text{NaGeH}_n(\text{SiH}_3)]_{3-n}$, $n = 0-2$. The silylation of sodium silylgermanide with silyl nonafluorobutanesulfonate proved to be particularly effective in the synthesis of Si—Ge containing process gases suitable for CVD (Scheme 1) \cite{11}.

Solutions of diaryldialkaligermanes were prepared by the reaction of alkali metals with the corresponding arylgermanes in HMPA/THF (equation 2) \cite{12}. Aryldialkaligermanes have never been isolated, but their formation was chemically confirmed by the $\text{Ar}_2\text{GeD}_2$ formed by deuteriolysis. Their reaction with organic halides was not taken as sufficient evidence of their formation. In $^{13}\text{C}$ NMR they show a deshielded ipso aromatic carbon compared

$^*$ $\text{M}_{14}$ denotes an element belonging to Group 14 of the periodic Table, such as Si, Ge, Sn, Pb.
to the starting arylgermane.

\[
\text{Ar}_2\text{GeH}_2 + 4 \text{ M } \xrightarrow{\text{HMPA/THF or THF}} \text{ Ar}_2\text{GeM}_2 + 2 \text{ M H } \quad (2)
\]

\[
\text{Ar} = \text{C}_6\text{H}_5, \ p-\text{CH}_3\text{C}_6\text{H}_4, \text{ M } = \text{Li, Na, K}
\]

Hydrogermalysis of alkylolithiums in ether or THF is one of the most general ways to synthesize organogermyllithiums and organohydrogermyllithiums (equation 3)\textsuperscript{3a,4a,9}. Highly basic solvents such as trialkylamines or DBU increase the yield of alkyl or arylhydrogermyllithiums, but also favor their dimerization through Li−H elimination.
\[
R^1R^2R^3GeH + R^4Li \xrightarrow{\text{ether or THF}} R^1R^2R^3GeLi + R^4H
\]  
(3)

- For \( R^1 = R^2 = R^3 = \text{Et}, R^4 = \text{Bu} \) (ether, 10% yield; THF + Et3N, 78% yield)
- For \( R^1 = R^2 = \text{Ph}, R^3 = H, R^4 = \text{Bu} \) (THF + Et3N, -40°C, 72% yield)

A retentive stereochemistry in these reactions has been established (equation 4)\(^1,13,14\).

\[
\alpha\text{-Naph}(\text{Ph})(R)GeH + n\text{-BuLi} \xrightarrow{\text{retention}} \alpha\text{-Naph}(\text{Ph})(R)GeLi + \text{BuH}
\]  
(4)

Various organogermyllithiums \( R_nH_3-nGeLi \) (\( R = \text{Ph, Mes etc., } n = 1-3 \)) were prepared easily following this general procedure\(^3a,4a,9\). Their stability depends on the nature of the \( R \) groups linked to germanium, on the possibility of complexation of the two metal centers and on the possibility of electron-pair delocalization.

Trimesitylgermyllithium was isolated as a yellow solid in the form of a THF complex in 62% yield (equation 5)\(^15\). The polarity of the germanium–lithium bond was evident from the high field shift of the Mes signals in \(^1H\) NMR spectra and the low field shift of the \textit{ipso}-aromatic carbons in \(^13C\) NMR spectra.

\[
\text{Mes}_3\text{GeH} + t\text{-BuLi} \xrightarrow{\text{THF, 20°C}} \text{Mes}_3\text{GeLi} + i\text{-BuH}
\]  
(5)

In the same way, bulky organohydrogermyllithiums were prepared and stabilized in complexes with a crown ether (equation 6)\(^16\). They were characterized by deuteriolysis, alkylation (MeI, Me\(_2\)SO\(_4\)) and reactions with acyl chlorides.

\[
R_2\text{GeH}_2 + t\text{-BuLi} \xrightarrow{\text{THF, -40°C to 20°C}} R_2\text{HGeLi} \xrightarrow{\text{12-crown-4, R = Mes}} R_2\text{HGe}^- (\text{Li(12-crown-4)})_2^+ \]  
(6)

- For \( R = \text{Ph} \) (-40°C, 95%)
- For \( R = \text{Mes} \) (-20°C, 84%)

Instead of solvent complexation, intramolecular chelation can also stabilize germanium-centered anions. Aryl(8-methoxy-1-naphthyl)hydrogermyllithiums, prepared from the corresponding chelated organogermane in 50–90% yield, are stable and their spectroscopic characteristics suggest a double-metal complexed structure (equation 7)\(^17\).

When the same reaction was conducted with two equivalents of \( n\text{-BuLi} \) followed by alkylation with MeI, it gave the expected dimethylated germanium derivative almost quantitatively. However, the reaction mechanism might be more complex than the expected nucleophilic substitution by a germanium-centered dianion. A more complex radical
process is probably involved\textsuperscript{17} (see also Scheme 5). Similar stabilization of germanium-centered anions using 2-(dimethylamino)phenyl as a chelating ligand allowed the isolation of crystalline germylanion as a monochelated monomer with the lithium atom coordinated to one of the amino groups and to two THF molecules as established by X-ray diffraction. The compound was prepared by deprotonation of the corresponding hydrogermane with \textit{t}-BuLi in THF at \(-40^\circ\text{C}\), in 93\% yield (equation 8). The yield was estimated by quenching with D\textsubscript{2}O. It was isolated as pale yellow monocrystals after recrystallization from toluene at \(-20^\circ\text{C}\).\textsuperscript{18}

\[
\begin{array}{cccc}
\text{H} & \text{NMe}_2 & \text{R}_2\text{Ge} \\
\text{R} = 2\text{-Me}_2\text{NC}_6\text{H}_4
\end{array}
\]

\[
\text{Ar}_3\text{GeH} + \text{K} \xrightarrow{\text{THF}} \text{THF} \rightarrow \text{Ar}_3\text{Ge}^- \quad \text{K}^+
\]

\[
\text{Ar} = (2\text{-CH}_2\text{NMe}_2)\text{C}_6\text{H}_4, (2\text{-MeO})(5\text{-Me})\text{C}_6\text{H}_3
\]

Another way to stabilize germanium-centered anions is to induce a partial delocalization of the lone pair. Germoly1 anions are easily available from the hydrogermolysis of \textit{BuLi}, \textit{PhCH}_2\text{K} or (\text{SiMe}_3)_2\text{NK} with 12-crown-4 or 18-crown-6 complexing lithium or potassium (Scheme 3).\textsuperscript{20–22} They are usually sufficiently stable to be isolated as yellow crystals in good yields. They display a pyramidal germanium center with weak bond localization in the diene portion of the ring.\textsuperscript{21} This conclusion emerges from structural studies of some of them (see Section IV).

A \textit{gem} germanium-centered dilithium has never been clearly observed, although it was postulated several times or characterized transiently in solution in reactions of alkali metals with arylhydrogermanes (equation 2), lithiosilolysis of a silylgermyllithium (equation 10)\textsuperscript{23} and hydrogermolysis of an excess of \textit{t}-BuLi (Scheme 4).\textsuperscript{16} In the last case, the pseudogermyldilithium intermediate reacted with alkyl or acyl halides to give the expected dialkylated or diacylated germanium compound in good yields, but its deuteriolysis gave
only the monodeuteriated organogermaine.

\[
\text{Me}_3\text{SiGeEt}_2\text{Li} + \text{Me}_3\text{SiLi} \xrightarrow{\text{HMPT}} \text{Me}_3\text{SiSiMe}_3 + \text{Et}_2\text{GeLi}_2 \quad (70\%)
\]

(10)

Analysis of pseudogermyldilithiums of this kind, obtained according to Scheme 4 and stabilized by steric hindrance, shows an aggregate between germyl and alkyllithiums. In an examination of the reaction pathway leading to dialkylation of the germanium center (Scheme 5)\textsuperscript{24}, it was shown that the reaction with alkyl halides is not an unequivocal probe for the characterization of metal-14-centered dianions. In the same way, germolyldianions have to be considered as delocalized dimeric sandwich structures with both alkali metals coordinated by the germolyldianions in an \( \eta^5 \) fashion (see Section IV, Figure 1)\textsuperscript{21}. Their aromaticity has been studied (see Section IV)\textsuperscript{22}. 

SCHEME 2
More metal centered are the vicinal organo 1,2-digermyldianions, easily prepared by metallation of the corresponding organo 1,2-dihydridgermanes with \( t\)-BuLi in THF. Perfectly stable at low temperature (\(-40^\circ C\)), 1,2-digermyldilithium compounds offer a convenient synthesis of cyclodigermanes by their \textit{in situ} reaction with 1,3-dibromopropane (equation 11) or with trans-(\( Et_3P\))\(_2\)PtCl\(_2\), as well as of cyclopolygermanes when reacted with \( R_2Ge(OMe)_2 \) or \( R_2(MeO)GeGe(MeO)R_2 \)\(^{25}\).

\[
\begin{align*}
\text{Ph}_2\text{GeH}_2 & \xrightarrow{t\text{-BuLi, excess}} \text{Ph}_2\text{HGeMe} (37\%) + \text{Ph}_2\text{GeMe}_2 (56\%) \\
& \xrightarrow{\text{MesCOCl, D}_2\text{O}} \text{Ph}_2\text{HGeCOMes} (15\%) + \text{Ph}_2\text{Ge(COMes)}_2 (19\%) \\
& \xrightarrow{\text{Ph}_2\text{HGeD} (-100\%)} \\
\end{align*}
\]

SCHEME 3

SCHEME 4

\[
\begin{align*}
\text{Ph}_2\text{HGeGeHPh}_2 & \xrightarrow{t\text{-BuLi, \(-40^\circ C\)}} \text{Ph}_2\text{LiGeGeLiPh}_2 \\
\text{Ph}_2\text{LiGeGeLiPh}_2 & \xrightarrow{\text{Br(CH}_3)_2\text{Br}} \text{Ph}_2\text{Ge} \\
\text{Ph}_2\text{Ge} & \xrightarrow{	ext{Ph}_2\text{Ge}} \\
\end{align*}
\]

In the reaction between (chlorodimesitylsilyl)diarylgermanes and \( t\)-BuLi in THF, new germyllithium compounds, resulting from an intramolecular hydrogermolysis of an intermediate silyllithium (Scheme 6), were characterized\(^{26}\). The silylated germylanion was characterized by deuteriolysis and alkylation.

Equimolar amounts of lithium diisopropylamide (LDA) and tin hydrides reacted in THF to form diisopropylamine and the corresponding stannyllithium (equation 12)\(^{27,28}\). In diethyl ether or hexane, an excess of tin hydride was required for complete reaction which leads to the ditin compound and lithium hydride (equation 13).
Mes₂GeH₂ + 2 n-BuLi $\xrightarrow{Et₂O}$ [Mes₂HGeLi, n-BuLi, Et₂O]

\[
\begin{align*}
\text{(a)} & : \text{Mes₂Ge} + \text{CH₃I} \\
\text{(b)} & : \text{CH₃Li} + \text{CH₃I} \\
\text{(c)} & : \text{Mes₂Ge} + \text{CH₃} \\
\text{(d)} & : \text{Mes₂Ge} + \text{CH₃I} \\
\end{align*}
\]

**SCHEME 5**

\[
\begin{align*}
\text{Ar}_2\text{Ge} & \xrightarrow{\text{SiMes}_2} \text{HCl} \\
\text{Ar}_2\text{Ge} & \xrightarrow{\text{Li} + \text{t-BuCl}} \text{THF} \\
\text{Ar}_2\text{Ge} & \xrightarrow{\text{MeOH-d₄}} \text{Ether} \\
\end{align*}
\]

**SCHEME 6**

\[
\begin{align*}
\text{R}_3\text{SnH} & \xrightarrow{\text{LDA}} \text{R}_3\text{SnLi} + \text{i-Pr}_2\text{NH} \\
\text{R} & = \text{Me, Bu} \\
2 \text{R}_3\text{SnH} & \xrightarrow{\text{LDA, ether}} \text{R}_3\text{SnSnR}_3 + \text{LiH} + \text{i-Pr}_2\text{NH} \\
\text{R} & = \text{Me}
\end{align*}
\]
It was shown that in equation 13 the formation of ditin proceeds from an intermediate hydrostannyllithium (equation 14)\(^27\).

\[
\text{Me}_3\text{SnLi} + \text{Me}_3\text{SnH} \rightarrow [\text{Me}_3\text{Sn(H)}\text{Me}_3^-] + \text{Li}^+ \\
\text{(Me}_3\text{Sn)}_2 + \text{LiH}
\]

Starting from diorganostannanes, the same reaction gave high yields of stannylanions (equation 15), but did not afford the gem-dilithium metal derivatives when an excess of LDA was used\(^29,30\).

\[
\text{Bu}_2\text{SnH}_2 \xrightarrow{\text{LDA}^*} \text{Bu}_2\text{SnHLi} \xrightarrow{\text{D}_2\text{O}} \text{Bu}_2\text{SnHD} \quad (15)
\]

\(*^\text{a} : \text{stoichiometric or excess}

However, as also observed in germanium chemistry, a mixture of dihydride with an excess of lithiated reagent behaves as a stannyldianion in reactions with organic halides, polyformaldehyde or epoxides (Scheme 7)\(^29\), and it thus appears as an interesting synthetic reagent.

\[
\begin{array}{c}
\text{Bu}_2\text{SnH}_2 + 2 \text{i-Pr}_2\text{NLi} \\
\text{Bu}_2\text{SnH}_2 + 2 \text{R}^2\text{Br} \\
\end{array}
\]

\[
\begin{array}{c}
\text{Bu}_2\text{Sn(CH}_2\text{CHR}^1\text{OLi)}_2 \\
\text{Bu}_2\text{Sn(CH}_2\text{OLi)}_2 \\
\end{array}
\]

\[
\begin{array}{c}
\text{R}^1 = \text{H, Me; R}^2 = \text{allyl, benzyl, Cl(CH}_2)_3 \\
\end{array}
\]

\text{SCHEME 7}

Whereas mixed methyleneophyltin hydrides reacted with NaH in DMSO to give the corresponding organotin sodium (60–70% yield) (equation 16), the more bulky trineophyltin hydride gave hexaneophylditin as the only product (equation 17)\(^31\).

\[
\text{MeNph}_2\text{SnH} + \text{NaH} \xrightarrow{\text{DMSO} - \text{H}_2} \text{MeNph}_2\text{SnNa} \quad (16)
\]

\[
\text{Nph}_3\text{SnH} + \text{NaH} \xrightarrow{\text{DMSO}} \text{Nph}_3\text{SnSnNph}_3 \quad (17)
\]

The same neophyltin hydrides did not react with LDA, possibly because of steric hindrance.
2. Substitution halogen/metal

The formation of a metal anion from metal halide and lithium can be rationalized by a double and successive mono-electronic transfer, with (or without when weak $M_{14}$−$M_{14}$ bond is involved) formation of a transient digermane (Scheme 8).

![Scheme 8](image)

SCHEME 8

Following this scheme, $\text{Me}_3\text{GeLi}$ was prepared from $\text{Me}_3\text{GeCl}$ and lithium in HMPA/Et$_2$O (equation 18)$^{32}$ and then used in the preparation of germasilanes, which are useful in the synthesis of stable silyllithiums (equation 19)$^{32}$.

$$4 \text{Me}_3\text{GeCl} + 8 \text{Li} \xrightarrow{\text{HMPA/Et}_2\text{O}(-78^\circ\text{C})} 4 \text{Me}_3\text{GeLi} \xrightarrow{\text{SiCl}_4} (\text{Me}_3\text{Ge})_4\text{Si}$$  (18)

$$\text{(Me}_3\text{Ge})_4\text{Si} + \text{MeLi} \xrightarrow{\text{THF}, 20^\circ\text{C}} \text{Me}_4\text{Ge} + (\text{Me}_3\text{Ge})_3\text{SiLi}$$  (19)

A series of aryl and alkylarylgermyllithiums and stannyllithiums were synthesized in the same way with the purpose of transforming them by laser photolysis into the corresponding metal-centered radicals$^{33}$ (equation 20).

$$\text{(Ph}_n\text{Me}_3-\text{nE})_2 \xrightarrow{\text{Li}} 2 \text{Ph}_n\text{Me}_3-\text{nE}^- \xrightarrow{\text{hv}} 2 \text{Ph}_n\text{Me}_3-\text{nE}^\bullet$$  (20)

$E = \text{Si, Ge, Sn}; n = 1-3$

The substitution of halogen by metal was also used to prepare metalloyl anions and, more specifically, the dianions of germoles (equation 21)$^{34-37}$.

$$\text{Ge}_2^- \xrightarrow{\text{THF}} 2 \text{Li}^+ \xrightarrow{2 \text{Me}_3\text{SiCl} \text{THF}} \text{Me}_3\text{Si}^- + \text{SiMe}_3$$  (21)

$R = \text{Et, Ph}$

The compound with $R = \text{Ph}$ was prepared by stirring a THF solution of the corresponding dichloride with lithium for 12 h at room temperature, followed by extraction with dioxane and recrystallization at $-20^\circ\text{C}$. The crystallographic study showed two structurally distinct forms depending on the crystallization temperature (see Section IV, Figure 8). The two forms can be considered as highly aromatic$^{35}$.

Germolyl dianion having $R = \text{Et}$ was synthesized following a similar process but using a mixture of THF and TMEDA. An X-ray crystal structure of the resulting (2,3,4,5-tetraethyl-1-germacyclopentadiene)$^{2-}$ 2 Li$^+$ showed three lithium cations around one
germole ring in \(\eta^1\), \(\eta^5\) and \(\eta^5\) sites, giving the composition \([\eta^5\text{-Li.TMEDA}][\eta^5\text{-Li}]_{1/2}\) \([\eta^1\text{-Li}]_{1/2}\). Nearly equal C–C bond distances in the \(\text{Et}_4\text{C}_4\text{Ge}\) ring suggest a delocalized \(\pi\)-system. Conversion of 1,1-dichloro-2,3-diphenyl-1-germaindene to the lithium (or sodium) dianion according to reaction 21 in THF–TMEDA led to an unusual phenomenon of aromatization of the \(\text{GeC}_4\) portion of 1-germaindene at the expense of the aromatic \(\text{C}_6\) ring.

The reaction of divalent \(\text{M}_{14}\) halides (Ge, Sn) with an excess of alkali metal (Na, K) in benzene led to vicinal-centered digermyl and distannyl dianions (equation 22). These compounds were isolated as red crystals (Ge: 23%, Sn: 30% yield). Their X-ray structures are similar (Figure 1), but the crystals are not isomorphous. The structure of the digermyl disodium compound is characterized by an inversion center at the midpoint of the Ge–Ge bond, whereas the distannyldipotassium has a twofold axis of symmetry along the potassium–potassium vector. In each structure the alkali metal counterions are associated with each dianion by coordination in a \(\pi\) sandwich fashion, and the alkali–metal \(14\) distances are longer than the normal single bond. By treating \(\text{ClGeC}_6\text{H}_3\cdot2,6\text{-Mes}_2\) with \(\text{KC}_8\), the same authors obtained a crystallized trigermylallyl anion formed from the corresponding cyclotrigermyl radical (equation 23). The structure of the trigermylallyl anion, isolated as dark green crystals, indicates a planar geometry at the central germanium and the K counterion complexed in a \(\pi\) fashion with two mesityl ligands. The complexing mesityl rings form a bent sandwich structure at the \(\text{K}^+\) ion.

\[
\text{Cl}-\text{E}-2,6\text{-Tip}_2\text{C}_6\text{H}_3 \xrightarrow{\text{M}} \text{E} \cdots \text{M} \cdots \text{E}
\]

\(\text{E} = \text{Ge}, \text{M} = \text{Na}\)
\(\text{E} = \text{Sn}, \text{M} = \text{K}\)

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\]

\(\text{E} = \text{Ge}, \text{M} = \text{Na}\)
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\[
\text{Cl}-\text{E}-2,6\text{-Tip}_2\text{C}_6\text{H}_3 \xrightarrow{\text{M}} \text{E} \cdots \text{M} \cdots \text{E}
\]

\(\text{E} = \text{Ge}, \text{M} = \text{Na}\)
\(\text{E} = \text{Sn}, \text{M} = \text{K}\)

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Bulky stannyl anions which are not available from stannyl hydrides (see Section I.A.1) were prepared by using the reaction of alkali metals with tin halides (equations 24–26)\textsuperscript{31,40,41}.

\[
\begin{align*}
\text{(Me)}_n\text{(Nph)}_{3-n}\text{SnBr} + \text{Li} & \rightarrow \text{(Me)}_n\text{(Nph)}_{3-n}\text{SnLi} \quad (24) \\
n &= 0, 1, 2 (70–75\% \text{ yields})
\end{align*}
\]

\[
\begin{align*}
\text{Bu}_3\text{SnX} & \rightarrow \text{Bu}_3\text{SnK} \quad (25) \\
\text{Ph}_3\text{SnCl} + \text{Na} & \rightarrow \text{Ph}_3\text{SnNa} \quad (26)
\end{align*}
\]

In a similar way, but in a one-pot experiment (equation 27)\textsuperscript{42}, a stable silylated stannyl anion was prepared in 44\% yield and isolated as white crystals. X-ray crystallography showed a distorted tetrahedral tin atom with a Sn–Li distance (2.87 Å) which is shorter than those published for [Li(THF)\textsubscript{3}.Sn\{(4-MeC\textsubscript{6}H\textsubscript{4})NSiMe\textsubscript{2}\}_3CH] (2.89 Å) and [Li(PMDETA).SnPh\textsubscript{3}] (2.87 Å), but longer than the Li–M\textsubscript{14} distances in the Ge and Si analogues: (2.67 Å) and (2.64 Å), respectively.

\[
\begin{align*}
\text{Me}_3\text{SiCl} & \rightarrow \text{Me}_3\text{SiLi}(\text{THF})_3 \quad (44\%) \\
\text{Me}_3\text{PbBr} & \rightarrow \text{Me}_3\text{PbLi} \quad (29)
\end{align*}
\]

3. Nucleophilic cleavage of M\textsubscript{14}–M\textsubscript{14} bonds and transmetallation reactions

Nucleophilic cleavage by potassium t-butoxide of digermanes, distannanes and diplumbanes in N, N\textsuperscript{′}-dimethylpropyleneurea (DMPU) as solvent provided a facile and general
method for preparations of germyl-, stannyl- and plumbyl-centered anions in good yields (60–90%) (equation 30)\(^45\). Cleavage of mixed \(M_{14}—M_{14}'\) bonds have also been investigated\(^46\).

\[
\text{Ph}_3E\text{-EPh}_3 + \text{Me}_3\text{COK} \rightarrow \text{Ph}_3\text{EK} + \text{Ph}_3\text{EOCMe}_3
\]  
\(E = \text{Ge, Sn, Pb}\)  

Other nucleophilic reagents have been used, such as \(\text{MeLi}^{32,47}\) (equation 31), \(\text{PhCH}_2\text{K}\) (equation 32)\(^21\) and \(\text{Bu}_4\text{NF}\) (equation 33)\(^48\).

\[
(\text{Me}_3\text{Si})_4\text{Ge} + \text{MeLi} \rightarrow \text{Me}_4\text{Si} + (\text{Me}_3\text{Si})_3\text{GeLi} (\text{THF})_3
\]  

Tris(trimethylsilyl)germyl lithium obtained according to equation 31 as a THF complex\(^32,47\) was isolated as colorless needles (88% yield). By using PMDETA in hexane, a new complexed \((\text{Me}_3\text{Si})_3\text{GeLi(pmdeta)}\) was also obtained as colorless crystals. Both germyllithium derivatives have a similar Ge–Li distance (2.666 Å and 2.653 Å) and a tetrahedral germanium. The ammonium germanate obtained in equation 33 is highly ionic, as revealed by a bathochromic effect \((\Delta \lambda = +125\text{nm})\) observed by comparison with the starting silagermane. It gives classical nucleophilic reactions with alkyl halides and nucleophilic additions to carbonyl compounds\(^48\).

Cleavage with cesium fluoride was used in the case of stannylsilanes (equation 34)\(^49\). The generated stannyl anions are very effective in synthetic applications, mainly in abstraction of halogen to initiate organic \(4+2\) cycloadditions (equation 35)\(^49\), a reaction which constitutes one of its chemical characterizations.

\[
\text{Bu}_3\text{SnSiMe}_3 + \text{CsF} \rightarrow [\text{Bu}_3\text{SnSi(F)Me}_3]^- + \text{Bu}_3\text{Sn}^- + \text{Me}_3\text{SiF}
\]  

Treatment of \(\text{Sn}_2(\text{CH}_2\text{Bu-t})_6\) with potassium naphthalenide in THF at 25 °C afforded crystalline \(K[\text{Sn(\text{CH}_2\text{Bu-t})_3}] (\text{THF})_2\) which in toluene gave \(K[\text{Sn(\text{CH}_2\text{Bu-t})_3}] (\eta^6-\text{C}_6\text{H}_5\text{Me})_3\) (equation 36)\(^50\). The X-ray structure of the latter revealed that potassium is in a distorted tetrahedral environment with a K–Sn bond length of 3.55 Å (See Section IV).
Nucleophilic cleavage of the lead–lead bond is one of the few ways to form plumbyl anions (equations 30, 37 and 38)\textsuperscript{45,51,52}, but in the case of a sterically hindered and thus weak lead–lead bond, a metal–metal cleavage is required (equation 39)\textsuperscript{45,51–53}.

\[
\text{Bu}_3\text{PbPbBu}_3 \xrightarrow{n\text{-BuLi}} \text{Bu}_4\text{Pb} + \text{Bu}_3\text{PbLi} \tag{37}
\]

\[
\text{Ph}_3\text{PbPbPh}_3 + \text{PhLi} \xrightarrow{\text{THF}} \text{Ph}_4\text{Pb} + \text{Ph}_3\text{PbLi} \tag{38}
\]

\[
\text{Mes}_3\text{PbPbMes}_3 + \text{Li} \xrightarrow{} 2[\text{Mes}_3\text{Pb}]^{-}\text{Li}^+ \tag{39}
\]

When they can be used, transmetallation reactions are also interesting synthetic routes to $\text{M}_{14}$ anions. In trialkylgermyl alkali metal compounds, the alkali metal is easily displaced by a less electropositive alkali metal (equation 40)\textsuperscript{54}.

\[
\text{Et}_3\text{GeLi} \xrightarrow{\text{+Na}} \text{Et}_3\text{GeNa} \xrightarrow{\text{+K}} \text{Et}_3\text{GeK} \xrightarrow{\text{+Cs}} \text{Et}_3\text{GeCs} \tag{40}
\]

In the same way, organodigermylmercury compounds led to germyllithium compounds (equations 41 and 42)\textsuperscript{1,3a,55}.
\[
(R_3\text{Ge})_2\text{Hg} + 2\ M \xrightarrow{\begin{array}{c} \text{C}_6\text{H}_6 \\
\text{or } n-\text{C}_6\text{H}_{14} \\
\end{array}} \text{Hg} + 2\ R_3\text{GeM} \tag{41}
\]

\[
\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}
\]

\[
[\text{GeR}_2-\text{GeR}_2-\text{Hg}]_n \xrightarrow{\text{Li}} n\text{R}_2\text{LiGe-GeLiR}_2 \xrightarrow{\text{MeI}} n\text{R}_2\text{MeGeGeMeR}_2 \tag{42}
\]

\[
\text{R} = \text{Ph, Et}
\]

4. Other syntheses and other metal-14 anions

There are other examples of reactions leading to or involving the formation of metal-centered anions, sometimes of a new type.

For example, treatment of a digermene with an equivalent of lithium naphthalenide in DME provided a digermenyl lithium species isolated as red microcrystals and identified by its reaction with methanol (equation 43)\textsuperscript{56}.

\[
\text{R}_2\text{Ge} \equiv \text{GeR}_2 \xrightarrow{\text{excess Li.Np/DME}} \text{R}_2\text{Ge} \equiv \text{GeR} \xrightarrow{\text{MeOH}} \text{R}_2(\text{H})\text{Ge} \equiv \text{GeR} \xrightarrow{\text{OMe}} \text{Li(DME)}_2
\]

Oxidative addition of an organometallic compound to a halogermylene also leads to a germylanion when the reaction is carried out at low temperature to prevent the nucleophilic substitution of the germanium–halogen bond. The transient halogermylsodium thus formed (Scheme 9) undergoes a fast ‘condensation’ to a more stable digermanylsodium characterized \textit{in situ} by NMR from the two different $\delta$\textsuperscript{29}Si signals: 21.9 and 23.7 ppm, and by chemical means from its reaction with alkyl halides\textsuperscript{57}.

\[
\text{GeCl}_2\text{dioxane} + t-\text{Bu}_3\text{SiNa} \xrightarrow{\text{THF, } -78^\circ\text{C}} \left[ \begin{array}{c} \text{Cl} \\
\text{t-Bu}_3\text{Si} \end{array} \right] \xrightarrow{\text{dioxane}} \left[ \begin{array}{c} \text{GeNa} \\
\text{Cl} \\
\end{array} \right] \xrightarrow{-\text{NaCl}} \text{t-Bu}_3\text{Si} \xrightarrow{\text{RX}} \text{t-Bu}_3\text{Si} \xrightarrow{-\text{NaCl}} \text{Cl} \xrightarrow{\text{Cl}} \text{Cl} \xrightarrow{\text{Cl}} \text{Cl}
\]

\[
\text{SCHEME 9}
\]

Synthesis of a cyclotetragermyl dianion from a vicinal digermyl dianion was achieved through nucleophilic attack of $t$-BuLi (equation 44)\textsuperscript{58}. This compound, isolated as yellow crystals, was characterized by X-ray diffractometry. It contains a planar four-membered ring of germanium atoms.
Heterobinuclear complexes featuring the bridging germole dianion ligand have been described (equation 45)\(^{59,60}\).

\[
\text{2 (Et}_2\text{O)LiCH}_2\text{Ph} \rightarrow \text{2 Me}_3\text{SiCH}_2\text{Ph}
\]

Germylanions have been generated electrochemically (equation 46)\(^{61}\).

\[
\text{Ph}_n\text{Me}_{3-n}\text{GeH} \rightarrow \text{Ph}_n\text{Me}_{3-n}\text{Ge}^- + \text{NBu}_4^+
\]

\[\text{Bu}_4\text{N}^+\text{BF}_4^-\]
The reaction of these electrochemically generated anions with phenylacetylene (i) was compared with the same reaction with the corresponding germyllithiums (ii). The stereochemistry of the resulting vinyl intermediates was different. Reaction (ii) produced a mixture of \(Z\) (33%) and \(E\) (57%) 2-organogermylstyrene, while reaction (i) led to \(Z\) (75%) and \(E\) (25%) 2-organogermylstyrene. These differences were interpreted in terms of the dependence of the activation energy for the isomerization of the intermediate on the nature of the counterion and its state of solvation\(^{61}\).

Sonication of 1,1-dichloro-2,3,4,5-tetraethylgermole with an excess of lithium in THF and TMEDA gave a red solution of trigermole dianion which was crystallized and characterized by X-ray analysis. It showed that one lithium cation is engaged in a lithocene structure, while the second one is in an environment similar to those in common organolithium compounds complexed by THF and TMEDA (equation 47)\(^{62}\).

\[
\begin{align*}
\text{Li/THF} & \quad \text{TMEDA} \\
\begin{array}{c}
\text{Ge} \\
\text{Cl} \\
\text{Cl}
\end{array} & \quad \begin{array}{c}
\text{Et}_4 \\
\text{Et}_4 \\
\text{Et}_4 \\
\text{Li (THF)(TMEDA)}
\end{array}
\end{align*}
\]

Anionic pentacoordinated 1,2-oxagermetanide was synthesized quantitatively by deprotonation of the corresponding \(\beta\)-hydroxygermane (Scheme 10)\(^{63}\). Upon heating at 150 °C for 30 days, this compound equilibrated with another diastereoisomer and underwent a Peterson-type reaction with elimination of olefins (Scheme 10).

In a formal oxidative coupling reaction, a dimeric deltahedral Zintl ion was obtained in high yield as green-brown crystals (equation 48)\(^{64}\). The X-ray structural determination revealed that the distance between the two Ge\(_9\) clusters is about 2.49 Å, which corresponds to a simple two-center, two-electron localized bond. There are two different cesium sites in the structure: one caps the open square face of each Ge\(_9\) cluster and one the Ge—Ge edge of its partner in the dimer. A more interesting role is played by the second cesium cation, since it not only caps faces and edges, but does that for two neighboring clusters and thus connects the clusters into chains. The positioning of the ethylene diamine molecules is such that the chains are enveloped by them and the cryptated potassiums are located between the chains\(^{64}\).

\[
\begin{align*}
\text{KCs}_2\text{Ge}_9 & \quad \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \\
\text{cryptand} & \rightarrow \\
\text{Cs}_4(\text{K-cryptand})_2[(\text{Ge})_9-(\text{Ge})_9].6\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2
\end{align*}
\]

\[
\text{cryptand: 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane}
\]

Germanates are ammonium salts in which the counterion is a germylanion (equation 49)\(^{65}\). They are generally prepared from ‘acidic’ hydrogermanes by reaction with a Lewis base \(N\). Sometimes they decompose reversibly to germylene in the presence of
K + CD3CN

KH, 18-crown-6/THF −72 °C to r.t.

Ge 
HO
CF3
Bu-
Ph
F3CC F3

80-150 °C CD3CN

150 °C CD3CN

30 days

SCHEME 10

K +

Ge
Ph
F3CC

Bu-
CF3

O

Bu-
CF3

O

Bu-
CF3

F3CC

Bu-
CF3

SCHEME 10
an excess of base N. When the base is DBU, the germanate can be isolated as an oil which precipitates in benzene.

\[
\text{PhCl}_2\text{GeH} \xrightarrow{N} \text{(PhCl}_2\text{Ge)}^- (\text{NH})^+ \xrightarrow{(a) - \text{NHCl}} \text{PhGeCl} \quad (49)
\]

Another way to germanates consists in the protonation of an amino ligand linked to germanium. Using HF, the germanium center was hexacoordinated by fluorine anions (Scheme 11)\(^\text{66}\). The germanate has a structure, obtained by single crystal X-ray diffractionometry, in which the germanium center is a slightly distorted octahedron with Ge–F (axial) bond lengths of 1.84 Å, while the Ge–F (equatorial) bond lengths are different (1.79 Å, 1.87 Å)\(^\text{66}\).

\[
\text{SCHEME 11}
\]

The reaction of a lithium tripodal silylamide with dichlorogermylene resulted in a dianimation of the germylene center coupled with an oxidative addition of one of the lithium amides (equation 50)\(^\text{67}\). The resulting triaminogermyllithium was isolated as colorless parallelepipedic crystals in 80% yield. An X-ray analysis revealed relatively large Ge–N bond lengths (1.98 Å) along with a large Ge–Li bond length (2.90 Å), suggesting a high localization of negative charge on the germanium center, which forms a close ion-pair with the THF complexed lithium counterion.

\[
\text{t-Bu} - \text{Si} - \text{O} - \text{Si} - \text{N Li} - \text{Ph} + \text{GeCl}_2\text{dioxane} \rightarrow \text{2LiCl, dioxane} \xrightarrow{\text{THF/75 °C}} \text{t-Bu} - \text{Si} - \text{O} - \text{Si} - \text{N Ge Li(THF)}_3 \quad (50)
\]
Metal-centered radical anions have recently received increased interest. Usually formed by SET reactions from derivatives of tetravalent or divalent metal-14 (equation 51), they have been characterized by ESR and radiofluorescence.

\[
[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{E} + \text{Na} \xrightarrow{20^\circ\text{C}/10–15 \text{s}} \text{THF} \] \rightarrow [(\text{Me}_3\text{Si})_2\text{CH}]_2\text{E}^-\text{Na}^+ \tag{51}
\]

\(\text{E} = \text{Ge, Sn}\)

Further contact between solutions of radical anions and sodium resulted in the complete disappearance of their ESR signals because of their transformation to a diamagnetic dianion through a second single electron transfer (equation 52).

\[
[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Ge}^-\text{Na}^+ + \text{Na} \xrightarrow{20^\circ\text{C}} \text{THF} \] \rightarrow [(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Ge}^{2(\text{aq})}2\text{Na}^+ \tag{52}
\]

Several publications about oxidative addition of metal or organometal derivatives to stannylenes describe a new and efficient way to stannyl anions. The reaction of CpLi with \(\text{Cl}_2\text{Sn}\) resulted in a mononuclear complex as colorless cubic crystals obtained in 48% yield (equation 53). Its structure was resolved by X-ray diffraction and shows a complete separation of the ion-pair.

\[
n\text{Cp}_2\text{Sn} + \text{CpLi} \xrightarrow{\text{12-crown-4}} \text{THF} \] \rightarrow \text{Cp}_3\text{Sn}^-\text{[Li(12-crown-4)2]}^+ \tag{53}
\]

The reduction of bivalent aryltin chloride by sodium anthracenide in THF gave a new way to a bulky distannylanion in the form of a stable very close ion-pair (equation 54). The X-ray crystal structure reveals a normal Sn–Sn distance (2.81 Å) in the distannylanion and a Sn–Na bond length of 3.24 Å.

\[
\text{ArSnCl} + \text{Na(anthracenide)} \xrightarrow{\text{THF}} \] \rightarrow (\text{THF})_3\text{Na}^+ \text{[SnAr]}_2 \tag{54}
\]

\(\text{Ar} = 2,6\text{-Tip}_2\text{C}_6\text{H}_3\)

New compounds having a trigonal-planar ‘paddle wheel’ triorganostannate ion were obtained from the reaction of sodium cyclopentadienide with bis(cyclopentadienyl)tin(II) and PMDETA, in a molar ratio of 1 : 1 : 1 in THF (equation 55). The reaction product, isolated as yellow crystals, was investigated by X-ray diffractometry. The structure is different from that of the cyclopentadienyl stannyl lithium obtained in equation 53. It displays a \((\eta^5\text{-Cp})_3\text{Sn}\) unit as a ‘paddle wheel’ triorganostannate anion in which one Cp ligand is additionally involved in a Sn(\(\mu\)-\(\eta^5\)-Cp)Na bridge. The Sn center is nearly trigonal planar, being separated from the complexed (PMDETA) sodium center by a Cp ring, with Sn–Cp and Cp–Na bond lengths of 2.73 Å and 2.55 Å.

\[
\text{Cp}_2\text{Sn} + \text{CpNa} \xrightarrow{\text{PMDETA/THF}} \] \rightarrow (\eta^5\text{-Cp})_3\text{Sn} \rightarrow (\mu\text{-}\eta^5\text{-Cp}) \rightarrow \text{Na} \cdot \text{PMDETA} \tag{55}
\]

A triaminostannyl lithium, prepared by oxidative addition of the corresponding amide to the stannylene bearing the same substituents (equation 56), was characterized by methylation (MeI, 71% yield) and halogenation (I\(_2\), 62% yield).

\[
\text{[Sn(NRAr)\_2]} \xrightarrow{\text{Li(NRAr)(OEt}_2\text{)}} \] \rightarrow [\text{LiSn(NRAr)\_3}] \tag{56}
\]

\(R = \text{C(CD}_3\text{)_2Me; Ar} = 3,5\text{-Me}_2\text{C}_6\text{H}_3\)
Similarly, the reaction of dichlorostannylene with \([\text{LiR}^N\text{(tmeda)}]_2\) \([\text{R}^N = \text{CH(SiMe}_2\text{Bu-t)}\text{C}_5\text{H}_4\text{N-2}]\) afforded a lithium trialkylstannate zwitterionic cage molecule having Li—Cl chloro-bridges according to X-ray structural determination (equation 57)\(^{74}\).

\[
\begin{align*}
[\text{LiR}^N\text{(tmeda)}_2] & \xrightarrow{1.8 \text{ SnCl}_2, \text{Et}_2\text{O}} \text{(tmeda)Li}_2\text{SnCl}_2, \text{Et}_2\text{O} \\
\text{R}^N & = \text{CH(SiMe}_2\text{Bu-t)}\text{C}_5\text{H}_4\text{N-2} \\
\text{R}^* & = \text{SiMe}_2\text{Bu-t}
\end{align*}
\]

Equation 57

Stannyl anions with a highly coordinated tin center are also known. A hydridostannyl anion in the shape of a trigonal bipyramid in which two iodine atoms occupy the apical positions was obtained by oxidative addition of lithium iodide to the corresponding tin hydride (equation 58)\(^{75}\). It was characterized by \(^{119}\text{Sn}\) NMR. Since apical iodines are more nucleophilic than the hydrogen, in its reactivity with \(\alpha\)-ethylenic carbonyl compounds, attack by iodine precedes reduction by hydrogen, achieving regioselective 1,4 reductions.

\[
\begin{align*}
\text{LiI} & \xrightarrow{\text{I}} \text{Bu}_2\text{Sn}_2\text{H} \xrightarrow{\text{Li}} \text{Bu}_2\text{Sn}_2\text{H} \xrightarrow{\text{Bu}} \text{Li}^+
\end{align*}
\]

Equation 58

A 1,2-oxastannetanide, which is an example of an anionic pentacoordinate tin compound with a four-membered ring oxygen and one organic substituent in apical position, was prepared at room temperature by deprotonation of the corresponding \(\beta\)-hydroxystannane using KH in THF and 18-crown-6 (equation 59)\(^{76}\). The presence of a stannyl anion was evident by the appearance of a double quartet with \(\delta_F\) centers at \(-75.09\) ppm.
Other stannates having four tin–carbon bonds were prepared by the reaction of tetracoordinate 1,1-dialkyl-3,3′-bis(trifluoromethyl)-3H-2,1-benzoxastannoles with RLi at 0 °C in THF (equation 60)\(^7\).
A stable zwitterionic carbene–plumbylene adduct has been reported (equation 64)\textsuperscript{80}. According to its X-ray crystal structure, the central carbon atom is almost planar while the lead atom is pyramidal. As expected, the P−C+ bond length (2.54 Å) is longer than a covalent P−C (about 2.38 Å) and a P≡C bond, which is expected to be about 2.05 Å\textsuperscript{80}.

A dianionic compound with trigonal-planar coordinated lead was obtained from the reaction of disodium decacarbonyldichromate with lead nitrate (equation 65)\textsuperscript{81}. The authors found that its \textsuperscript{207}Pb NMR signal (δ: 7885 ppm) supports an unsaturated character. The π system was also chemically evident. Below 213 K, in the presence of PMe\textsubscript{3}, a pyramidal adduct is formed quantitatively, the structure of which confirms coordination of the Lewis base PMe\textsubscript{3} to the coordinatively unsaturated lead center (Pb−P: 2.84 Å).

**B. M\textsubscript{14}–Group (II) Metal Compounds**

For several years many reactions were rationalized in terms of transient germyl-Grignard reagents\textsuperscript{3a,4a}. Then, a few of these compounds, along with symmetrical
11. Alkaline and alkaline earth metal-14 compounds

digermylmagnesium, were isolated mainly in transmetallation reactions\textsuperscript{82–84}. Their structures were confirmed by chemical characterization, spectroscopic analysis and sometimes by X-ray structural studies. They possess the reactivity of nucleophilic germylanions (Scheme 12)\textsuperscript{82}.

\[
\begin{align*}
R_2\text{HGeLi} + \text{MgBr}_2 & \quad \overset{-10^\circ\text{C}}{\longrightarrow} \quad [R_2\text{HGeMgBr}] \\
R = \text{Ph}, 56\%; R = \text{Mes}, 67\% \\
\end{align*}
\]

SCHEME 12

Bis(trimethylgermylmagnesium was the first symmetrical bis(organogermyl) magnesium isolated. It was obtained from the reaction of bis(trimethylgermyl)mercury with magnesium in DME and isolated as colorless crystals complexed with DME (equation 66)\textsuperscript{83}. The X-ray structure analysis shows a germanium–magnesium bond length of 2.7 Å (Figure 2)\textsuperscript{84}.

\[
\begin{align*}
\text{(Me}_3\text{Ge})_2\text{Hg} + \text{Mg} & \quad \overset{\text{DME}}{\longrightarrow} \quad \text{(Me}_3\text{Ge})_2\text{Mg} \cdot 2\text{DME} \\
\end{align*}
\]

Addition of a Grignard reagent to a germasilene or a digermene also leads to germyl Grignard compounds. The addition to unsymmetrical germasilene is regioselective with

FIGURE 2. Solid state structure of (Me\textsubscript{3}Ge\textsubscript{2})\textsubscript{Mg} \cdot 2 DME with hydrogen atoms omitted. Reproduced by permission of Verlag der Zeitschrift für Naturforschung from Reference 84
the alkyl group adding to silicon to produce a germyl magnesium halide (equation 67)\textsuperscript{85}. As expected, upon hydrolysis, the germyl Grignard leads to the corresponding germanes.

\[
\text{Mes} \quad \text{M} = \text{Si, Ge} 
\]

Stannyl Grignard reagents are more easily available from tin hydrides (equation 68)\textsuperscript{86,87}.

\[
\text{Bu}_3\text{SnH} + i-\text{PrMgCl} \xrightarrow{\text{ether, } -\text{C}_3\text{H}_8} \text{Bu}_3\text{SnMgCl} 
\]

Triphenyllead Grignard reagent, prepared by the reaction of a Grignard reagent with PbCl\textsubscript{2} in THF, is always used \textit{in situ}, like a classical Grignard. It reacts as a plumbyl anion leading to substitution reactions, for example with allylic or propargylic halides (Scheme 13)\textsuperscript{88}.

\[
\begin{align*}
3 \text{PhMgBr} + \text{PbCl}_2 & \rightarrow \text{Ph}_3\text{PbMgBr} \\
\text{Ph}_3\text{Pb} + 3 \text{PhMgBr} & \rightarrow \text{Ph}_3\text{PbCH}_2\text{C} & \equiv & \text{CH} \\
\text{(94\%)} & + \\
\text{(6\%)}
\end{align*}
\]

\textbf{SCHEME 13}

\[
\begin{align*}
\text{R}_3\text{GeCl} + \text{Ca} & \xrightarrow{900 \, ^\circ\text{C}, 0.01 \text{torr}} \text{R}_3\text{GeCaCl} \\
\text{H}_2\text{O} & \rightarrow \text{R}_3\text{GeH} \\
\text{PhBr} & \rightarrow \text{R}_3\text{GePh} \\
\end{align*}
\]

\textbf{SCHEME 14}

Insertion reactions of calcium atoms into \text{M}_{14}—\text{M}_{14} bonds yield symmetrical or unsymmetrical \text{M}_{14}—\text{Ca} compounds according to Scheme 14 and equation 69\textsuperscript{89}. A trimethylsilyl trimethylstannyl calcium was also characterized chemically in the cocondensation of calcium with trimethylsilyl trimethylstannane\textsuperscript{90}. Calcium bis(stannide) (equation 69) crystallizes in the form of colorless cuboids in a centrosymmetric space group P1. The calcium atom lies on the crystallographic center of inversion in the middle of the linear Sn—Ca—Sn chain. The calcium atom is coordinated in a distorted octahedral fashion by two tin atoms.
and four oxygen atoms of the THF ligands in a trans configuration (Figure 3)\(^8^9\).

\[
\text{Me}_3\text{SnSnMe}_3 + \text{Ca} \rightarrow \text{[(Me}_3\text{Sn)}_2\text{Ca}] \cdot 4\text{THF} \quad (69)
\]

When the bis(trimethylstannyl)calcium was reacted with an excess of hexamethyldistannane, a new polystannylcalcium was formed quantitatively according to equation 70\(^8^9\).

\[
\text{[(Me}_3\text{Sn)}_2\text{Ca}] \cdot 4\text{THF} + 6\text{Me}_3\text{SnSnMe}_3 \rightarrow \text{[(Me}_3\text{Sn)}_3\text{Sn}\text{Ca}] \cdot 4\text{THF} + 6\text{SnMe}_4 \quad (70)
\]

Similar insertions of strontium or barium atoms into M\(_{14}\)-group (II) compounds (equation 71)\(^3^a\).

\[
\text{Ph}_3\text{GeGePh}_3 + \text{MNH}_3 \rightarrow 
\begin{array}{c}
\text{Ph}_3\text{Ge} \\
\text{THF}
\end{array} 
\rightarrow 
\begin{array}{c}
\text{Ph}_3\text{Ge} \\
\cdot \text{M} \\
\cdot \text{THF}
\end{array} \quad (71)
\]

\(\text{M} = \text{Sr, Ba}\)

Other compounds displaying a M\(_{14}\)-metal bond with a nucleophilic center can be considered as reacting like M\(_{14}\) anions (Scheme 15, equation 72)\(^3^a, ^4^a\), but they usually behave in a different way (Schemes 16 and 17, equation 73)\(^3^a, ^4^a, ^9^1\) and therefore will not be discussed here.

\[
\begin{align*}
\text{[(F}_3\text{C)}_3\text{Ge)}_2\text{Zn} + \text{Cp}_2\text{TiCl}_2 & \rightarrow \text{Cp}_2\text{ClTiGe(FC)}_3 \quad (72) \\
\begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array} 
& \begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array} 
& \begin{array}{c}
\text{Ph} \\
\text{GeHgGeHg}
\end{array} 
& \begin{array}{c}
\text{Ge:} \\
\text{Hg}
\end{array} 
& \text{hν} 
& \begin{array}{c}
\text{Ph} \\
\text{Cl}
\end{array} 
& \begin{array}{c}
\text{Cl}
\end{array} 
& n 
\end{align*}
\]
(R₃Ge)₂M + ROH → R₃GeMOR + R₃GeH

M = Hg, Cd; R = alkyl, aryl, acyl

+ROH → R₃GeOR

R₃ = Ph₃, Ph₂Me, PhMe₂

**SCHEME 15**

(R₃Ge)₂Hg → \text{hv or } T \text{°C} \rightarrow 2 \text{R₃Ge}^* \rightarrow \text{R₃GeGeR₃}

PhCH₈NOBu-t → \text{R₃GeCH(Ph)NBu-t}

ESR characterized

**SCHEME 16**

\[ [(\text{R₃Ge})_2\text{HAl}]^- \text{Li}^+, \text{THF} \]

H₂O → \text{R₃GeH (96%)}

R’X → \text{R₃GeR’}

R’ = Me, Ph
X = I, Br

**SCHEME 17**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Starting reagents</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₃GeLi</td>
<td>Me₃GeCl or (Me₃Ge)₂/Li</td>
<td>92–94, 32</td>
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<tr>
<td>Et₃GeLi, Et₃GeK, Et₃GeNa</td>
<td>(Et₃Ge)₂Hg/Li, K, Na</td>
<td>95, 96</td>
</tr>
<tr>
<td>Ph₃GeLi</td>
<td>Ph₃GeH/BuLi, (Ph₃Ge)₂GeLi</td>
<td>33, 97–99</td>
</tr>
<tr>
<td>Ph₃GeK</td>
<td>(Ph₃Ge)₂/Me₃COK</td>
<td>45</td>
</tr>
<tr>
<td>Ph₂MeGeLi</td>
<td>Ph₂MeGeCl/Li</td>
<td>33</td>
</tr>
<tr>
<td>PhMe₂GeLi</td>
<td>PhMe₂GeCl/Li</td>
<td>33</td>
</tr>
<tr>
<td>Mes₃GeLi</td>
<td>Mes₃GeH/t-BuLi</td>
<td>15</td>
</tr>
<tr>
<td>(2-Me₂NC₆H₄)₃GeLi</td>
<td>(2-Me₂NC₆H₄)₃GeH/t-BuLi</td>
<td>18</td>
</tr>
<tr>
<td>(2-Me₂NCH₂C₆H₄)₃GeK</td>
<td>(2-Me₂NCH₂C₆H₄)₃GeH/PhCH₂K</td>
<td>19</td>
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<tr>
<td>(PhCH₂)₃GeLi</td>
<td>(PhCH₂)₄GeLi</td>
<td>100</td>
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<td>(Me₃Si)₃GeLi</td>
<td>(Me₃Si)₄Ge/MeLi</td>
<td>47, 101</td>
</tr>
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<td>Mes₂HGeLi</td>
<td>Mes₂HGeH/t-BuLi</td>
<td>16</td>
</tr>
<tr>
<td>Ph₂HGeLi</td>
<td>Ph₂HGeH/t-BuLi</td>
<td>16</td>
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<tr>
<td>Tip₂HGeLi</td>
<td>(Tip)₂HGeH/t-BuLi</td>
<td>26</td>
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</tbody>
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**TABLE 1. Representative metallated germlyl compounds**
<table>
<thead>
<tr>
<th>Compound</th>
<th>Starting reagents</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>(8-MeONp)$_2$HGeLi</td>
<td>(8-MeONp)$_2$GeH$_2$/t-BuLi</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>$\text{t-BuSi(OSiMe}_2$NLiPh)$_3$/\text{Cl}_2\text{Ge.dioxane}$</td>
<td>67</td>
</tr>
<tr>
<td>MesH$_2$GeLi</td>
<td>MesGeH$_3$/t-BuLi</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>Ph(C$_4$Me$_4$)GeH/n-BuLi</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>(Me$_3$Si)$_3$Si(C$_4$Me$_4$)GeH/n-BuLi, 2 (12-crown-4)</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>Mes(C$_4$Me$_4$)GeH/n-BuLi, 2 (12-crown-4)</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>(Me$_3$Si)$_2$(C$_4$Me$_4$)Ge/PhCH$_2$K, 18-crown-6</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>[Me(C$_4$Me$_4$)Ge]$_2$/2 Na, 15-crown-5</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>[Li$(\text{THF})(\text{TMEDA})]$ {2,3,4,5-Et$_4$-Ge,Ge-{Li(2,3,4,5-Et$_4$C$_4$Ge)$_2$}C$_4$Ge]}</td>
<td>62</td>
</tr>
</tbody>
</table>

**TABLE 1. (continued)***
TABLE 2. Representative dimetallated germyl and digermyl compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Starting reagents</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph₂GeK₂</td>
<td>Ph₂GeH₂/K</td>
<td>12</td>
</tr>
<tr>
<td>Et₂GeLi₂</td>
<td>Me₃SiGeEt₂Li/Me₃SiLi</td>
<td>103</td>
</tr>
<tr>
<td>Ph₂LiGeGeLiPh₂</td>
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<td>25</td>
</tr>
</tbody>
</table>

TABLE 3. Representative metallated stannyl compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Starting reagents</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₃SnLi</td>
<td>(Me₃Sn)₂/MeLi or BuLi, Me₃SnH/LDA, Me₃SnCl/Li</td>
<td>27, 104–106</td>
</tr>
<tr>
<td>Bu₃SnLi</td>
<td>Bu₃SnH/LDA, (Bu₃Sn)₂/MeLi or BuLi,</td>
<td>28, 104, 106</td>
</tr>
<tr>
<td>Ph₃SnLi</td>
<td>Ph₃SnCl/Li</td>
<td>105</td>
</tr>
<tr>
<td>Me₂NphSnLi</td>
<td>Me₂NphSnBr/Li</td>
<td>31</td>
</tr>
<tr>
<td>MeNph₂SnLi</td>
<td>MeNph₂SnBr/Li</td>
<td>31</td>
</tr>
<tr>
<td>Nph₃SnLi</td>
<td>Nph₃SnBr/Li</td>
<td>31</td>
</tr>
<tr>
<td>(Me₃Si)₃SnLi</td>
<td>(Me₃Si)₃SnMeLi, Me₃SiLi/SnCl₄</td>
<td>42, 107</td>
</tr>
<tr>
<td>Bu₂HSnLi</td>
<td>Bu₂SnH₂/LDA</td>
<td>29, 30</td>
</tr>
<tr>
<td>Ph₂HSnLi</td>
<td>Ph₂SnH₂/LDA</td>
<td>29, 30</td>
</tr>
<tr>
<td>(c-C₆H₁₁)₂HSnLi</td>
<td>(c-C₆H₁₁)₂SnH₂/LDA</td>
<td>29, 30</td>
</tr>
<tr>
<td>Me₃SnNa</td>
<td>Me₃SnCl/Na, (Me₃Sn)₂/Na</td>
<td>41, 108</td>
</tr>
<tr>
<td>Bu₃SnNa</td>
<td>Bu₃SnCl/Na</td>
<td>41</td>
</tr>
<tr>
<td>Ph₃SnNa</td>
<td>Ph₃SnCl/Na</td>
<td>41</td>
</tr>
<tr>
<td>Me₂NphSnNa</td>
<td>Me₂NphSnH/NaH</td>
<td>31</td>
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<td>MeNph₂SnNa</td>
<td>MeNph₂SnH/NaH</td>
<td>31</td>
</tr>
<tr>
<td>Me₃SnK</td>
<td>Me₃SnH/⁻BuOK</td>
<td>109</td>
</tr>
<tr>
<td>Bu₃SnK</td>
<td>Bu₃SnCl/[K⁺/K⁻]</td>
<td>40</td>
</tr>
<tr>
<td>Ph₃SnK</td>
<td>(Ph₃Sn)₂/⁻BuOK, Ph₃SnH/⁻BuOK</td>
<td>45, 109</td>
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<tr>
<td>Bu₃SnCs</td>
<td>(Bu₃Sn)₂/CsF</td>
<td>49</td>
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TABLE 4. Representative metallated plumbyl compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Starting reagents</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₃PbLi</td>
<td>Me₃PbBr/Li</td>
<td>44</td>
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<tr>
<td>Bu₃PbLi</td>
<td>(Bu₃Pb)₂/BuLi,</td>
<td>51</td>
</tr>
<tr>
<td>(t-Bu)₃PbLi</td>
<td>((t-Bu)₃Pb)₂/Li</td>
<td>110</td>
</tr>
<tr>
<td>Ph₃PbLi</td>
<td>(Ph₃Pb)₂/PhLi, Li</td>
<td>53, 111</td>
</tr>
<tr>
<td>Mes₃PbLi</td>
<td>(Mes₃Pb)₂/Li</td>
<td>52</td>
</tr>
<tr>
<td>o-Tol₃PbLi</td>
<td>(o-Tol₃Pb)₂/Li</td>
<td>111</td>
</tr>
<tr>
<td>p-Tol₃PbLi</td>
<td>(p-Tol₃Pb)₂/Li</td>
<td>111</td>
</tr>
<tr>
<td>(2,4-Xyl)₃PbLi</td>
<td>((2,4-Xyl)₃Pb)₂/Li</td>
<td>111</td>
</tr>
<tr>
<td>Ph₃PbK</td>
<td>(Ph₃Pb)₂/t-BuOK</td>
<td>45</td>
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</tbody>
</table>

IV. SPECTROSCOPIC AND STRUCTURAL STUDIES

UV and ¹H NMR, and more particularly ¹³C NMR, spectroscopies are excellent tools for the analysis of molecular and electronic structures of metal-14 anions. Calculations are also very useful for evaluating the charge delocalization, particularly in the metalole series, in connection with UV studies. X-ray structural analyses are conclusive when single crystals are isolated.

A. UV-visible Spectroscopy

In UV-visible studies of metal-14 anions showed bathochromic shifts of their absorption maxima in comparison with those of the precursor organogermanes. This absorption band (Table 5) can be explained in terms of a transition from the non-bonding orbital of the metal (HOMO) to the lowest anti-bonding orbital (LUMO) of the metal–carbon bonds for alkyl metal-14 anions⁹³ or of the phenyl groups in the aryl series¹⁷,³³,¹¹². Moreover, the bathochromic shifts on going from lithium to potassium are indicative of CIP (Contact Ion Pair) formation for the aryl group-14 anions¹¹² with an electron localization at the metal.

Under laser photolysis, these metal-14 anions easily gave the corresponding radicals by direct photo-ejection from the group-14 element³³ (equation 74).

\[
\text{Ph}_n\text{Me}_{3-n}E^- \xrightarrow{hv} \text{Ph}_n\text{Me}_{3-n}E^+ + e^- \\
E = \text{Si, Ge, Sn}; \ n = 1-3 \\
1/2 (\text{Ph}_n\text{Me}_{3-n}E)_2
\] (74)

CIDEP studies indicated that photo-ejection reactions probably occurred from triplet anions³³. Oxidation potentials (−0.29 to −0.90 V, versus SCE)¹¹³ confirmed the electron-donor properties of the anions.

B. NMR Spectroscopy

NMR spectroscopy (¹H, ¹³C, ⁷Li, ...) is widely used to clarify the nature of the metal-14–alkalimetal bond and the possible interactions between the metal-14 anion center and its substituents. The upfield shifts of the proton NMR signals of Ge—H correlate with the negative charge on germanium¹⁶, but the most interesting conclusions about charge delocalization in these compounds were obtained from ¹³C studies of arylgermylanions (Table 6). A comparison of their chemical shifts with those of the starting arylgermanes
TABLE 5. UV spectra $\lambda_{\text{max}}$ for group-14 centered anions

<table>
<thead>
<tr>
<th>Anion</th>
<th>$\lambda_{\text{max}}$ (nm) for M =</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me$_3$Ge</td>
<td>280</td>
<td>280</td>
</tr>
<tr>
<td>$n$-Bu$_3$Ge</td>
<td>&lt;280</td>
<td>~280</td>
</tr>
<tr>
<td>Ph$_3$Ge</td>
<td>308</td>
<td></td>
</tr>
<tr>
<td>PhMe$_2$Ge</td>
<td>290</td>
<td></td>
</tr>
<tr>
<td>(8-MeONp)PhHGe</td>
<td>348</td>
<td></td>
</tr>
<tr>
<td>Ph$_3$Sn</td>
<td>298(sh)</td>
<td>350(sh)</td>
</tr>
<tr>
<td>Ph$_3$Pb</td>
<td>298(sh)</td>
<td>348</td>
</tr>
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</table>

TABLE 6. $^{13}$C chemical shifts (ppm) of metallated arylanions

<table>
<thead>
<tr>
<th>Compound</th>
<th>ipso</th>
<th>ortho</th>
<th>meta</th>
<th>para</th>
<th>$\Delta\delta$(ipso)$^a$</th>
<th>$\Delta\delta$(ortho)$^a$</th>
<th>$\Delta\delta$(meta)$^a$</th>
<th>$\Delta\delta$(para)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph$_3$GeNa$^b$</td>
<td>163.3</td>
<td>139.6</td>
<td>127.7</td>
<td>124.1</td>
<td>+31.7</td>
<td>+3.6</td>
<td>−1.4</td>
<td>−5.6</td>
</tr>
<tr>
<td>Mes$_3$GeLi$^c$</td>
<td>153.7</td>
<td>144.0</td>
<td>128.7</td>
<td>130.9</td>
<td>+26.4</td>
<td>−0.1</td>
<td>0</td>
<td>−8.3</td>
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<tr>
<td>Ph$_3$HGeNa$^b$</td>
<td>164.4</td>
<td>137.8</td>
<td>126.8</td>
<td>123.5</td>
<td>+29.7</td>
<td>+2.0</td>
<td>−2.3</td>
<td>−6.3</td>
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<tr>
<td>Ph$_3$HGeLi$^c$</td>
<td>159.4</td>
<td>137.6</td>
<td>127.0</td>
<td>124.1</td>
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<td>−2.4</td>
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</tr>
<tr>
<td>Mes$_2$HGeLi$^c$</td>
<td>153.9</td>
<td>144.4</td>
<td>127.2</td>
<td>132.6</td>
<td>+22.0</td>
<td>0</td>
<td>−2.3</td>
<td>−6.8</td>
</tr>
<tr>
<td>8-MeO−Np$^e$</td>
<td>161.7</td>
<td>137.4</td>
<td>126.6</td>
<td>123.8</td>
<td>+23.5</td>
<td>+2.5</td>
<td>−2.1</td>
<td>−5.2</td>
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<td>PhHGeLi$^f$</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ph$_3$GeNa$^b$</td>
<td>165.3</td>
<td>137.3</td>
<td>126.9</td>
<td>123.8</td>
<td>+28.9</td>
<td>+1.5</td>
<td>−2.1</td>
<td>−6.0</td>
</tr>
<tr>
<td>Ph$_3$GeLi$^d$</td>
<td>173.1</td>
<td>135.0</td>
<td>124.8</td>
<td>120.7</td>
<td>+35.4</td>
<td>+2.0</td>
<td>−3.3</td>
<td>−7.9</td>
</tr>
<tr>
<td>Ph$_3$GeK$^e$</td>
<td>166.3</td>
<td>137.3</td>
<td>126.6</td>
<td>123.5</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Mes$_3$GeLi$^f$</td>
<td>152.5</td>
<td>142.8</td>
<td>129.3</td>
<td>139.3</td>
<td>+17.3</td>
<td>−0.9</td>
<td>0</td>
<td>−0.8</td>
</tr>
<tr>
<td>Ph$_3$LiGeGeLiPh$_2$</td>
<td>157.0</td>
<td>137.7</td>
<td>127.0</td>
<td>124.5</td>
<td>+20.4</td>
<td>+1.5</td>
<td>−2.6</td>
<td>−1.6</td>
</tr>
<tr>
<td>Ph$_3$GeK$_2$</td>
<td>164.0</td>
<td>138.3</td>
<td>127.6</td>
<td>124.3</td>
<td>+28.3</td>
<td>+0.6</td>
<td>−2.6</td>
<td>−6.6</td>
</tr>
<tr>
<td>(p−Tol)$_2$GeK$_2$</td>
<td>160.0</td>
<td>138.7</td>
<td>128.8</td>
<td>133.0</td>
<td>+19.3</td>
<td>+1.7</td>
<td>−2.2</td>
<td>−0.6</td>
</tr>
<tr>
<td>Ph$_3$SnK$^e$</td>
<td>167.7</td>
<td>139.2</td>
<td>126.9</td>
<td>124.3</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td>Ph$_3$PbK$^e$</td>
<td>191.1</td>
<td>140.2</td>
<td>128.1</td>
<td>123.7</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

$^a\Delta\delta = \delta(\text{Ar}_3MLi) - \delta(\text{Ar}_3MH)$.
$^b$Solutions in NH$_3$; benzene resonance occurs at 129.04 ppm.
$^c$In THF-d$_8$.
$^d$In HMPA.
$^e$In DMPU; cyclohexane used as an internal reference at 27.7 ppm.

showed a strong downfield shift of the ipso carbon and a moderate high field shift of the para carbon which was observed in all the M$_{14}$ series$^{6,9,16,45,114–116}$. Chemical shifts of the meta and ortho carbons were less affected by the metatlation of the arylgermane. These results can be attributed to a polarization of the phenyl ring, resulting in decreased electron density at the ipso carbon. Such a polarization can be induced by a localized negative charge on the germanium center which is consistent with predominant inductive $\pi$-polarization effects and negligible (or absent) mesomeric effects.

In the particular case of germoles (C$_4$Ge rings), the corresponding anions (MLi, MK) had either a localized non-aromatic structure with a negative charge localized on germanium$^{20,21}$, or delocalized aromatic structure$^{34,35}$, depending on the nature of the metal and the substituents.

The $^{119}$Sn NMR chemical shifts (Table 7) seem not to be correlated to the negative charge on the metal. Moreover, the $^{207}$Pb resonance of Ph$_3$Pb$^-$ appeared at an extremely low field shift (+1040 to +1060 ppm)$^{116}$ (Table 7).
The role of covalency in group 14 atom–alkali metal interactions has been widely discussed from proton and lithium NMR chemical shifts. Cox and coworkers\textsuperscript{117} suggested that the degree of association between the group-14 atom and lithium increased in the order Pb < Sn < Ge, and that the germanium–lithium bond had a considerable degree of covalent character. Other spectroscopic studies (\textsuperscript{7}Li, \textsuperscript{119}Sn, \textsuperscript{207}Pb NMR) of phenyl-substituted group-14 anions showed that the structure in solution can be described by a classical ion-pair model\textsuperscript{116} with variations from CIP to SSIP (Solvent Separated Ion Pair) depending on the solvent (ether to tetrahydrofuran).

Within the alkyl series\textsuperscript{118}, the nature of the Ge–metal bond in Et\textsubscript{3}GeM (M = Li, Na, K and Cs) was studied by proton NMR methods by measuring variations of \(\delta_{\text{CH}_{2}}\) of the ethyl groups (\(\Delta = \delta_{\text{CH}_{3}} - \delta_{\text{CH}_{2}}\)) according to the metal or the solvent. It was concluded that under these conditions, the Ge–M grouping is a contact ion-pair which becomes a solvent separated ion-pair when HMPT is added.

The weakness of these bonds was also demonstrated by NMR studies of (trimethylstannyl) and (tributylstannyl) lithiums\textsuperscript{119} in solution. The addition of more than two equivalents of HMPA produced the ion-separated complex Bu\textsubscript{3}Sn\textsuperscript{−}/Li(HMPA)\textsubscript{2}\textsuperscript{+} both in ether and in THF. By contrast, the observation of a Sn–Li coupling at low temperature seemed to indicate a significant covalent interaction. For example, (tributylstannyl)lithium in ether at \(-119^\circ\text{C}\) showed Li–Sn coupling (\(J_{\text{Li}–\text{Sn}} = 402.5\text{ Hz}\)) in both the \textsuperscript{119}Sn and \textsuperscript{7}Li spectra\textsuperscript{119}. In the \textsuperscript{119}Sn NMR spectra, both the 1 : 1 : 1 : 1 quartet from coupling of \textsuperscript{119}Sn to \textsuperscript{7}Li and the 1 : 1 : 1 triplet derived from the natural abundance of \textsuperscript{6}Li were observed. The expected \textsuperscript{117}Sn and \textsuperscript{119}Sn satellites were also well resolved in the \textsuperscript{7}Li spectra. The same large coupling constant (\(J_{\text{Li}–\text{Sn}} = 412\text{ Hz}\)) was previously observed for Ph\textsubscript{3}SnLi–PMDETA\textsuperscript{120}. According to the authors, large coupling constants could imply that there is a significant amount of covalent character in these Sn–Li bonds. Another reason might be the use of a predominantly 5s orbital in Sn–Li bonds\textsuperscript{6}. In the potassium series, the presence of a Sn–K bond in [K{Sn(CH\textsubscript{2}Bu-t)\textsubscript{3}]}(THF)\textsubscript{2}] was confirmed by a solid state \textsuperscript{119}Sn cross-polarization magic angle spinning (CP-MAS) NMR spectral study in which the coupling \textsuperscript{119}Sn–\textsuperscript{39}K (with \(J\) of 289 Hz) was observed for the first time\textsuperscript{50}.

The configurational stability of germyllithium compounds has been studied by temperature variation of the proton NMR spectra\textsuperscript{121}. The selected system Ph(i-Pr)\textsubscript{2}GeLi possesses groups (methyl of the i-Pr groups) which are diastereotopic. The methyl non-equivalence was observed in diglyme up to 185°C, which is the upper experimental limit. Assuming that rotation around the Ge–C bond was fast on the NMR time scale, the non-equivalence

---

**TABLE 7.** \textsuperscript{119}Sn and \textsuperscript{207}Pb chemical shifts and \(J\) couplings of group-14 anions

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\delta_{\text{M}_{14}}(\text{ppm}))</th>
<th>(J(\text{M}_{14}–\text{M}))</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph\textsubscript{3}SnLi</td>
<td>-106.7</td>
<td></td>
<td>THF</td>
</tr>
<tr>
<td>Ph\textsubscript{3}SnLi</td>
<td>J(\textsuperscript{7}Li–\textsuperscript{119}Sn) = 412 Hz</td>
<td>Toluene-d\textsubscript{8}</td>
<td></td>
</tr>
<tr>
<td>Ph\textsubscript{3}SnK</td>
<td>-108.4</td>
<td></td>
<td>THF</td>
</tr>
<tr>
<td>Me\textsubscript{3}SnLi</td>
<td>-179</td>
<td></td>
<td>THF</td>
</tr>
<tr>
<td>Et\textsubscript{3}SnLi</td>
<td>-99</td>
<td></td>
<td>THF</td>
</tr>
<tr>
<td>Bu\textsubscript{3}SnLi</td>
<td>-155</td>
<td></td>
<td>Et\textsubscript{2}O</td>
</tr>
<tr>
<td>[(t-BuCH\textsubscript{2})\textsubscript{3}SnK(η\textsuperscript{6}-C\textsubscript{6}H\textsubscript{5}Me)\textsubscript{3}]</td>
<td>-221</td>
<td></td>
<td>Toluene</td>
</tr>
<tr>
<td></td>
<td></td>
<td>J(\textsuperscript{39}K–\textsuperscript{119}Sn) = 289 Hz</td>
<td>Solid state</td>
</tr>
<tr>
<td>Ph\textsubscript{3}PbLi</td>
<td>1062.6</td>
<td></td>
<td>THF</td>
</tr>
<tr>
<td>Me\textsubscript{3}PbLi</td>
<td>512</td>
<td></td>
<td>THF</td>
</tr>
<tr>
<td>(t-Bu\textsubscript{3}PbLi</td>
<td>1573.8</td>
<td></td>
<td>THF</td>
</tr>
</tbody>
</table>
of these groups was taken as evidence for slow inversion about germanium. A lower limit to inversion about trivalent germanium could therefore be set at about 24 kcal mol\(^{-1}\).

C. X-ray Diffraction Studies

The sterically hindered compound \((\text{Me}_3\text{Si})_3\text{GeLi}\) (donor) (donor = THF or PMDETA) was the first germanium–metal bonded complex to be characterized by X-ray structure analysis at low temperature (153 K)\(^47\). The germanium–lithium distances of 2.666(6) Å (THF) and 2.653(9) Å (PMDETA) are slightly greater than the sum of the covalent radii of Ge and Li (2.56 Å). The reduction of angles around the central germanium was explained by the polar nature of the Ge–Li bond (Figure 4).

A shorter Ge–Li bond of 2.598(9) Å\(^18\) was observed for tris(2-dimethylaminophenyl) germyllithium. In this case, the distortion of the geometry around the germanium center was explained by the interaction between the lithium atom and the amino group.

X-ray structural studies of the anions of germoles have recently stimulated a great deal of interest\(^21\),\(^22\),\(^35\),\(^36\). Crown ethers (12-crown-4 for Li and 16-crown-6 for K) were used in monometallation reactions, giving free germacyclopentanenide ions\(^21\),\(^22\). They have a non-aromatic ring with a pyramidal germanium center (Figure 5).

Several types of metal coordination to germole dianions have been described\(^21\),\(^35\),\(^36\): \(\eta^5\), \(\eta^5\) (a), \(\eta^1\), \(\eta^5\) (b) and \(\eta^1\), \(\eta^5\) and \(\eta^5\) (c) (Figure 6).

An example of \(\eta^5\) bonding type is evident in the case of the bis(germole dianion) complex \([\text{K}_4(18\text{-crown}-6)]_3[\text{C}_4\text{Me}_4\text{Ge}]_2\) (Figure 7)\(^21\).

The dilithium salt of the tetraphenylgermole dianion has the very interesting property of crystallizing from dioxane in two structurally distinct forms (a and b) depending upon the crystallization temperature. The crystals obtained from dioxane at \(-20^\circ\text{C}\) have a reverse sandwich structure (a), while crystals obtained at 25°C have one lithium atom \(\eta^5\)-coordinated to the ring atoms and the other \(\eta^1\)-coordinated to the germanium atom (b)\(^35\) (Figure 8).

The X-ray structure determination of the germole dianion \([\eta^5\text{-Li.TMEDA}][\eta^5\text{-Li}]_{1/2}[\eta^1\text{-Li}]_{1/2}[\text{Et}_4\text{C}_4\text{Ge}]_{36}\) showed three lithium cations around one germole ring in the \(\eta^1\), \(\eta^5\) and \(\eta^5\) sites (Figure 9).

---

**FIGURE 4.** Solid state structure of \((\text{Me}_3\text{Si})_3\text{GeLi}(\text{THF})_3\) with hydrogen atoms omitted. Reprinted with permission from Reference 47. Copyright 1996 American Chemical Society
FIGURE 5. Solid state structure of [Me₄C₄GeSi(SiMe₃)₃] with hydrogen atoms omitted. Reproduced by permission of Wiley-VCH from Reference 22.

FIGURE 6. Coordination states of germolylic anions

The germole dianions in these structures appear to possess delocalized π-systems, as evident by nearly equivalent C−C bond lengths in the five-membered rings. In the sandwich structure, the two metal atoms (K or Li) lie above and below the C₄Ge ring within bonding distance of all five ring atoms. Other structures of germylanions have also been described. These compounds do not have metal–Ge contact, but are ion-separated species.

Although many alkali and alkaline earth stannate complexes have been structurally characterized, there are only a few reports of stannyl compounds containing true metal–Sn
bonds. [Ph₃SnLi(PMDETA)] was the first metal–Sn bonded complex to be characterized in the solid state [120] (Figure 10). The Sn–Li bond of 2.817(7) Å (average of two independent molecules) is a little greater than the sum of the covalent radii (2.74 Å). The Sn center shows a pyramidal geometry which was also observed for the Ph₃Sn⁻ ion in the solid state structure of [(18-crown-6) K⁺−SnPh₃][122].

The Pb analogue complex Ph₃PbLi(PMDETA)[123] shows very similar structural features. The Pb–Li distance is slightly greater than the sum of the covalent radii of Pb and Li (average over both independent molecules: 2.858 Å; sum of covalent radii: 2.81 Å). The Ph₃Pb moiety is, however, more pyramidal than the Ph₃Sn unit (average C−Sn−C angle: 96.1°; average C−Pb−C angle: 94.3°). The significant distortion in the Ph₃E unit, away from a tetrahedral geometry, is consistent with the expected increase in the effective energetic separation of s and p orbitals on descending group 14.

Depending upon the coordinated solvent around the metal, several interesting features have been described. The complex [Li(dioxane)]₄⁺[Sn(furyl)₃Li(furyl)₃Sn]⁻.2dioxane is an ion-pair consisting of lithium ion coordinated by four dioxanes and a complex anion. The latter consists of two pyramidal (furyl)₃Sn⁻ ions linked by their furyl O-atoms to a central 6-coordinated Li center[124]. The stannyl potassium compound [K(Sn(CH₂Bu-t)₃)] (η⁶-C₆H₅Me)₃] is the first example of a complex in which the alkali metal ion is
not stabilized by heteroatom donors (O, N, etc.)\textsuperscript{50}. Three \(\pi\)-bonded toluene molecules solvate the K\(^+\) cation. The tin environment is pyramidal and the Sn–K distance is 3.548(3) Å.

More recently, complexes containing ‘paddle wheel’ \([(\eta^5\text{-C}_5\text{H}_5)_3E^-](E = \text{Sn, Pb})\) anions were prepared and structurally characterized\textsuperscript{126,127} (Figure 11).

These monomeric complexes are essentially isostructural and contain trigonal-planar \((\eta^5\text{-C}_5\text{H}_5)_3E^-(E = \text{Sn, Pb})\) units (Sn and Pb: 0.14 Å out of the plane of the three Cp centers), linked through a \(\mu\)-Cp bridge to a [Na(PMDETA)]\(^+\) cation. When the cation was
exchanged for magnesium, a separate $[(\eta^3\text{-Cp})_3\text{Sn}]^-$ ion was observed (Figure 12). The Cp ligands of the anion are bonded equivalently to the Sn center. The Cp (centroid)–Sn contacts were also significantly shorter than those found in the Na complex and a more pyramidal geometry was observed for this anion.

Table 8 gives some examples of metal 14–metal bond distances.
V. REACTIVITIES

A. Hydrolysis

Hydrolysis and more particularly deuteriolysis of the M\textsubscript{14}−M\textsubscript{1} or M\textsubscript{2} bond is one of the best ways to characterize M\textsubscript{14} anions, mainly used in germanium, tin and lead chemistry\textsuperscript{3,4,8} (equations 75 and 76)\textsuperscript{20,86}. This characterization reaction becomes very typical in the case of hydrometal-14 anions from the coupling constant between hydrogen and deuterium observed in $^1$H NMR spectra (equation 77)\textsuperscript{16,29,30}. The reaction of plumbyllithium or sodium with water was reported to be more complicated and lead to PbO\textsuperscript{8}.

\begin{equation}
\text{Ph}_3\text{GeLi} + \text{D}_2\text{O} \rightarrow \text{Ph}_3\text{GeD} + \text{LiD}
\end{equation}

The stereochemistry of the hydrolysis of the germanium–lithium bond (retention) was established\textsuperscript{8}.

B. Oxidation

Oxygen, sulfur or selenium insert in the germanium alkali–metal bond\textsuperscript{8} (equation 78\textsuperscript{67} and equation 79\textsuperscript{128}).

\begin{equation}
\frac{1}{2} \text{O}_2 + \text{Li(THF)}_3 \rightarrow 3 \text{THF} + \text{MeSiOSiMe}_2\text{GeLi} \rightarrow 2 \text{MeSiOSiMe}_2(\text{SiMeN})\text{GeLi}
\end{equation}
11. Alkaline and alkaline earth metal-14 compounds

The treatment of arylhydrogermyllithium with elemental selenium produced tetraselena germolanes (equation 80)^9.

The reaction of Ph₃SnLi with selenium in THF at room temperature led to the lithium triphenyltin selenide, which had been trapped by reaction with metal-14 halides (Scheme 18)^2.

C. Substitution

Metal-14 anions react with alkyl halides (RX) mostly by nucleophilic substitution (SN2), the stereochemistry of which is dependent on the structure of R and X, the solvent and the nature of the counterion. Other reactions were also observed: nucleophilic substitution at halogen [also called halogen/metal exchange (HME)] and single electron processes. In some cases steric hindrance around the reactant results in elimination.

1. Substitutions at carbon

The reaction of organogermylmetal compounds with organic halides is an effective route to form germanium–carbon bonds. The stereochemistry of these reactions was established as predominantly retention (equation 81)^129,130,131; see Section V.C.2.

\[
R^1R^2R^3Ge^*Li + R^4Cl \xrightarrow{\text{Retention}} R^1R^2R^3Ge^* + LiCl
\]  

Methyl iodide was widely used for the characterization of metal-14 centered anions. Generally, the reaction occurs at room temperature and leads to almost quantitative yields (equation 82). However, it was shown in germanium chemistry that one has to be careful in the interpretation of the results because complexes such as [GeLi, RLi, ether] lead to
the same dialkylation on metal-14 (see Section III. A. 1, Scheme 5).

\[
\begin{align*}
\text{M}_{14} & - \text{M} + \text{MeI} \rightarrow \text{M}_{14} - \text{Me} + \text{MI} \\
\text{M} & = \text{group I or group II metal}
\end{align*}
\] 

(82)

Because of steric hindrance and high coordination of the germanium center, in some cases methyl iodide undergoes halogen/metal exchange (equation 83)\(^\text{17}\).

\[
\begin{align*}
\text{OMe} & \text{GeH}_2 \text{Mes} \\
& \xrightarrow{1. \ 2 \ n-\text{BuLi} \ 2. \ \text{MeI}} \text{OMe} \text{GeMe} \text{Mes} \text{I} \\
\end{align*}
\] 

(83)

Within the tin series, the trimethylstannyl anion has to be considered as one of the most powerful simple nucleophiles available; thus an \(S_N^2\) reaction at carbon with inversion of configuration is often observed (equation 84)\(^\text{4b}\).

\[
\begin{align*}
\text{R}_1^3\text{Sn}^- & + \text{R}_2\text{X} \rightarrow \text{R}_1^3\text{SnR}_2^- + \text{X}^- \\
\text{R}_1^- & = \text{Me, Bu, Ph}
\end{align*}
\] 

(84)

\(S_N^2\) substitutions at the halogen were also observed (equation 85)\(^\text{4b}\).

\[
\begin{align*}
\text{R}_1^3\text{Sn}^- & + \text{R}_2\text{X} \rightarrow \text{R}_1^3\text{SnX} + \text{R}_2^- \\
\text{R}_1^- & = \text{Me, Ph}
\end{align*}
\] 

(85)

\(S_{RN1}\) reactions with aryl halides were also observed. Their general mechanism is presented in Scheme 19\(^\text{4b}\) and illustrated in the subsection on SET reactions.

\[
\begin{align*}
\text{R}_3\text{Sn}^- & + \text{R}'\text{X} \rightarrow (\text{R}'\text{X})^- + \text{R}_3\text{Sn}^- \\
(\text{R}'\text{X})^- & \rightarrow \text{R}'^- + \text{X}^- \\
\text{R}'^- & + \text{R}_3\text{Sn}^- \rightarrow (\text{R}_3\text{SnR}')^- \\
(\text{R}_3\text{SnR}')^- & + \text{R}'\text{X} \rightarrow \text{R}_3\text{SnR'}^- + (\text{R}'\text{X})^- \\
\end{align*}
\] 

SCHEME 19

Formal nucleophilic substitutions have been studied by simple trapping techniques designed to separate and estimate contributions of reactions proceeding by way of free radicals, by way of anions, geminate or synchronous processes\(^\text{108}\). Reactions of trimethyltin sodium with organic halides in THF at 0 °C were examined using dicyclohexylphosphine for trapping free radicals and \(t\)-butylamine for trapping free anionoids. Among the twenty-two halides included in this study, nine were shown to involve two or all three of the mechanistic pathways.
Primary chlorides reacted predominantly by a direct mechanism (SN2 or a multicentered
process). Isobutyl or neopentyl halides led to contributions from electron transfer (free
radicals) and halogen–metal exchange (anionoid) mechanisms.

Secondary bromides reacted predominantly by an electron transfer and competitive but
minor halogen–metal exchange, while the relative contribution from these were reversed
in the case of iodides.

Triethyldiethylcarbinyl chlorides reacted exclusively by elimination while the bromide reacted
by electron transfer in competition with elimination.

1- and 2-bromoadamantanes reacted, because of high steric hindrance, by electron
transfer, and 1-chloroadamantane, which is less reactive, gave no reaction under the same
conditions.

The results obtained in the case of primary halides were confirmed by kinetic studies
of their reactions with stannylanions using a stopped flow technique. The resulting rate
constants were much greater than those calculated for an electron transfer according to
the Hush–Marcus theory which supports a nucleophilic reactivity rather than a single
electron transfer pathway. On the contrary, in the case of 1-iodonorbornane (a tertiary halide), the result of the
reaction with trimethylstannyl reagents (Me₃SnM, M = Li, Na), both in the absence and
in the presence of trapping agents, confirmed that the nucleophilic substitution process is
governed by competition between polar and radical mechanisms.

As in germanium chemistry, MeI was also mainly used to characterize stannylanions
(equation 86). The structure of the methylated compound was determined by X-ray
analysis.

Substitution of alkyl halides by triphenylplumbyl anions also easily gave alkylation of
the metal-14 center through a process which proceeds with inversion of configuration at
the carbon center (equation 87).

Non-classical metal-14 anions often react in the same way. Thus, ammonium ger-
manates were alkylated with MeI (equation 88).

Metal dianions and polymetal anions were also alkylated by MeI or other alkyl halides
RX (equations 89 and 90) in high yields (70–80%).
All of these reactions which lead to $M_{14}$-carbon bonds allow the synthesis of various functional metal-14 organometallic compounds.

The reaction of germyllithiums with chloromethyl methyl ether gave the germymethyl methyl ether in good yield (equation 91)\(^9,136\).

\[
R_3\text{GeLi} + \text{ClCH}_2\text{OCH}_3 \rightarrow R_3\text{GeCH}_2\text{OCH}_3
\]  

(91)

$R_3\text{Ge}$: PhH$_2$Ge (73% yield)

$R_3\text{Ge}$: TMS$_2$(Me$_3$Ge)Ge (89% yield)

The reaction of Ph$_3$MLi ($M = \text{Ge, Sn}$) or Me$_3$SnNa with 6-bromo-1-heptene gave the expected 6-$M_{14}$-1-heptene as the major product, but also (2-methylcyclopentyl)methyl derived metal-14 compound (equation 92)\(^137\). An intermediate 1-methyl-5-hexenyl radical was proposed, but its participation was not clearly established. Distannylation of haloalkylpropene was also described (equation 93)\(^138\).

\[
\text{MPh}_3 + \text{ClBr} \rightarrow \text{MPh}_3
\]  

(92)

\[
2 \text{R}_3\text{SnLi} \rightarrow \text{R}_3\text{SnSnR}_3
\]  

(93)

The arylstannylation of the aniline skeleton using $o$-, $m$- or $p$-bromo-$N,N$-dimethylanilines has been reported (equation 94)\(^139\). In the case of the three bromoanilines, a modified process was used (Scheme 20)\(^139\).

\[
o\text{-BrC}_6\text{H}_4\text{NMe}_2 + \text{Me}_3\text{SnLi} \rightarrow o\text{-Me}_3\text{SnC}_6\text{H}_4\text{NMe}_2 + \text{LiBr}
\]  

(94)

Organic $gem$-di- and tri-halides, or carbon tetrachloride gave complete stannylation because $\alpha$-stannylalkyl halides are much more reactive than $\alpha$-stannylalkyl $gem$-dihalides.
11. Alkaline and alkaline earth metal-14 compounds

\[ x\text{-BrC}_6H_4NH_2 + 3 \text{BuLi} \rightarrow x\text{-LiC}_6H_4NLi_2 \rightarrow \]
\[ x\text{-BrMgC}_6H_4NLi_2 \rightarrow x\text{-Ph}_3\text{SnC}_6H_4NLi_2 \rightarrow H_2O \]
\[ x\text{-Ph}_3\text{SnC}_6H_4NH_2 \]
\[ x = o, m, p \]

**SCHEME 20**

(equations 95 and 96) \(^{4b}\).

\[ 3 \text{Me}_3\text{SnLi} + \text{HCCl}_3 \rightarrow \text{HC(SnMe}_3)_3 \] (95)

\[ 2 \text{Me}_3\text{SnLi} + (\text{TMS})_2\text{CCl}_2 \rightarrow (\text{TMS})_2\text{C(SnMe}_3)_2 \] (96)

In lead chemistry, the level of metallation was temperature-dependent (equation 97) \(^{3c}\).

\[ \text{Ph}_3\text{PbLi} + \text{CCl}_4 \rightarrow \text{Ph}_3\text{PbCCl}_3 \] (97)

In the case of 1,2-dihaloethanes and 1,3-dihalopropanes, an elimination was observed (equation 98) \(^{3c}\); see Scheme 21 \(^{140}\).

\[ 2 \text{Ar}_3\text{PbMgX} + X\text{CH}_2\text{CH}_2X \rightarrow \text{Ar}_6\text{Pb}_2 + \text{CH}_2 = \text{CH}_2 + 2 \text{MgX}_2 \] (98)

\[ X = \text{Cl, Br} \]

\[ \text{R}_3\text{SnNa} + X\text{CH}_2\text{CH}_2\text{H} \rightarrow \text{R}_3\text{SnH} + X\text{CH}_2\text{CH} = \text{CH}_2 + \text{NaX} \]
\[ \text{R}_3\text{SnNa} + \text{XCH}_2\text{CH} = \text{CH}_2 \rightarrow \text{R}_3\text{SnCH}_2\text{CH} = \text{CH}_2 + \text{NaX} \]

\[ 2\text{R}_3\text{SnH} \rightarrow \text{R}_3\text{SnSnR}_3 + \text{H}_2 \]

**SCHEME 21**

When the chain becomes longer, dimetallation occurs preferentially (equation 99) \(^{140}\).

\[ 2 \text{Me}_3\text{SnNa} + \text{Cl(CH}_2)_n\text{Cl} \rightarrow \text{Me}_3\text{Sn(CH}_2)_n\text{SnMe}_3 \] (99)

\[ n = 4–6 \]

2-stannylpyrimidines were synthesized by stannylamion substitution of 2-chloro- or 2-bromopyrimidines (equation 100) \(^{141}\).
Another application of the direct alkylation of metal-14 anions is the synthesis of polymer-supported organotin hydrides. These were prepared by the reaction of \(\omega\)-haloalkylpolystyrenes with hydridobutylstannyllithium. The stannyl group was separated from the phenyl ring of polystyrene by two, three or even four carbon spacers. These polymers were found to contain 0.8–1.4 mmol of Sn–H per gram. The reducing ability of the polymer-supported organotin hydrides was monitored by reactions with haloalkanes (Scheme 22)\(^{142}\).

A convenient, general and efficient (96% yield) synthesis of primary \(\alpha\)-alkoxyorganostannanes from stannylanions and \(\alpha\)-haloethers has been reported (equation 101)\(^28\).

\[
\text{Bu}_3\text{SnLi} \quad \text{ROCH}_2\text{Cl} \quad \xrightarrow{-78\,^\circ\text{C}} \quad \text{Bu}_3\text{SnCH}_2\text{OR} \quad (101)
\]

The substitution of aromatic acyl chloride by organogermyl groups occurs undoubtedly by an addition–elimination process (\(S_N\) acyl), but under particular conditions SET processes were also involved\(^{143}\) (see Section V.E). These reactions yield as major products either \(\alpha\)-germylketones (equations 102 and 103)\(^{15,16,144}\) or bis(organogermyl) carbinols, depending on reagents and conditions.\(^8\)

\[
\text{Ph}_3\text{GeLi} + \text{ArCOCl} \quad \xrightarrow{-\text{LiCl}} \quad \text{Ph}_3\text{GeCOAr} \quad (102)
\]

\(\text{Ar} = \text{Ph}, \, p\text{-MeOC}_6\text{H}_4, \, p\text{-FC}_6\text{H}_4, \, p\text{-CF}_3\text{C}_6\text{H}_4\)
11. Alkaline and alkaline earth metal-14 compounds

\[ \text{Ar}_2\text{HGeLi} + \text{PhCOCl} \rightarrow \text{Ar}_2\text{HGeCOPh} \] (103)

\[ \text{Ar} = \text{Ph, Mes} \]

With the more sterically hindered 2,4,6-trimethylbenzoyl chloride, the expected reaction occurred but it also gave an unexpected germa-β-diketone which might be formed through a benzoylgermyllithium (Scheme 23)\textsuperscript{16}. Digermyl diketones were synthesized in the same way (equation 104)\textsuperscript{9}.

\[ \begin{align*}
\text{Ph}_2\text{HGeLi} & \rightarrow \text{MesCOCl} & \rightarrow \text{MesCOCl} \\
\text{Ph}_2\text{HGeCOMes} & + \text{Ph}_2\text{Ge(COMes)}_2 & + \text{Ph}_2\text{GeH}_2 \\
\rightarrow & \text{Ph}_2\text{GeH}_2 & \text{MesCOCl} \\
\text{Ph}_2\text{LiGeCOMes} & + \text{Ph}_2\text{HGeLi} & \rightarrow \text{Ph}_2\text{HGeLi} \\
\text{Ph}_2\text{HGeLi} & \rightarrow \text{Ph}_2\text{HGeLi} \\
\text{Ph}_2\text{LiGeCOMes} & \rightarrow \text{Ph}_2\text{LiGeCOMes} \\
\end{align*} \]

\textbf{SCHEME 23}

\[ \begin{align*}
\text{Ph}_2\text{HGeLi} + 2 \text{MesCOCl} & \rightarrow \text{Ph}_2\text{GeCOMes} + \text{Ph}_2\text{Ge(COMes)}_2 + \text{Ph}_2\text{GeH}_2 \\
-2\text{LiCl} & \rightarrow \text{MesCOCl} \\
\text{(45%)} & \rightarrow \text{Ph}_2\text{GeCOMes} \\
\end{align*} \] (104)

The reaction of PhH\textsubscript{2}GeLi with MesCOCl gave an unexpected triacylgermane, no doubt by successive trans-lithiation of a transient hydrogermyl ketone (equation 105)\textsuperscript{102}.

\[ 3 \text{PhH}_2\text{GeLi} + 3 \text{MesCOCl} \rightarrow 3\text{LiCl} & \rightarrow \text{PhGe(COMes)}_3 + 2 \text{PhGeH}_3 \\
\text{hydrolysis} & \rightarrow \text{PhGe(COMes)}_3 \\
\text{(81%)} & \rightarrow \text{PhGe(COMes)}_3 \\
\] (105)

When the steric effect around germanium and the carbonyl did not prevent subsequent addition of the germyllithium to the germyl ketone, the reaction gave mainly the α-digermyl alcohol (equation 106)\textsuperscript{102}.

\[ \begin{align*}
\text{MesH}_2\text{GeLi} + \text{PhCOCl} & \rightarrow \text{MesH}_2\text{GeLi} + \text{PhCOCl} \\
1. -40^\circ\text{C} & \rightarrow \text{MesH}_2\text{GeLi} + \text{PhCOCl} \\
2. \text{H}_2\text{O} & \rightarrow \text{MesH}_2\text{GeLi} + \text{PhCOCl} \\
\rightarrow & \text{(MesH}_2\text{Ge)}_2\text{C(OH)Ph} \\
\text{(29%)} & \rightarrow \text{(MesH}_2\text{Ge)}_2\text{C(OH)Ph} \\
\end{align*} \] (106)

The reaction of a stannylanion with an acyl chloride also constitutes a general access to acylstannanes, but in low yields (equation 107)\textsuperscript{145}. These can be improved by using other functions derived from carboxylic acids\textsuperscript{8} (see equation 118 below).

\[ \begin{align*}
\text{R}_3''\text{SnLi} & + \text{RCOCl} \rightarrow \text{R}_3''\text{SnLi} + \text{RCOCl} \\
-\text{LiCl} & \rightarrow \text{R}_3''\text{SnLi} + \text{RCOCl} \\
\rightarrow & \text{R}_3''\text{SnLi} + \text{RCOCl} \\
\text{R} = \text{aryl}; R' = \text{allyl}, \text{aryl} \\
\end{align*} \] (107)

In lead chemistry, the reaction between the trimesitylplumbyllithium and acyl chlorides led to acylplumbanes in high yield and to the first isolable acylplumbane as a yellow crystalline compound, whose structure was confirmed by single crystal X-ray analysis.
(equation 108)\(^5\)\(^2\).

\[
\text{Mes}_3\text{PbLi} + \text{RCOCl} \rightarrowforewordt{\text{LiCl}} \rightarrow \text{Mes}_3\text{PbCOR} \quad (108)
\]

\(R = \text{Me, Ph}

Other less stable acylplumbanes were not isolated but characterized \textit{in situ} (equation 109)\(^3\)\(^c\).

\[
\text{Ph}_3\text{PbLi} \rightarrowforewordt{\text{PhCOCl}} \rightarrow \text{LiCl} \rightarrowforewordt{\text{Ph}_3\text{PbCOR}} \quad (109)
\]

\(R = \text{Me, Ph, OEt, NEt}_2\)

The reaction of vicinal \(M_{14}\) dianions with organic dihalides gave heterocyclization (equation 110)\(^9\),\(^2\)\(^5\).

\[
\text{Ph}_2\text{LiGeGeLiPh}_2 + \text{Br(CH}_2)_3\text{Br} \rightarrowforewordt{2\text{LiBr}} \rightarrowforewordt{\text{Ph}_2\text{Ge}} \rightarrowforewordt{\text{Ph}_2\text{Ge}} \quad (26\%\)\(^)\)
\)

In the case of benzyl halides, a lithium halogen exchange prevents the cyclization and the reaction gives only oligomers (equation 111)\(^9\),\(^2\)\(^5\).

\[
\text{Ph}_2\text{LiGeGeLiPh}_2 \rightarrowforewordt{\text{Br}} \rightarrowforewordt{\text{Ph}_2\text{GeGeLiPh}_2 \rightarrowforewordt{\text{2LiBr}} \rightarrowforewordt{\frac{1}{n} \text{(Ph}_2\text{Ge})_n}} \quad (111)
\]

In tin chemistry, this type of reaction was used to prepare a distannacyclooctane, but in low yield (11%) (equation 112)\(^1\)\(^4\)\(^0\).

\[
\text{Me}_2(\text{Na})\text{SnSn(Na)Me}_2 + \text{Br(CH}_2)_3\text{Br} \rightarrowforewordt{2\text{NaBr}} \rightarrowforewordt{\text{Me}_2\text{SnSnMe}_2} \quad (112)
\]

Other carbon–heteroelement bonds have also been used to obtain substitution at carbon by metal-14 anions.

Methylation of germylanions was achieved with Me\(_2\)SO\(_4\) (equation 113)\(^1\)\(^6\).

\[
\text{R}_2\text{HGeLi} \rightarrowforewordt{1. \text{Me}_2\text{SO}_4} \rightarrowforewordt{2. \text{H}_2\text{O}} \rightarrowforewordt{\text{R}_2\text{HGeMe}} \quad (113)
\]

\(R = \text{Ph (95%)}; R = \text{Mes (95%)}\)

Tosylate and other alkoxy groups have been used as leaving groups (equations 114\(^4\)\(^b\), 115\(^1\)\(^4\)\(^6\) and 116\(^1\)\(^4\)\(^7\)).

\[
\text{Me}_3\text{SnLi} + \text{R} \rightarrowforewordt{\text{OTS}} \rightarrowforewordt{\text{TsOLi}} \rightarrowforewordt{\text{R}} \quad (114)
\]
11. Alkaline and alkaline earth metal-14 compounds

\[
\text{Bu}_3\text{SnMgCl} + \text{AcOCH(OR)}_2 \xrightarrow{-\text{AcOMgCl}} \text{Bu}_3\text{SnCH(OR)}_2 \quad (115)
\]

\[
\begin{align*}
\text{Bu}_3\text{SnLi} + \text{THF} & \xrightarrow{-78^\circ C} \text{Bu}_3\text{SnCH(OR)}_2 + \text{EtOLi} \\
& \quad (116)
\end{align*}
\]

Amino groups are also suitable leaving groups, as shown in equation 117\textsuperscript{148,149}.

\[
\begin{align*}
\text{NR} & \xrightarrow{0 \text{ to } 38^\circ C} \text{SnBu}_3 \\
& \quad (117)
\end{align*}
\]

\(\alpha\)-Metal-14 ketones were obtained by the reaction of metal-14 anions with esters or amides (equation 118)\textsuperscript{143,145,150}. The yields were often better than those obtained using acyl chlorides\textsuperscript{8}.

\[
\text{R}'_3\text{MLi} + \text{RCOX} \xrightarrow{-\text{LiX}} \text{R}'_3\text{MCOR} \quad (118)
\]

2. Substitutions at metal

Transmetallation occurs between metal-14 anions and various halometal compounds to yield a variety of organometallic compounds.

Organogermyllithiums have been used to prepare germanium–magnesium compounds which could not be isolated but led to selective germylation (Scheme 24)\textsuperscript{9,82}. Similarly, germylmercury compounds were obtained (equation 119)\textsuperscript{9,15}.

\[
\begin{align*}
\text{Mes}_3\text{GeLi} + \text{HgCl}_2 & \xrightarrow{-\text{LiCl}} \text{Mes}_3\text{GeHgCl} \\
& \xrightarrow{-\text{LiCl}} (\text{Mes}_3\text{Ge})_2\text{Hg} \\
& \quad (119)
\end{align*}
\]

The reaction of dimesitylgermyllithium etherate with diethylchloroaluminium gave an etherate of the corresponding germyl–aluminium compound in 66% yield (equation 120)\textsuperscript{151}. 
The same reaction was observed in tin chemistry (equation 121)\textsuperscript{4b} and applied also to the synthesis of a tin–zinc compound (equation 122)\textsuperscript{4b}.

\[
\text{Bu}_3\text{SnLi} + \text{Et}_2\text{AlCl} \rightarrow \text{Bu}_3\text{SnAlEt}_2 \quad (121)
\]

\[
2\text{Bu}_3\text{SnLi} + \text{ZnBr}_2 \rightarrow (\text{Bu}_3\text{Sn})_2\text{Zn} \quad (122)
\]

The reaction of trimethylgermyllithium with silicon tetrachloride, because of steric hindrance, gave a low yield of tetra(trimethylgermyl)silane, and hexamethyldigermane was obtained as the major product. The digermane resulted from a lithium/halogen exchange reaction (equation 123)\textsuperscript{32}.

\[
4\text{Me}_3\text{GeLi} + \text{SiCl}_4 \rightarrow (\text{Me}_3\text{Ge})_4\text{Si} + \text{Me}_3\text{GeGeMe}_3 \quad (19%) + \text{Me}_3\text{GeGeMe}_3 \quad (30%) \quad (123)
\]

Less bulky germyllithiums gave higher yields of germasilanes (equation 124)\textsuperscript{105}.

\[
\text{PhMe}_2\text{GeLi} + t\text{-BuMe}_2\text{SiCl} \rightarrow 25^\circ\text{C} \rightarrow \text{PhMe}_2\text{GeSiMe}_2\text{Bu-}t + \text{LiCl} \quad (71%) \quad (124)
\]

In the same way catenated stannyl, germyl silanes were prepared (equation 125)\textsuperscript{105}. The structure of an aryl compound was resolved by X-ray analysis\textsuperscript{105}.

\[
t\text{-BuMe}_2\text{SiGeMe}_2\text{Cl} + \text{R}_3\text{SnLi} \rightarrow t\text{-BuMe}_2\text{SiGeMe}_2\text{SnR}_3 \quad (125)
\]

\[\text{R} = \text{Me}, \text{Ph}\]

Transmetallations of germoles have also been studied starting from the localized monoanion and the germolyldianion (equations 126 and 127)\textsuperscript{20,35}.
Starting from a metal-14 dihalide, selective monogermylation or complete germylation can be obtained by using germylpotassium or germyllithium compounds (equations 128 and 129)\(^{152}\).

\[
\text{Ph}_2\text{SiCl}_2 + \text{Ph}_3\text{GeK} \xrightarrow{\text{Et}_2\text{O}, -78^\circ\text{C}, 5\ h} \text{Ph}_3\text{GeSiClPh}_2 + \text{KCl} \tag{128}
\]

\[
\text{Ph}_2\text{SiCl}_2 + 2\ \text{Ph}_3\text{GeLi} \xrightarrow{\text{DME}, -78^\circ\text{C}} \text{Ph}_3\text{GeSiPh}_2\text{GePh}_3 + 2\ \text{LiCl} \tag{129}
\]

Non-symmetrical organohydopopolymgermanes are usually difficult to obtain. In some cases, the reaction of a germylanion with an organohalohydrogermane allows their synthesis (Scheme 25, a), but when the organohalohydrogermane is too ‘acidic’, a competitive lithiation reaction (Scheme 25, b) gives polygermanes through \(\alpha\)-elimination\(^{16}\).

\[
\text{R}_2\text{GeHLi} + \text{PhClGeH}_2 \xrightarrow{(a)} \text{R}_2\text{HGeGeH}_2\text{Ph} \quad \text{R} = \text{Ph}, 35\% \\
\text{R} = \text{Mes}, 44\% \\
\xrightarrow{(b)} \text{R}_2\text{GeH}_2 + [\text{PhHGeClLi}] \\
\xrightarrow{-\text{LiCl}} (1/n) (\text{PhGeH})_n
\]

**SCHEME 25**

Novel half-sandwich complexes with divalent Ge, Sn and Pb were obtained from the reaction of CpSnCl with the corresponding metal-14 anion in more than 80% yield (equation 130)\(^ {153}\). The single crystal X-ray crystallographic analysis of the compound with
M = Ge revealed an average effect of $\eta^3$ and $\eta^1$ bonding modes of the cyclopentadienyl ring to the tin atom\textsuperscript{153}.

\[
\text{CpSnCl} + \text{KM (OBU-t)$_3$} \xrightarrow{\text{Toluene 25 °C}} \text{CpSnO} \xrightarrow{\text{MOBu-t + KCl}} t-\text{Bu}
\]

\[
M = \text{Ge, Sn, Pb}
\]

The X-ray analysis of diphenylbis[tris(trimethylsilyl)germyl]plumbane, obtained from the reaction of diphenyldichlorolead with the appropriate germyllithium (equation 131), showed a staggering of methyl groups around the lead center\textsuperscript{154}.

\[
(C_6H_5)_2PbCl_2 + 2(THF)_{25}LiGe(SiMe$_3$)$_3 \xrightarrow{-78 °C \text{ to r.t.}} (C_6H_5)_2Pb(Ge(SiMe$_3$)$_3$)$_2 + 2 \text{ LiCl}
\]

Metal-14-metal-14 compounds were also prepared from tin- or lead-centered anions as shown in equations 132 and 133\textsuperscript{155}.

\[
(o-\text{Tol})_3ML \xrightarrow{\text{THF}} (o-\text{Tol})_3\text{SnM(Tol-o)$_3$}
\]

\[
M = \text{Sn, 2 h, r.t., 66% yield (X-ray: Sn–Sn bond length : 2.883 Å)}
\]

\[
M = \text{Pb, -78 °C, 57% yield}
\]

\[
R_3\text{PbLi} + \text{Ph$_3$SnCl} \xrightarrow{\text{THF}} R_3\text{PbSnPh$_3$}
\]

\[
R = o-\text{Tol, 67% yield (X-ray: Sn–Pb bond length : 2.845 Å)}
\]

\[
R = \text{Mes, 44% yield}
\]

The reaction of one equivalent of $[\text{Li(THF)$_3$Sn(SiMe$_3$)$_3$}]$ with $[\text{Sn(2-}(-(\text{Me$_3$Si})_2\text{C})-\text{C$_5$H$_4$N)}\text{Cl]}$ in Et$_2$O at ambient temperature gave the corresponding divalent Sn–tetravalent Sn–compound in high yield (equation 134)\textsuperscript{156}. A single crystal X-ray diffraction study revealed the distannyl compound to be monomeric and the divalent Sn–tetravalent Sn–bond to be of length 2.869 Å. This was the first measurement of such a bond length. The $^{119}\text{SnNMR}$ spectrum exhibits two singlets at $\delta = 897$ ppm and 502 ppm, each with well resolved isotropically shifted $^{119}\text{Sn}$ and $^{117}\text{Sn}$ satellites ($J$: 6700 and 6400 Hz, respectively). This was also the first measurement of a $^{1}J$ coupling between Sn atoms of different valences.

Polygermanes $R_3\text{Ge(GeEt$_2$)$_n$GeR}_3$ ($R =$ alkyl, aryl) and polystannanes $\text{Ph$_3$Sn–(t-}Bu$_2$\text{Sn)$_n$SnPh$_3$} (n = 1 to 4)$ were prepared (equation 135) and studied by $^{119}\text{SnNMR}$ and UV. A relationship between the electronic excitation and $^{119}\text{SnNMR}$ chemical shifts of the central Sn atom was obtained, as well as a linear relationship between the coupling constant $^{2}J(119\text{Sn}/119\text{Sn})$ and the ‘non-bonding’ distance $d(\text{Sn} \cdots \text{Sn})$. These correlations
point to a smooth transition between the covalently bonded polystannanes and metallic tin.

\[
\begin{align*}
\text{Me}_3\text{Si} & \quad \text{Me}_3\text{Si} \\
\text{Cl} & \quad \text{Sn} \\
\text{SiMe}_3 & \quad \text{SiMe}_3 \\
\text{N} & \quad \text{N}
\end{align*}
\]

\[
\text{Li(THF)}_3\text{Sn(SiMe}_3)_3 \quad \text{Et}_2\text{O}
\]

\[
\begin{align*}
2 \text{R}_3\text{MLi} + X(t\text{-Bu}_2\text{Sn})_n \text{X} & \xrightarrow{\text{−78 °C}} R_3\text{M}(t\text{-Bu}_2\text{Sn})_n\text{MR}_3 \\
& \xrightarrow{\text{−2 LiX}} \text{R}_3\text{M}(t\text{-Bu}_2\text{Sn})_n\text{MR}_3
\end{align*}
\]

\[X = \text{Cl, Br} \quad \text{M} = \text{Ge, R} = \text{Et, Ph}\]

\[\text{M} = \text{Sn, R} = \text{Ph}\]

Treatment of a solution of tri(t-butyl)plumbyllithium or triarylplumbyllithiums in THF with a variety of group-14 electrophiles gave a number of dimetalla derivatives of lead (equations 136 and 137). The values and signs of the coupling constants \(1^J(^{207}\text{Pb}–^{29}\text{Si})\), \(1^J(^{207}\text{Pb}–^{119}\text{Sn})\) and \(1^J(^{207}\text{Pb}–^{207}\text{Pb})\) were determined.

\[
\begin{align*}
t\text{-Bu}_3\text{PbLi} & \xrightarrow{\text{RR}^{'2}\text{MCl(M=Si, Sn)}} t\text{-Bu}_3\text{PbMRR}^{'2} \\
& \xrightarrow{\text{or RR}^{'2}\text{MBr(M=Ge, Pb)}} (\text{THF}, \text{−30 °C})
\end{align*}
\]

\[\text{R, R}^{'} = \text{allyl, aryl}\]

\[
\begin{align*}
\text{Ar}_3\text{PbLi} + \text{Ar}^{'}_3\text{MX} & \xrightarrow{\text{THF}} \text{Ar}_3\text{PbMAr}^{'}_3 \\
& \xrightarrow{\text{−60 °C}} \text{Ar}_3\text{PbMAr}^{'}_3
\end{align*}
\]

\[\text{M} = \text{Ge, X} = \text{Cl, Br}\]

\[\text{M} = \text{Pb, X} = \text{Br, I}\]

\[\text{Ar, Ar}^{'} = \text{Ph, p-tolyl, 2,4-xylyl, p-anisyl, 2-Np}\]

A tin-containing silylferrocenes was prepared according to equation 138.

\[
\begin{align*}
2 \text{Me}_3\text{SnNa}, \text{NH}_3, \text{−78 °C} & \quad \xrightarrow{\text{−2 NaCl}} \quad 2 \text{Me}_3\text{SnNa}, \text{NH}_3, \text{−78 °C}
\end{align*}
\]

Various other compounds bearing another metal (usually a transition metal or a lanthanide) linked to the M\(_{14}\) (Ge, Sn, Pb) have been reported. Some of them were prepared from
metal-14 anions (equations 139\textsuperscript{160}, 140\textsuperscript{161}, 141\textsuperscript{4b}, 142\textsuperscript{162}, 143\textsuperscript{3c}, 144\textsuperscript{19} and 145\textsuperscript{163}).

\[ t-\text{Bu} \]
\[ \begin{array}{c}
\text{N} \\
\text{PCl} \\
\text{N} \\
t-\text{Bu}
\end{array} \quad + \quad \begin{array}{c}
\text{Et₃GeLi} \\
\text{LiCl}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{t-Bu} \\
\text{N} \\
\text{PGeEt₃}
\end{array} \quad \text{(71\%)} \] (139)

\[ 2 \text{Me₃GeLi} \xrightarrow{\text{CuBr} \cdot \text{Me₂S}} \text{THF, \textdegree78} \] (140)

\( 2 \text{Me₃SnLi} \xrightarrow{\text{CuBr}} (\text{Me₃Sn})₂\text{CuLi} \) (141)

\[ \text{R}^1\text{R}^2\text{MCl}₂ + \text{Ph₃GeLi} \xrightarrow{\text{THF, \textdegreeLiCl}} \text{R}^1\text{R}^2\text{M} \quad \text{GePh₃} \] (142)

\( \text{R}^1, \text{R}^2 = \text{Cp}, \text{Cp}^*; \text{M} = \text{Zr, Hf} \)

\[ \text{Ph₃PbLi} + [\text{Et₄N}][\text{ClM(CO)}₅] \xrightarrow{\text{LiCl}} [\text{Et₄N}][\text{Ph₃PbM(CO)}₅] \] (143)

\( \text{M} = \text{Cr, Mo, W} \)

\[ 2 \left[ \begin{array}{c}
\text{NMe₂} \\
\text{Ge}^-\text{K}^⁺ \\
\text{₃}
\end{array} \right] \xrightarrow{-2\text{KI}} \left[ \begin{array}{c}
\text{NMe₂} \\
\text{Ge} \\
\text{₃}
\end{array} \right] \text{Ln} \] (144)

\( \text{Ln} = \text{Yb (14\%); Sm (13\%)} \)

\[ \text{Ph₃GeK} + \text{Cp₃UCl} \xrightarrow{\text{THF, \textdegree20} \text{C}} \text{Ph₃GeUCp₃} + \text{KCl} \] (145)

An interesting application of M\textsubscript{14} anions in transition metal chemistry was the synthesis of optically active anions containing a transition metal–germanium bond. Thus, reaction of the optically active methyl (α-naphthyl) phenylgermyllithium R\textsubscript{3}GeLi with Mo(CO)\textsubscript{6}, W(CO)\textsubscript{6}, Fe(CO)\textsubscript{5}, \((\text{η}^5\text{-MeC}_5\text{H}_4)\text{Mn(CO)}₃\) or \((\text{η}^5\text{-C}_5\text{H}_5)(\text{Ph₃P})\text{NiCl} led to anionic complexes (equation 146)\textsuperscript{164} isolated for the four first ones as the Et₄N\textsuperscript{+} salts.

\[ \text{R₃GeLi} + \text{MCO} \xrightarrow{\text{Et₂O}} \text{R₃GeM}^-\text{Li}^+ \] (146)

\( \text{M} = \text{W(CO)}₅, \text{Mo(CO)}₅, (\text{η}^5\text{-MeC}_5\text{H}_4)\text{Mn(CO)}₂, \text{Fe(CO)}₄ \)

The reaction of metal-14 anions with the metal–halogen bond gave heterocyclization, as shown in equation 147\textsuperscript{9,165}. 

In some cases a competition between the reaction of metal-14 anions with the carbon–halogen and the metal–halogen bond was observed. For example, in the reaction of chloro(chloromethyl)dimethyl silane or germane with group-14 element nucleophiles $R_3M'Li$ ($M' = Si, Ge, Sn$), the expected monometallated $R_3M'−MMe_2−CH_2Cl$ was obtained in a very low yield, while disubstituted compounds $R_3M'−MMe_2−CH_2−M'R_3$ were mainly produced because, in the monometallated $M'$ compound, the carbon–halogen bond is activated by the $\beta$-effect of the $R_3M'$ group (equation 148)$^{165}$.}

\[
\begin{align*}
\text{Me}_2\text{MCH}_2\text{Cl} & \quad \text{1. } R_3M'\text{Li} \\
& \quad \text{2. } \text{H}_2\text{O} \\
& \quad \xrightarrow{\text{Cl}} \text{Me}_2\text{MCH}_2\text{Cl} + \text{Me}_2\text{MCH}_2\text{M'R}_3 \\
& \quad \xrightarrow{\text{M'R}_3} \text{M'R}_3 \\
M &= \text{Si, Ge} \\
R_3M' &= \text{Me}_3\text{Ge, PhMe}_2\text{Ge, Me}_3\text{Sn}
\end{align*}
\]

Nucleophilic substitutions at metal can also involve a leaving group other than halogen. Digermanes were obtained in high yields (80–85%) by the lithiogermolysis of germyl triflates (equation 149)$^{166}$. The stereochemistry of such nucleophilic substitution of an alkoxygermane by a germyllithium reagent was studied. The germyllithium reagents retain their configuration whereas inversion occurs for the alkoxygermane (equation 150 and Scheme 26)$^{167}$. Organohydrodigermanes (equation 151)$^9$ and cyclopolygermanes (equations 152 and 153)$^9,25$ were obtained in the same way.

\[
\begin{align*}
\text{R}_3\text{GeLi} + \text{R}_3'\text{GeOSO}_2\text{CF}_3 & \quad \longrightarrow \text{R}_3\text{GeGeR}_3' + \text{CF}_3\text{SO}_2\text{OLi} \\
\text{(-)-MePhNpGe*OMen} & \quad \xrightarrow{\text{Ph}_3\text{GeLi}} \text{(+)-MePhNpGe*GePh}_3 \\
|\alpha|^{25}_D : -49 & \quad |\alpha|^{25}_D : +7.5 \\
\text{MesH}_2\text{GeLi} + \text{MesH}_2\text{GeOMe} & \quad \xrightarrow{-\text{MeOLi}} \text{MesH}_2\text{GeGeH}_2\text{Mes} \\
& \quad (48\%) \\
\text{Ph}_2\text{LiGeGeLiPh}_2 + \text{Et}_2(\text{MeO})\text{GeGe(OMe)Et}_2 & \quad \xrightarrow{-\text{MeOLi}} \text{Ph}_2\text{Ge} \quad \text{GePh}_2 \\
& \quad \text{Et}_2\text{Ge} \quad \text{GeEt}_2 \\
& \quad (49\%) \\
\text{Ph}_2\text{LiGeGeLiPh}_2 + (\text{MeO})_2\text{Ge} & \quad \xrightarrow{-2 \text{MeOLi}} \text{Ph}_2\text{Ge} \quad \text{Ph}_2\text{Ge} \\
& \quad \text{Ph}_2\text{Ge} \quad \text{GePh}_2 \\
& \quad (56\%) 
\end{align*}
\]
The reaction of Ph$_3$SnNa with (Bu$_2$SnS)$_3$ gave the symmetric tin sulfide (Ph$_3$Sn)$_2$S (equation 154)$^{41}$.

$$\text{Ph}_3\text{SnNa} \xrightarrow{(\text{Bu}_2\text{SnS})_3} (\text{Ph}_3\text{Sn})_2\text{S} + \text{Ph}_3\text{SnSnPh}_3 \quad (154)$$

An important application of this method is in the preparation of (triphenylstannyl)diphenylphosphine (equation 155)$^{41}$.

$$\text{Ph}_3\text{SnNa} \xrightarrow{\text{Ph}_2\text{PX}} \text{Ph}_3\text{SnPPh}_2 + \text{NaX} \quad (155)$$

In transition metal complexes, the metal–carbonyl bond is also easily cleaved by M$_{14}$ anions (Scheme 27)$^{4a}$.

Cyclotrigermenes were obtained from the reaction of metal-14 anions with tris(tri-$t$-butylsilyl)cyclotrigermanium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, the TFPB behaving as the leaving group (equation 156)$^{168}$. The cyclotrigermene structure was established by X-ray determination.
D. Nucleophilic Additions

\( \text{M}_{14} \) anions were characterized by carbonation when the \( \text{M}_{14} \)-methanoic acids formed were sufficiently stable. The stereochemistry of this reaction was determined as retention (Scheme 28).

\[
\text{SCHEME 27}
\]

Reactions of \( \text{M}_{14} \)-anions with aldehydes resulted in facile 1,2-additions leading to \( \alpha \)-metallated alcohols (equations 157\textsuperscript{16,24} and 158\textsuperscript{9}). When the aldehyde was highly conjugated (equation 158), the nucleophilic addition did not occur and a SET reaction took place (see Section V.E). In the case of tin, the reaction was used for the synthesis of \( \alpha \)-stannylalcohol (equation 159)\textsuperscript{4b} and then applied to the preparation of \( \alpha \)-alkoxystannanes (equations 160 and 161)\textsuperscript{104,171} and \( \alpha \)-iodostannanes\textsuperscript{102,172}.
Trimethylgermyllithium reacted with aliphatic ketones to give the corresponding trimethylgermylcarbinols stereoselectively (equation 162) \(^{173}\).

\[
\text{Bu}_3\text{SnLi} + \text{RCHO} \xrightarrow{\text{after hydrolysis}} \text{Bu}_3\text{SnCH(OH)R}
\]

\[
\text{Bu}_3\text{SnLi} + \text{RCHO} \xrightarrow{\text{O}^-\text{Li}^+} \text{RCHSnBu}_3 \xrightarrow{\text{R'}X} \text{RCHSnBu}_3
\]

\[
\text{MOMCl} = \text{MeOCH}_2\text{Cl}
\]

In the reaction of acylgermanes with triethylgermyllithium (equation 163) \(^{174}\), gem-(bisgermyl)alcohols were isolated.

\[
\begin{align*}
\text{t-Bu} & \quad \text{Bu}_3\text{GeLi}, \text{Et}_2\text{O}-\text{HMPA}, -30^\circ\text{C} \\
& \rightarrow \quad \text{t-Bu} \quad \text{Bu}_3\text{Sn} \quad \text{OH} \\
& \quad \text{GeMe}_3 \\
\end{align*}
\]

\[(\text{cis}/\text{trans} = 15/85)\]
11. Alkaline and alkaline earth metal-14 compounds

\[
\begin{align*}
R_3ECR' + LiGeEt_3 & \xrightarrow{\text{hexane (H')}} R_3EGeEt_3 \\
R_3E &= Et_3Ge, Et_3GeGeEt_2, Me_3SiGeEt_2, \\
R' &= CMe_3, Ph
\end{align*}
\]

Thermostable silaenolate anions were obtained by the reaction of tris(trimethylsilyl)acylsilanes with triethylgermyllithium in THF (equation 164)^174.

\[
\begin{align*}
RCOEt_3GeLi & \xrightarrow{\text{Et}_3GeLi} RCO(Et_3Ge)SiMe_3 \\
R &= CMe_3, R' = SiMe_3, E = Si, Ge \\
R &= \text{adamantyl}, R' = SiMe_3, E = Si \\
R &= R' = CMe_3, E = Si
\end{align*}
\]

Ammonium germanates gave the same 1,2-addition to a carbonyl group (equation 165)^48.

\[
\begin{align*}
\text{Me}_3\text{Ge}^- \text{Bu}_4\text{N}^+ & \xrightarrow{1. \text{PhCOMe}} \text{MePh(Me}_3\text{Ge)COH} + \text{PhMeCHOH (75%)} \\
\end{align*}
\]

In the case of \(\alpha,\beta\)-unsaturated ketones, enolates of 3-M\(_{14}\) ketones were obtained regioselectively and characterized chemically (Scheme 29)^173. The reaction with \(\alpha,\beta\)-unsaturated amides is shown in equation 166^175.

\[
\begin{align*}
\text{Et}_3\text{GeLi} + \text{PhCH=CHCONMe}_2 & \xrightarrow{\text{after hydrolysis}} \text{Et}_3\text{GeCHCH}_2\text{CONMe}_2 \\
\end{align*}
\]

These 1,4-additions were also observed in tin chemistry (equations 167 and 168)^176–179.
These nucleophilic additions to a carbonyl group were also used to synthesize a germene by Peterson’s reaction (equation 169).\(^{180}\)
The complex Et₃GeNa-YCl₃ reacted as a strong base and abstracted the acidic hydrogen α to carbonyl, but did not lead to the expected nucleophilic addition (equation 170).\(^{181}\)

\[
\begin{align*}
\text{RCoC≡N} & \quad \text{ArCN} \\
& \quad \text{R₃GeLi·(THF)}_2
\end{align*}
\]

Metal-14 anions can add to activated ethylenic bonds. Thus, the reaction of Ph₃ELi (E = Ge, Sn) with cobaltocenium or decamethylcobaltocenium salts resulted in a...
nucleophilic addition forming cyclopentadiene–cyclopentadienyl–cobalt complexes and a competitive single electron reduction giving a cobaltocene. The proportion of the nucleophilic addition decreased from germanium to tin and also when Cp was changed to Cp* (Scheme 30). 

\[ [(C_5R_5)_2Co]PF_6 + Ph_3ElLi \]

\[ R = H, Me; E = Ge, Sn \]

**SCHEME 30**

The reaction of germyllithiums with C\(_{60}\) gave different 1,2-monoadducts (equation 175), the structures of which were resolved by X-ray analysis.

\[ R^1R^2R^3GeLi \xrightarrow{1. C_{60} \atop 2. \text{EtOH}} R^1R^2R^3Ge \quad R^1R^2R^3Ge \]

1,2 adduct 1,16 and 1,29 adducts

\[ (175) \]
Examples of additions of M\(_{14}\) anions to the acetylenic bond (equation 176)\(^{186}\) and to dienes (equation 177)\(^{187}\) have been described\(^8\).

\[
\begin{align*}
&\text{Bu}_3\text{SnLi-CuBr-Me}_2\text{S} \\
&\quad \text{Bu}_3\text{Sn} \\
&\quad \text{R} \\
&\quad \text{OPMB} \quad \text{Bu}_3\text{SnLi-CuBr-Me}_2\text{S} \\
&\quad \text{R} \quad \text{OPMB} \\
\end{align*}
\]

\[\text{R} = \text{H, COOMe (84–98\%)}\]

OPMB = \(p\)-methoxybenzyloxy

\[
\begin{align*}
&\text{CO}_2\text{Me} \\
&\quad \text{Bu}_3\text{SnLi} \\
&\quad \text{R}^1\text{R}^2\text{CO} \\
&\quad \text{Bu}_3\text{Sn} \\
&\quad \text{CO}_2\text{Me} \\
&\quad \text{R}^1 \quad \text{OH} \\
&\quad \text{R}^2 \quad \text{A} \quad \text{CO}_2\text{Me} \\
\end{align*}
\]

\[\text{R}^1\text{R}^2\text{CO} = \text{MeCOMe, PhCHO,}
\]

cyclohexanone, \(p\)-MeOC\(_6\)H\(_4\)CHO

E. SET Reactions

The notion that group-14 organometallic molecules react at ambient or moderate temperatures, preferentially by electron pair mechanisms involving concerted or polar (ionic) bond breaking, has prevailed for a long time. Homolytic cleavage, on the other hand, was thought to be a mechanism typical of high temperature or radical initiated (photo or chemically) reactions. During the last decade, new reactions involving the exchange of a single electron between closed-shell diamagnetic molecules, so-called SET reactions, have been largely regarded as a less and less exotic phenomenon\(^{188}\). Recent investigations in the field of the chemistry of organometal-14 compounds have shown that various functional compounds (\(A\)), strongly conjugated and, because of this, having a very low LUMO, react with organometal-14 compounds by inducing a single electron transfer. These reactions yield, depending on the polarity of the metal center, either a metal-centered intermediate radical (equation 178) or a metal-centered cation (equation 179)\(^{188}\).

\[
\begin{align*}
\delta^- & \quad \delta^+ & \quad \text{R}_3\text{M} - \text{Y} & \quad \text{A} & \quad \text{R}_3\text{M} - \text{Y}^{\text{+}} & \quad (\text{A})^{\text{-}} \\
\text{R}_3\text{Ge}^{\text{+}} & \quad (\text{A})^{-} & \quad \text{Y}^{\text{+}} & \quad \text{R}_3\text{Ge}^{\text{+}} & \quad (\text{A})^{-} & \quad \text{Y}^{\text{+}}
\end{align*}
\]

\[\text{Y} = \text{H, Li}\]
These reactions can be rationalized on the basis that the organometal-14 compound reacts as a prometal-centered radical (equation 178) and as a prometal-centered cation (equation 179)\textsuperscript{188}. Metal-14 anions react in SET reactions, according to equation 178.

1. **SET at carbon and metal**

The possibility of a single electron transfer process in substitution reactions at carbon and metal was at first gradually and now widely accepted.

In germanium chemistry the importance of free radical pathways in substitution reactions of secondary bromides with R\textsubscript{3}GeLi (R = CH\textsubscript{3}, C\textsubscript{6}H\textsubscript{5}) reagents is strongly indicated by product stereochemistry in cyclohexyl systems and by cyclization of the cis-heptene-2-yl moiety to yield [(2-methylcyclopentenyl)methyl]germanes, with the appropriate cis/trans ratio, as shown in equation 180, Table 9 and equations 181 and 182\textsuperscript{189}.

\[
\begin{align*}
\text{Br} & + \text{R}_3\text{MLi} & \text{solvent} & 15 \degree \text{C} & \text{Br} & + \text{R}_3\text{MLi} \\
(180) & & & & & \\
\text{R}_3 = (\text{CH}_3)_3 \text{CH} & + (\text{C}_6\text{H}_5)_3 \text{GeLi} & \text{THF} & \text{Br} & + (\text{C}_6\text{H}_5)_3 \text{GeLi} \\
(181) & & & & & \\
\text{Br} & + (\text{C}_6\text{H}_5)_3 \text{GeLi} & \text{THF} & \text{Br} & + (\text{C}_6\text{H}_5)_3 \text{GeLi} \\
\end{align*}
\]
Up on steady light illumination of aromatic compounds \( A \) in the presence of the triphenylstannyl anion metal cation pair \( \text{Ph}_3\text{Sn}^-, \text{M}^+ \) in tetrahydrofuran, radical anions of the aromatic compounds \( A^{*-}, \text{M}^+ \) were produced by electron transfer from \( \text{Ph}_3\text{Sn}^- \), \( \text{M}^+ \) to the excited aromatic compounds. After the light was cut off, the radical anions of perylene and tetracene persisted for a long time; for anthracene and pyrene, the radical anions formed transiently and decayed rapidly. The decay rate depended on the reduction potentials of \( A \). The decay processes were attributed to back electron transfer from \( A^{*-}, \text{M}^+ \) to the distannane \( \text{Ph}_3\text{SnSnPh}_3 \) which was produced by the coupling of \( \text{Ph}_3\text{Sn}^* \) radicals, since the rate constants calculated on the basis of the above reactions were in good agreement with the observed rate constants. Slow decay of \( A^{*-}, \text{M}^+ \) can be realized when the reduction potentials of \( A \) are less negative than that of the distannane (Scheme 31, Figure 13)\(^{190}\).

The reaction of trimethylstannyl sodium with primary halides has been studied in detail with emphasis on the effect of solvents and added radical and carbanion traps. By lowering
the viscosity of the solvent, lowering the cation coordinating ability of the solvent or running the reactions in the presence of a radical trap, it was shown that radical intermediates were involved (Scheme 32, Table 10)\textsuperscript{191}.

Furthermore, the reaction of a primary alkyl iodide having a cyclizable radical probe with Me\textsubscript{3}SnNa did not occur exclusively by SN\textsubscript{2} and HME pathways, as previously
\[
\begin{align*}
\text{Me}_3\text{SnNa} & \quad \text{SnMe}_3^+ \quad + \quad \text{NaBr} \\
\text{Me}_3\text{Sn} & \quad \text{Me}_3\text{Sn}^+ \quad + \quad \text{NaBr}
\end{align*}
\]

SH = hydrogen donor solvent

SCHEME 32
### TABLE 10. Reaction profile of Me$_3$SnNa with 6-bromo-1-hexene$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvents (ratio)</th>
<th>Yield of product$^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{SnMe}_3$</td>
<td>$\text{SnMe}_3$</td>
</tr>
<tr>
<td>1</td>
<td>THF-C$<em>2$H$</em>{26}$ (2 : 8)</td>
<td>92.2</td>
</tr>
<tr>
<td>2</td>
<td>THF-C$<em>2$H$</em>{26}$ (3 : 7)</td>
<td>94.1</td>
</tr>
<tr>
<td>3</td>
<td>THF-C$<em>2$H$</em>{26}$ (5 : 5)</td>
<td>95.5</td>
</tr>
<tr>
<td>4</td>
<td>THF-C$<em>2$H$</em>{26}$ (7 : 3)</td>
<td>98.0</td>
</tr>
<tr>
<td>5</td>
<td>THF-C$<em>2$H$</em>{26}$ (9 : 1)</td>
<td>98.8</td>
</tr>
<tr>
<td>6</td>
<td>THF-Et$_2$O (2 : 8)</td>
<td>86.4</td>
</tr>
<tr>
<td>7</td>
<td>THF-Et$_2$O (3 : 7)</td>
<td>93.5</td>
</tr>
<tr>
<td>8</td>
<td>THF-Et$_2$O (5 : 5)</td>
<td>98.8</td>
</tr>
<tr>
<td>9</td>
<td>THF-Et$_2$O (7 : 3)</td>
<td>98.5</td>
</tr>
<tr>
<td>10</td>
<td>THF-Et$_2$O (9 : 1)</td>
<td>99.1</td>
</tr>
<tr>
<td>11</td>
<td>THF-C$<em>5$H$</em>{12}$ (2 : 8)</td>
<td>83.4</td>
</tr>
<tr>
<td>12</td>
<td>THF-C$<em>5$H$</em>{12}$ (3 : 7)</td>
<td>89.9</td>
</tr>
<tr>
<td>13</td>
<td>THF-C$<em>5$H$</em>{12}$ (5 : 5)</td>
<td>95.0</td>
</tr>
<tr>
<td>14</td>
<td>THF-C$<em>5$H$</em>{12}$ (7 : 3)</td>
<td>98.7</td>
</tr>
<tr>
<td>15</td>
<td>THF-C$<em>5$H$</em>{12}$ (9 : 1)</td>
<td>98.5</td>
</tr>
</tbody>
</table>

$^a$Reactions were conducted by using 0.024 M concentrations of RBr and 0.048 M concentrations of Me$_3$SnNa at 0°C for 15 min.

$^b$Yields are based on the RBr consumed.

### TABLE 11. Reaction of endo-5-(2-iodoethyl)-2-norbornene with Me$_3$SnNa$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive$^b$ (molar equiv)</th>
<th>Temp (°C)</th>
<th>Yield of product$^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{SnMe}_3$</td>
<td>$\text{SnMe}_3$</td>
<td>$\text{SnMe}_3$</td>
</tr>
<tr>
<td>1</td>
<td>none</td>
<td>0</td>
<td>90.5</td>
</tr>
<tr>
<td>2</td>
<td>DCPH, 1</td>
<td>0</td>
<td>51.5</td>
</tr>
<tr>
<td>3</td>
<td>DCPH, 10</td>
<td>0</td>
<td>60.0</td>
</tr>
<tr>
<td>4</td>
<td>TBA$^c$, 1</td>
<td>0</td>
<td>75.3</td>
</tr>
<tr>
<td>5</td>
<td>TBA, 10</td>
<td>0</td>
<td>75.0</td>
</tr>
<tr>
<td>6</td>
<td>DCPH, 10; TBA, 10</td>
<td>0</td>
<td>48.6</td>
</tr>
<tr>
<td>7</td>
<td>none</td>
<td>−23</td>
<td>96.0</td>
</tr>
<tr>
<td>8</td>
<td>DCPH, 10</td>
<td>−23</td>
<td>80.0</td>
</tr>
<tr>
<td>9</td>
<td>TBA, 10</td>
<td>−23</td>
<td>95.0</td>
</tr>
<tr>
<td>10</td>
<td>none</td>
<td>−78</td>
<td>97.0</td>
</tr>
<tr>
<td>11</td>
<td>DCPH, 10</td>
<td>−78</td>
<td>90.0</td>
</tr>
<tr>
<td>12</td>
<td>TBA, 10</td>
<td>−78</td>
<td>96.0</td>
</tr>
</tbody>
</table>

$^a$Reactions were conducted by using 0.05 M concentration of RI and 0.1 M concentration of Me$_3$SnNa in THF for 15 min.

$^b$Yields are based on the RI consumed.

$^c$TBA = $t$-butylamine.
reported, but also by an electron transfer pathway to a significant extent (Scheme 33, Table 11)\textsuperscript{191}.

Evidence for an intermediate stannyl radical implication in such SET processes was obtained directly by a stopped flow technique in the reaction of tributylstannyl anion with \textit{s}- and \textit{t}-butyl bromides and iodides (Scheme 34, Figure 14)\textsuperscript{192}. 

\textbf{SCHEME 33}
FIGURE 14. Time profiles observed at 400 nm for the reaction of tributylstannyl anion with (a) s-BuI ($5.0 \times 10^{-3}$ mol dm$^{-3}$), (b) t-BuI ($1.25 \times 10^{-3}$ mol dm$^{-3}$), (c) s-BuBr ($2.5 \times 10^{-3}$ mol dm$^{-3}$) and (d) t-BuBr ($1.25 \times 10^{-2}$ mol dm$^{-3}$). Reprinted with permission from Reference 192. Copyright 1998 American Chemical Society

Another example of SET substitution at carbon and metal by metal-14 anions was evident in the reaction of Me$_3$SnNa with 2-chloropyridine, p-chlorobenzonitrile, o- and m-dichlorobenzene, 1,3,5-trichlorobenzene, 2,5-, 2,6- and 3,5-dichloropyridine, which gave good yields of substitution products through a suggested SRN1 mechanism (equation 183)$^{193}$.

$$\text{Cl} \quad \text{X} \quad \text{Me}_3\text{Sn}\text{X} \quad \text{SnMe}_3$$

X = CH, N; 11 examples, yield = 4–90%

When p-bis(trimethylstannyl)benzene was treated with sodium metal in liquid ammonia, a dianion was formed which upon photostimulation with C$_6$H$_5$Cl afforded the disubstitution product in 70% yield (Scheme 35)$^{193}$.

The reaction between triorganostannyl ions and haloarenes in liquid ammonia can lead to substitution and reduction products. It was found that in some cases the reaction can follow an SRN1 mechanism exclusively. With triphenylstannyl ions, good yields of products of the SRN1 mechanism were obtained when reactions were conducted with chloroarenes
11. Alkaline and alkaline earth metal-14 compounds

\[
\text{Bu}_3\text{Sn}^-\text{K}^+ + \text{R}'\text{X} \\
\downarrow\text{Electron transfer} \\
[\text{Bu}_3\text{Sn}^{\text{R}'\text{X}^-}] \text{K}^+ \\
\downarrow\text{Dissociation} \\
[\text{Bu}_3\text{Sn}^{\text{R}''\text{X}^-}] \text{K}^+ \\
\text{Bu}_3\text{SnR}' \rightarrow \text{Bu}_3\text{Sn}^+ + \text{R}''
\]

**SCHEME 34**

The reaction of trimethylstannylsodium with two geminal dihalides, 6,6-dichloro-5,5-dimethyl-1-hexene and 6,6-diiodo-5,5-dimethyl-1-hexene, gave evidence of a single electron transfer pathway. An initial electron transfer from Me\text{3Sn}^- to the geminal dihalides leads to the haloradical (X'), which then serves as the precursor to all the reactions and products detailed in Scheme 37\textsuperscript{195}.

\[(p\text{-chlorotoluene}, p\text{-dichlorobenzene, 1-chloronaphthalene and 1-chloroquinoline}) \text{ and with some bromoarenes as shown in Scheme 36}^{194}\.\]

The reaction of trimethylstannylsodium with two geminal dihalides, 6,6-dichloro-5,5-dimethyl-1-hexene and 6,6-diiodo-5,5-dimethyl-1-hexene, gave evidence of a single electron transfer pathway. An initial electron transfer from Me\text{3Sn}^- to the geminal dihalides leads to the haloradical (X'), which then serves as the precursor to all the reactions and products detailed in Scheme 37\textsuperscript{195}.
Scheme 36
11. Alkaline and alkaline earth metal-14 compounds

Scheme 37
When steric hindrance makes nucleophilic substitution difficult, germyllithiums reacted with acyl chlorides to give a competitive SET reaction (equation 184 and Scheme 38)\textsuperscript{15}.

\[ n \text{Mes}_3\text{GeLi} + m \text{PhCOCl} \longrightarrow \text{Mes}_3\text{GeCOPh} + \text{Mes}_3\text{GeCl} + \text{Mes}_3\text{GeH} + \text{PhCOCOPh} \]  

(184)

Diethyl arylphosphates have also been shown to react with alkali metaltriorganostannides through a SET mechanism involving stannyl radicals and affording arylstannane in excellent yields (equation 185)\textsuperscript{196}.

\[ \text{OPO(OEt)}_2 \text{SnPh}_3 + \text{Ph}_3\text{Sn} \xrightarrow{\text{hv}} \text{SnPh}_3 + \text{1-OPO(OEt)}_2 \]  

(185)

Aluminum alkoxides have been shown to influence the selectivity of reactions involving a single electron transfer stage. Triethylgermyllithium reacts with amides $\text{R}_2\text{NCO}−\text{X}$ ($\text{X} = \text{Cl}, \text{OMe}, \text{NM}_{2}, \text{Ph}$) by a mechanism which includes a free radical stage. The radical anion salt of $\text{N,N}$-diethylbenzamide, which is thermally stable in hydrocarbons, was detected in the course of these reactions which gave ($\text{N,N}$-dialkylcarbamoyl)germanes when they were performed in the presence of an equimolar amount of ($\text{s}$-BuO)$_3\text{Al}$ (Scheme 39)\textsuperscript{143}.

2. SET additions

Single electron processes were also evident in addition reactions of metal-14 anions to conjugated carbonyl compounds and other conjugated molecules having a low LUMO. When organogermyllithiums $\text{R}_3\text{GeLi}$ ($\text{R} = \text{Ph}, \text{Mes}$) were reacted with several carbonyl conjugated substrates (2-furan carboxaldehyde, 2-thiophene carboxaldehyde and their corresponding nitro derivatives), only germylation of the carbonyl groups was observed with a regioselectivity depending on the nature of the unsaturated ring. With 2-furancarboxaldehyde and 2-thiophenecarboxaldehyde, the germylcarbinols were obtained by mainly nucleophilic C-germylation (equation 186)\textsuperscript{197}. In the case of the nitro compounds, O-germylation was dominant, and a single electron transfer mechanism was corroborated by
ESR measurements. The presence of the intermediate organic radical anion was confirmed by comparison with a similar intermediate obtained from the SET of the nitro-substituted aldehyde with an electron-rich olefin (Scheme 40, equation 187, Figures 15 and 16).

\begin{equation}
\text{R}_3\text{GeLi} + \begin{array}{c}
\text{CHO} \\
\text{X} = \text{O}, \text{R}_3 = \text{Ph}_3, \text{Ph}_2\text{H}, \text{Mes}_2\text{H} \\
\text{X} = \text{S}, \text{R}_3 = \text{Ph}_3, \text{Mes}_2\text{H}
\end{array} \xrightarrow{\text{H}_2\text{O}} \begin{array}{c}
\text{CHO} \\
\text{R}_3\text{GeH} + \text{C}_2\text{H}_5\text{OH}
\end{array}
\end{equation}

\begin{equation}
\text{NO}_2\text{CHO} + \text{ERO} \rightarrow \begin{array}{c}
\text{C}_2\text{H}_5\text{N} - \text{C} = \text{C} - \text{N} - \text{C} = \text{N} - \text{C}\text{H}_3 \\
\text{EO} = \begin{array}{c}
\text{CHO} \\
\text{R}_3\text{GeLi}
\end{array}
\end{array} \rightarrow \begin{array}{c}
\text{CHO} \\
\text{R}_3\text{GeH} + \text{C}_2\text{H}_5\text{OH}
\end{array}
\end{equation}
\[ \text{NO}_2 \text{CHO} + R_3\text{GeLi} \rightarrow \left[ \begin{array}{c} \text{NO}_2 \\
\text{CHO} \\
\end{array} \right]^- + [R_3\text{GeLi}]^{++} \]

\[ \begin{array}{c} \text{NO}_2 \\
\text{CHO} \\
\end{array} \rightarrow \begin{array}{c} \text{NO}_2 \\
\text{CHO} \\
\end{array} \ \\
\text{Li}^+ + R_3\text{Ge}^* \]

\[ \text{Me}_3\text{NHCl} \rightarrow \text{Me}_3\text{N} \rightarrow \text{LiCl} \]

\[ \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} \]

\[ \text{NO}_2 \text{CHO} \rightarrow \text{NO}_2 \text{CH}_2\text{OGeR}_3 \rightarrow \text{NO}_2 \text{CH}_2\text{OH} + (\text{R}_3\text{Ge})_2\text{O} \]

\[ R_3 = \text{Ph}_3, \text{Ph}_2\text{H}, \text{Mes}_2\text{H} \]

\[ X = \text{O}, \text{S} \]

**Scheme 40**

**Figure 15.** ESR spectrum of the radical anion generated from the reaction of 5-nitrothiophene-2-carboxaldehyde with germillyiums.12-crown-4. From Reference 197 with permission from Gordon and Breach Publishing, copyright Taylor & Francis
The reaction of trimethyl and triphenylstanny1 potassium with mono- and di-substituted enones in acetonitrile as solvent led in nearly quantitative yields either to a mixture of diastereomers or to a pure diastereomer of β-stannylketones (Scheme 41). There was experimental support for the existence of a SET mechanism, i.e. partial or total inhibition of the reaction by addition of a free radical scavenger (galvinoxyl) or a radical anion scavenger (p-dinitrobenzene). The possibility of a SET depends on the one-electron donor ability of the nucleophile and the electron acceptor ability of the ketone. These reactions are stereoselective.

Reactions between organogermyllithiums $R_3GeLi$ and several substrates favoring SET reactions (3,5-di-$t$-butyl-$o$-quinone, fluorenone, tetracyanoquinodimethane, 2,4,6-tri-$t$-butynitrosobenzene, etc.) led mainly to the digermanes and O- or N-germyl adducts. These reactions mainly proceed by a SET. An ESR study of the reaction showed transient organic radical anions and germanium-centered radicals $R_3Ge•$. The digermanes were formed by recombination of $R_3Ge•$ radicals, as well as by lithiogermolysis of the reaction adducts.

In the case of SET addition of $R_3GeLi$ to 3,5-di-$t$-butyl-$o$-quinone (Scheme 42), the two radical intermediates were observed by ESR when $R = Mes$. The dominance of this mechanism was demonstrated by the reaction between $R_3GeLi$ and a paramagnetic quinonic species, the galvinoxyl radical, which was almost completely transformed into a diamagnetic anion (Scheme 43).

A study by ESR of the reaction between $R_3GeLi$ ($R = Ph, Mes$) with fluorenone showed the transient formation of the radical anion derived from fluorenone. The reaction results were, however, influenced by the experimental procedure. When fluorenone was added slowly to an excess of germyllithium, digermane was mainly formed (equation 188), whereas when the germyllithium was added to fluorenone, only traces of digermanes were observed (equation 189). These results were explained by the fact that fluorenone also behaved as a spin trap for the transient germyl radical leading to an O-germylated adduct, the lithiogermolysis of which in the presence of excess germyllithium gave digermane (Scheme 44).
The possibility of an internal spin trapping of the transient germanium-centered radical by the starting single electron acceptor was evident in the reaction of germyllithium with tri-t-butylnitrosobenzene (BNB) (Scheme 45). The transient germylated anilino radicals were observed (R = Ph, Mes), but the formation of digermane was hindered by steric effects in the case of R = Mes. Steric effects inhibited coupling of the radical (e) and the lithiogermolysis of the O-germylated adduct (f).
11. Alkaline and alkaline earth metal-14 compounds

\[
\text{R}_3\text{GeLi} + \begin{array}{c}
\text{O} \\
\text{LiO} \\
\text{LiO}
\end{array}
\rightarrow
\begin{array}{c}
(R_3\text{GeLi})^{++} + \\
\text{O}
\end{array}
\]

\[
\begin{array}{c}
\text{R}_3\text{GeLi} \\
\text{R}_3\text{Ge} \\
\text{R}_3\text{GeGeR}_3
\end{array}
\]

\[
\begin{array}{c}
\text{R}_3\text{Ge} \\
\text{H}^+ \\
\text{R}_3\text{GeO}
\end{array}
\]

\[
\begin{array}{c}
\text{g} = 2.0045 \\
\alpha_H = 2.6 \text{ G}
\end{array}
\]

\[
\begin{array}{c}
\text{R} = \text{Mes} \\
g = 2.0084 \\
\alpha_H = 0.69 \text{ G}
\end{array}
\]

SCHEME 42
Scheme 43
The change in the addition mechanism from nucleophilic to single electron transfer is often initiated by high conjugation of the substrate and steric effects which are able to prevent the nucleophilic attack by the $M_{14}$ anion. For example, in the case of benzophenone, $Ph_2HGeLi$ gave a nucleophilic addition, while Mes$_2HGeLi$ gave a SET addition (Scheme 46)$^{16}$.

3. SET cleavages

Triethylgermyllithium, which added easily to benzoyl triethylgermane in hexane to give, after hydrolysis, bis(triethylgermyl)phenylcarbinol in 70% yield (equation 190)$^{200}$,
underwent in HMPA a completely different reaction which led to digermane and phenyllithium. This reaction proceeded through a SET mechanism as shown by detection of the transient radical anion of benzoylgermane using ESR (Scheme 47):200.

\[
\begin{align*}
\text{Et}_3\text{GeLi} + \text{Et}_3\text{GeCOPh} & \quad \text{hexane} \\
& \quad \text{after hydrolysis} \\
\xrightarrow{\text{R} = \text{Ph}} & \quad (\text{Et}_3\text{Ge})_2\text{C(OH)Ph} \\
\xrightarrow{\text{R} = \text{Mes}} & \quad H(\text{Mes}_2\text{Ge})_2\text{H} + 1/n (\text{Mes}_2\text{Ge})_n \\
& \quad + \text{Ph}_2\text{CHOH} + \text{Ph}_2\text{CO}
\end{align*}
\]

SCHEME 46

\[
\begin{align*}
\text{Et}_3\text{GeLi} + \text{Et}_3\text{GeCOPh} & \quad \text{HMPA} \\
& \quad [\text{Et}_3\text{GeLi}]^{\bullet\bullet} + [\text{Et}_3\text{GeCOPh}]^{\bullet\bullet} \\
& \quad -\text{CO} \\
\xrightarrow{\text{Et}_3\text{GeEt}_3} & \quad 2\text{Et}_3\text{Ge}^\bullet + \text{PhLi}
\end{align*}
\]

SCHEME 47
F. Miscellaneous Reactions

1. Decomposition

Organohydrogermyllithiums $R_2HGeLi$ have a stability in solution which depends on the solvent used and the nature of the R group linked to the metal. For example, dimethylhydrogermyllithium is stable in solvents such as pentane, THF and amines, but diphenylhydrogermyllithium decomposed slowly in THF at 20 °C within 24 h. This decomposition was faster in the presence of an amine ($Et_3N$ or $Et_2NMe$), and gave di-, tri- and tetra-germyllithiums as confirmed by hydrolysis (equation 191). The nature of these polygermanes depends mainly on the reaction time. The selective synthesis of di-, tri- or tetra-germanes can be achieved and monitored by GC analysis.

$$Ph_2GeH_2 + t-BuLi \xrightarrow{Et_3N, BuH, LiH} Ph_2HGe(GePh_2)_nGeLiPh_2 \xrightarrow{H_2O} Ph_2HGe(GePh_2)_nGeHPh_2$$

2. Rearrangement reactions

Treatment of hydrogermanium cyclopentadiene transition metal complexes with LDA can lead initially to a competition between the deprotonation of the hydrogen linked to germanium or to the cyclopentadienyl ring, but a migration of the germyl group to cyclopentadiene was actually observed (equation 192).

$$LDA \xrightarrow{FeMeOC} FeLiOCGeHPh_2 \xrightarrow{MeI} GeHPh_2$$

3. Insertion of a bivalent metal-14

The insertion of a bivalent metal-14 derivatives into a germanium–metal bond led to poly-metal anions which gave, after alkylation, polygermanes (equations 193 and 194).

$$3Et_3GeLi + GeI_2 \rightarrow (Et_3Ge)_3GeLi \xrightarrow{MeI} (Et_3Ge)_3GeMe$$

$$R_3SnLi + R_2Sn \rightarrow R_3SnSnR_2Li$$

4. Insertion of a transition metal complex

Insertion of copper(I) cyanide into the Sn–Li bond resulted in an oxidation of Cu to cuprates (equation 195).
Bis(naphthalene)titanium complexes were prepared by insertion of freshly prepared Ti(C\textsubscript{10}H\textsubscript{8})\textsubscript{2} into the Sn–K bond (Scheme 48\textsuperscript{203}).

\[
\text{Me}_3\text{SnK} + [\text{Ti(C}_{10}\text{H}_8)_2] \xrightarrow{\text{THF, } -78^\circ C} \left[\text{K(15.C.5)}_2\right]_{\text{2}} [\text{Ti(C}_{10}\text{H}_8)_2(\text{SnMe}_3)]
\]

15.C.5 = 15-crown-5
C\textsubscript{10}H\textsubscript{8} = naphthalene

\[\text{Me}_3\text{SnK} \xrightarrow{\text{THF,} 15.C.5} [\text{K(15.C.5)}_2\text{2}][\text{Ti(C}_{10}\text{H}_8)_2(\text{SnMe}_3)_2]\]

55%

\[\text{SCHEME 48}\]

5. **Ligand exchange**

The reaction of tri(substituted allyl) stannyllithium with (substituted allyl)lithium formed an equilibrium mixture of tri(substituted allyl) stannyllithiums having all possible combinations of substituents (equation 196\textsuperscript{204}).

\[
\begin{align*}
\text{(substituted allyl)stannyllithium} & \xrightarrow{\text{1. MeI}} \text{(substituted allyl)lithium} \\
+ n_2 & \xrightarrow{\text{2. MeI}} \text{(substituted allyl)stannyl} + n_3 \text{(substituted allyl)stannyl} + n_4 \text{stannyl}
\end{align*}
\]

(196)

6. **Heterocyclic rearrangements initiated by nucleophilic addition to carbonyl**

The reaction of Brook's ketone with an excess of Et\textsubscript{3}GeLi followed by hydrolysis gave a 1 : 2 mixture of a trisilacyclobutane and (adamantoyl) adamantyl carbinol. It was suggested that this reaction involves the formation of a transient disilene. The structure of the trisilacyclobutane was established by X-ray analysis (equation 197\textsuperscript{205}).
11. Alkaline and alkaline earth metal-14 compounds

\[ \text{(Me}_3\text{Si)}_2\text{SiCAd} \rightarrow \text{Et}_3\text{GeLi} \rightarrow \text{Me}_3\text{SiSi(SiMe}_3)_2\text{AdC} \rightarrow \text{Et}_3\text{GeO} \]

\[ \text{Me}_3\text{SiSi(SiMe}_3)_2\text{AdC} \rightarrow \text{Me}_3\text{SiSi(SiMe}_3)_2\text{AdC} + \text{O} + \text{OH} \]

7. Elimination reactions

Metal-14 anion centers have been used to initiate elimination reactions for the synthesis of doubly bonded metal-14 compounds, as shown in equation 198206.

\[ \text{Tip}_2\text{SnGeMes}_2 \rightarrow \text{Et}_3\text{GeLi} \rightarrow \text{Et}_3\text{GeH} \]

8. Base activity

It was shown, using NMR analysis, that gradual introduction of HMPT into a benzene solution of Et\text{3GeM} (M = Li, Na, K and Cs) caused increased solvation of the M\(^+\) cation and the formation of a real ion-pair separated by solvent. Comparison of the reactivity of Et\text{3GeM} in benzene solution and (Et\text{3Ge}^-) (M\(^+\), HMPT) with methyl \(t\)-butyl ketone showed a drastic difference. As expected, Et\text{3GeM} gave the germylcarbinol while the ion-pair (Et\text{3Ge}^-) (M\(^+\), HMPT) gave almost quantitative proton abstraction (90%) with formation of Et\text{3GeH} (equations 199 and 200).

9. Photoreduction

Direct photo-ejection of an electron from the corresponding metal-14 anion reduced it to a metal-14 centered radical (equation 74).

G. Synthetic Applications

Because of the high cost of germanium and the high toxicity of lead, these metal-14 elements have been little used in organic synthesis compared with tin. The use of tin compounds in syntheses has been reviewed\(^4b,207\). We shall here illustrate the particular application of metal-14 anions.

Metal-14 anions have been used due to their high basic reactivity. They are able to abstract acidic hydrogen (equation 201)\(^181\), induce elimination (equation 202)\(^49\) and lead
to stereospecific cyclization (equations 203 and 204)\(^49\).

\[
\begin{align*}
\text{1. Et}_3\text{GeNa-} \text{YCl}_3 & \; 3:1 \text{ THF/HMPA} \; -78^\circ \text{C} \\
\text{2. MeI} & \; -78^\circ \text{C}
\end{align*}
\]

\[\text{R, R'} = \text{Ph, cyclohexyl, } C_6H_{11}, \text{ Me}_2\text{CHCH}_2, \text{ Me, Et}\]

A few key steps in the synthesis of optically active forskolin were achieved using allylation of aldehydes by a tin route (equation 205)\(^208\).
11. Alkaline and alkaline earth metal-14 compounds

\[
\begin{align*}
\text{Cl} & \rightarrow \text{Bu}_3\text{SnLi} & \text{Bu}_3\text{Sn} \\
\text{OR} & & \text{OR}
\end{align*}
\]

or

1. SnCl₂ or InCl₃
2. R’CHO

1. BuLi
2. R’CHO

\[
\begin{align*}
\text{OH} & \quad \text{OR} \\
\text{R'} & \quad \text{OH} \\
\text{RO} & \quad \text{OR}
\end{align*}
\]

\( R = \text{H, CH}_2\text{Ph} \)
\( \text{R'}\text{CHO} = \text{PhCHO} \)

(205)

\[
\begin{align*}
\text{R}_3\text{SiO} & \rightarrow \text{Bu}_3\text{SnLi} \\
\text{THF, } & -78 \degree \text{C} \\
\text{2. Separation} & \\
\text{Bu}_3\text{SnLi, THF, } & -78 \degree \text{C}
\end{align*}
\]

1. AcCl

\[
\begin{align*}
\text{R}_3\text{SiO} & \rightarrow \text{Bu}_3\text{SnLi} \\
\text{and} & \\
\text{inversion} & & \text{BuLi, } -78 \degree \text{C}
\end{align*}
\]

SCHEME 49
α-(Trialkylstannyl) ether, obtained from the stannylation of α-chloroallyl ether by Bu₃SnLi, allowed the stereoselective synthesis of lithioether and then, after Wittig rearrangement, the corresponding alcohol (Scheme 49)²⁰⁹.

A one-pot sequential Michael–Michael ring closure (MIMIRC) reaction using 2-cyclohexenone as the initial Michael acceptor allowed an effective construction of various polyfunctionalized polycyclic compounds (Scheme 50)²¹⁰.

Sulfuration of hypervalent anionic tin complexes led to a practical synthesis of disulfides involving non-odorous reagents and avoiding the use of H₂S (equation 206)²¹¹.

\[
\begin{align*}
n-Bu₄N^+ & \quad \begin{array}{c}
\text{F} \\
\text{Ph} \\
\text{Sn} \\
\text{Ph} \\
\text{F}
\end{array}
\rightarrow \quad \begin{array}{c}
\text{F} \\
\text{Ph} \\
\text{Sn} \\
\text{Ph} \\
\text{F}
\end{array} \\
\text{1. Elemental sulfur} \\
\text{2. Acid}
\end{align*}
\]

(206)

The stannylation of conjugated ethylenic ketones coupled with an oxidative destannylation provided the synthetic means to various new carbonyl compounds (equations 207 and 208)¹⁰⁶.
Oxyfunctional organolithium reagents which are very useful synthons are easy to make by stannylation of aldehydes followed by a destannylation with an organolithium (equations 209 and 210)\textsuperscript{104}.

\[
\text{RCHO} \xrightarrow{1. \text{Bu}_3\text{SnLi}, 2. \text{R'X}} \text{R} \xrightarrow{\text{BuLi}} \text{R} \xrightarrow{\text{OR'}} \Li
\]

RCHO = furan-3-carboxaldehyde, R'X = 2-chloroethyl ether
Tributylstannylmagnesium chloride and tributylstannyalkalis reacted with immonium salts to form non-substituted, α-substituted or α,α-disubstituted aminomethyltributyltins. Transmetallation of the aminomethyltributyl tins with butyllithium followed by condensation with carbonyls provided a regiospecific route to β-aminoalcohols (Scheme 51)\textsuperscript{87}.

Trimethylstannyllithium can catalyze the rearrangement of 1,4-bis(trimethylstannyl)-2-butyne to 2,3-bis(trimethylstannyl)-1,3-butadiene, which is a useful reagent in the preparation of their silicon analogues (Scheme 52)\textsuperscript{212}.
11. Alkaline and alkaline earth metal-14 compounds

\[
\text{Cl} \quad \text{Cl}
\]
\[
\text{Cl} \quad \text{Cl}
\]

or

\[
\text{Me}_3\text{Si} \quad \text{SnMe}_3
\]
\[
\text{Me}_3\text{Si} \quad \text{SnMe}_3
\]

THF, −78 °C

2. Me$_3$SnLi

Me$_3$Sn

SnMe$_3$

THF, HMPA

25 °C

1. 3 MeLi, THF, −78 °C

2. −40 °C, 100 min

3. Me$_3$SiCl

Me$_3$Si

SiMe$_3$

98%

SCHEME 52

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Spectroscopic studies and quantum-chemical calculations of short-lived germylenes, stannylenes and plumbylenes

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I. LIST OF ABBREVIATIONS

AM1 semiempirical method based on the modified neglect of diatomic overlap approximation using radial gaussian functions to modify the core–core repulsion term
ANO atomic natural orbital
12. Spectroscopic studies and quantum-chemical calculations

AO atomic orbital
B3LYP Becke’s three-parameter hybrid functional using the Lee, Yang and Parr correlation functional
BLYP Becke’s exchange functional and the Lee, Yang and Parr correlation functional
CA carbene analog
CAS SCF complete active space self-consistent field
CCSD(T) coupled cluster calculations, using single and double substitutions from the Hartree–Fock determinant. Include triple excitations non-iteratively
CI configuration interaction
CIS configuration interaction with single excitations
CNDO semiempirical method based on the complete neglect of differential overlap approximation
CVD chemical vapor deposition
DFT density functional theory
DHF Dirac–Hartree–Fock
DZ double-zeta
DZ + d double-zeta + polarization functions on heavy atoms
DZP double-zeta + polarization functions on all atoms
$E_a$ activation energy
EA electron affinity
$\Delta E_{ST}$ energy difference between the first singlet and triplet states

$$\Delta E_{ST} = E_{\text{triplet}} - E_{\text{singlet}}$$

ECP effective core potential
EHMO extended Hückel MO method
EIMS electron impact mass spectrometry
ESR electron spin resonance
G2 Gaussian-2 methods that correspond effectively to energy calculations at the QCISD(T)/6–311+G(3df,2p)//MP2(full)/6–31G(d) level with ZPE from HF/6–31G(d) level and higher level corrections
HF Hartree–Fock
HOMO highest occupied molecular orbital
ICLAS intracavity laser absorption spectroscopy
IE ionization energy
IR infrared spectroscopy
IRDLKS infrared diode laser kinetic spectroscopy
IRDLs infrared diode laser spectroscopy
ISEELS inner-shell electron energy loss spectroscopy
LIF laser-induced fluorescence
LIP laser-induced phosphorescence
LRAFKS laser resonance absorption flash kinetic spectroscopy
LUMO lowest unoccupied molecular orbital
MNDO semiempirical method based on the modified neglect of diatomic overlap-approximation
MO molecular orbital
$\text{MP}_n(n = 2–4)$ $n$-th order of Møller–Plesset correlation energy correction
MRSDCI multireference single + double configuration interaction
MRSDCI + Q multireference single + double configuration interaction plus a Davidson-correction for uncoupled quadruple clusters
MW microwave spectroscopy
II. INTRODUCTION

Carbene analogs are electrically neutral species, which are characterized by the presence of an atom possessing either at least one lone pair of s or p electrons and at least one unoccupied p orbital or two unpaired electrons in s and p or in two p orbitals, but having no unoccupied d level with a quantum number lower than that of the valent p electrons\(^1,2\). Carbene analogs of the Group 14 elements (CAs), silylenes (\(\text{SiR}_2\)), germynes (\(\text{GeR}_2\)), stannylenes (\(\text{SnR}_2\)) and plumbylenes (\(\text{PbR}_2\)), represent an important class of chemical derivatives of these elements. Short-lived representatives of CAs play a significant role in chemical transformations of organogermanium, -tin and -lead compounds, including those of practical interest. Since the 1970s the synthetic approaches to the preparation of stable CAs have also been developed and a lot of stable CAs have been synthesized. The chemistry of CAs has been surveyed in many reviews and monographs in detail, the most recent being those on silylenes\(^3,4\), germynes\(^5–7\) and stannylenes\(^5\).

The first spectroscopic studies of CAs were performed in the 1930s\(^8–10\). A great number of CAs have since been characterized by different spectroscopic methods. Application of molecular spectroscopy to studies of short-lived CAs has enabled us to obtain the most unambiguous experimental evidence of their existence as kinetically independent species. It also provided very important information on the nature of bonding in these molecules, their electronic structures and geometries, necessary for understanding their chemical reactivity. Information on spectral characteristics of some CAs has already found analytic use for their detection in complex reaction mixtures (for example, in CVD processes), for studies of their further transformations and for identification of the simplest CAs in interstellar clouds. In spite of extensive data on molecular spectroscopy of CAs and the fast growing number of publications in this field, there is still no comprehensive review devoted to spectroscopic studies of CAs, although their spectral characteristics were partially listed in different reviews. The most complete consideration of spectroscopic studies of silylenes is presented in a recent review by Gaspar and West\(^3\). Spectral characteristics of many CAs are collected in a compilation by Nefedov and coworkers\(^11\), some data on vibrational and electronic spectroscopy can be found in a serial compilation of Jacox\(^12–15\) and those on ionization energies and electron affinities in the compilation.
Spectroscopic studies and quantum-chemical calculations of Lias and coworkers\textsuperscript{16}. Results of matrix IR studies of CAs have been presented in a review by Korolev and Nefedov\textsuperscript{17}. Different physicochemical properties of CAs are collected in the NIST Chemistry WebBook\textsuperscript{18}.

The present review is devoted to spectroscopic studies of short-lived germylenes, stannylenes and plumbylenes, and their complexes with Lewis bases. Some data on silylenes are also given for comparison, though detailed consideration of all available data on silylenes is beyond the scope of this review. The spectroscopic studies of monoxides, EO (E = Si, Ge, Sn, Pb), and related diatomic molecules with formal divalent E, as well as those of isonitrile analogs, ENR (E = Si, Ge, Sn, Pb), are not considered here, as the parent carbon monoxide and C≡NH are not classified as carbenes. Since the electronic structure of carbonylgermylene, GeCO, and carbonylstannylene, SnCO, differ significantly from the electronic structure of carbenes and CAs\textsuperscript{19}, their spectra too are not discussed here. At the same time spectroscopic data for complexes of germylenes, stannylenes and plumbylenes with Lewis bases are included, because such complexes are closely related to free germylenes, stannylenes and plumbylenes and, as is obvious now, they play an important role in chemical transformations involving these reactive intermediates.

The results of electronic, vibrational, microwave and photoelectron spectroscopy studies will be discussed below. The data obtained by these methods for stable germylenes, stannylenes and plumbylenes (except those for cyclopentadienyl derivatives because of their quite specific electronic structure) and their complexes are also discussed in this review owing to their importance for understanding the general trends. At the same time, nuclear magnetic resonance data available for most stable CAs and Mössbauer spectroscopy data available for a huge number of stable Sn(II) compounds are not included, as these methods were solely applied to study the stable CAs (with only one exception\textsuperscript{20} where Mössbauer spectra of SnMe\textsubscript{2} and SnMeH were measured in low-temperature Ar matrices). Consideration of the microwave spectroscopy studies of short-lived germylenes, stannylenes and plumbylenes is supplemented with analysis of their geometries obtained by different experimental methods. The structures of stable germylenes, stannylenes and plumbylenes are not discussed here. Discussion of the structures of stable germylenes and their stable complexes can be found in earlier reviews\textsuperscript{6,21}. Structural data for stable plumbylenes and their stable complexes are available in a recent compilation\textsuperscript{22}. Section IX devoted to photoelectron spectroscopy studies is supplemented with data on ionization energies and electron affinities measured by mass spectrometry and also with a short overview of the electrochemistry of germylenes and stannylenes.

Quantum-chemical calculations are employed extensively for the interpretation of experimentally observed spectra. Increasing accuracy of modern quantum-chemical methods in the prediction of spectral characteristics, geometries and energies allows one to a certain extent to fill the gaps in experimental data available for germylenes, stannylenes and plumbylenes. Therefore we review in Section X the results of quantum-chemical studies of germylenes, stannylenes and plumbylenes.

### III. ELECTRONIC TRANSITIONS IN TRIATOMIC AND TETRAATOMIC GERMYLENES, STANNYLENES AND PLUMBYLENES

This and subsequent sections are devoted to the electronic spectra of germylenes, stannylenes and plumbylenes. All experimentally known CAs have a singlet ground state. Typically, in this state the HOMO of the CA represents the nonbonding lone-pair orbital of n type and \( \sigma \) symmetry with significant localization on the divalent silicon, germanium, tin or lead atom and the LUMO is a \( \pi \)-type MO with the main contribution from the empty p orbital of the same atom (see Section IX). Therefore, the first allowed electronic transition between HOMO and LUMO in CAs belongs to the n–\( \pi \) type and the corresponding
bands lie in the visible or in the near-UV region. Thus, the UV-vis absorption spectroscopy is a very convenient tool for a direct detection of CAs. Indeed, a great number of CAs have been characterized by low resolution UV-vis absorption spectra in the condensed phase, mainly in low-temperature matrices with the standard absorption technique and also in solutions using a flash photolysis technique. The spectra obtained by these methods usually consist of one or more broad bands, each being actually an unresolved superposition of a series of overlapping vibronic lines broadened due to interactions with the environment, and it will be considered in the next section. Generation of CAs in the gas phase and use of a high resolution probe technique allow one to resolve vibronic and in some cases even rotational structure in the electronic spectra, provided that the molecule has not too many degrees of freedom. Currently it has been done only for some triatomic germynes, stannylenes and plumbylenes of two types: EX$_2$ and EXY, E = Ge, Sn, Pb, and for germylidene, H$_2$C=Ge. The spectra of the tri- and tetraatomic germynes, stannylenes and plumbylenes will be considered in this section.

The assignment of the observed bands to the particular CA is typically based on the following data: the stoichiometry of the precursor decomposition, exclusion of alternative possible products with known spectral characteristics, correspondence of the observed rovibronic band structure with that expected on the basis of selection rules, agreement of some frequencies obtained from analysis of vibronic structure with the ground state frequencies determined from vibrational spectra, use of different precursors for generation of the same CA, and also on some other criteria, depending on the method of generation and on the probing technique. Lately, high level quantum-chemical calculations have found wide application in interpretation of the main features of the observed spectra and in assignment of the bands to the particular electronic transition. At present reliable and self-consistent data have been obtained for most of the triatomic germynes, stannylenes and plumbylenes.

The singlet ground state ($S_0$) of the triatomic CAs is designated as $\tilde{X}^1A_1$ for EX$_2$ and $\tilde{X}^1A'$ for EXH in accordance with the symmetry of their HOMO. The first excited electronic state of these molecules is the low-lying triplet ($T_1$) state: $\tilde{a}^3B_1$ for EX$_2$ and $\tilde{a}^3A''$ for EXH, followed by the excited singlet ($S_1$) state $\tilde{A}^1B_1$ for EX$_2$ and $\tilde{A}^1A''$ for EXH. Transition $T_1 – S_0$ is forbidden by the selection rules. However, this type transitions could have nonzero probability and thus appear in the spectra as relatively weak bands. Due to its low intensity the detection of this transition is quite complicated. The lifetime of the $T_1$ state is usually quite long ($\text{ca} \ 10^{-5}$s). Transition $S_1 – S_0$ is allowed by the selection rules; the typical lifetime of the $S_1$ state is $10^{-9} – 10^{-6}$s. The bands corresponding to this transition are usually intensive. The lifetime of the excited state can be used as a criterion for the assignment of the observed transition to a $T_1 – S_0$ or to an $S_1 – S_0$ band. With rare exceptions (see below) all the observed and thoroughly studied electronic bands of triatomic germynes, stannylenes and plumbylenes are attributed to these two transitions. A particular vibrational level of an electronic state of a triatomic CA will be designated as $T(v_1, v_2, v_3)$, where $T$ is the corresponding electronic term (like $^1A''$ or $^1B_1$), and $v_i$ are the quantum numbers for vibrational levels of $i$-th fundamental modes.

The following important data can be obtained from analysis of the rovibronic structure of the electronic transition band: the difference between zero vibrational levels of the upper and lower electronic states, $T_{00}$, fundamental frequencies for the fully symmetric vibrational modes (for symmetric stretching, $v_1$, and bending, $v_2$, modes of the EX$_2$, or stretching, $v_1$ and $v_3$, and bending $v_2$ modes of EXH) in both states (designated as $v_i'$ for the lower electronic state and as $v_i''$ for the upper state), rotational constants for each of the vibrational levels of the electronic states involved (if rotational structure is resolved), and, from the rotational constants, two geometrical parameters (because only two rotational constants are independent for the planar molecules) for the corresponding electronic state.
Some conclusions on the excited state dynamics (such as the existence of nonradiative and, particularly, predissociative processes, the estimation of dissociation limit, etc.) can be derived from a detailed consideration of the rovibronic structure and measurements of the lifetimes. It is noteworthy that the observation of the fine rovibronic structure can be hampered and its analysis can be complicated by the presence of several isotopes of the constituent atoms (e.g., Ge, Sn, Pb, Cl and Br) and also by a significant increase in the principal moments of inertia due to the presence of heavy elements in the molecule.

Some numerical characteristics of the observed electronic transitions in triatomic germynes, stannylenes and plumbylenes of the EX$_2$ and EXY types are collected in Table 1 and Table 2, respectively. Similar data on the triatomic silylenes are included for comparison in these tables. Some molecular constants of germylidene and its silicon analog are compared in Table 3.

### A. Prototype EH$_2$ Molecules

The laser-induced fluorescence (LIF) excitation and dispersed fluorescence spectra of the $^{1}B_1 - ^{1}A_1$ transition in the prototype germylene, GeH$_2$, and its deuterated derivative, GeD$_2$, were first measured by Saito and Obi under supersonic jet conditions$^{23-25}$. GeH$_2$ and GeD$_2$ were produced by 193-nm laser photolysis of PhGeH$_3$ and PhGeD$_3$, respectively. The LIF spectra consisted of progressions of the upper state bending vibrations ($\nu_2$) up to vibrational quantum number 4 for GeH$_2$ and 6 for GeD$_2$ in the 650–470 nm region. The term value, $T_e$ (the energy of the vibrational zero point of the upper state relative to that of the ground state), of the $^{1}B_1$ state has been determined to be 16330 cm$^{-1}$.$^{23}$ The observed predominant excitation of the bending mode is compatible with the large change in bond angle between the ground and the excited states. From the absence of transitions from higher vibrational levels of the $^{1}B_1$ state it has been suggested that a predissociation channel to Ge($^1$D) + H$_2$ (or D$_2$) opens at ca 20000 cm$^{-1}$.$^{24,25}$ Based on these findings the heat of formation of GeH$_2$ is estimated to be within 19053–19178 cm$^{-1}$ (228–229 kJ mol$^{-1}$)$^{25}$. All vibronic bands had simple rotational structure due to the cooling of the internal degrees of freedom under the jet conditions$^{23-25}$. Isotopic splitting of the rotational lines due to germanium isotopomers was well resolved. The missing rotational $r$-subbranch in the LIF excitation spectra has been noted, suggesting a heterogeneous (rotational dependent) $K_a'$ dependent predissociation to Ge($^3$P) + H$_2$ (or D$_2$) in the $^{1}B_1$ state of germylene. The presence of $J$-dependent predissociation has been noted too$^{25}$. Mechanisms for all the predissociation processes have been proposed. The fluorescence lifetimes of single rovibronic levels of the upper state have been measured$^{25}$. It has been found that the lifetimes decrease from ca 2.5 to ca 0.5 µs with increasing vibrational quantum number. This trend could be related to a nonradiative process. However, the decrease in lifetimes calculated in the framework of this hypothesis deviated from that observed experimentally. From the dispersed fluorescence spectra the bending frequencies of the ground state have been obtained for both GeH$_2$ and GeD$_2$.$^{23}$

Later$^{26}$, in the LIF spectra of jet-cooled GeH$_2$ (produced from GeH$_4$ by an electric discharge) a set of additional vibronic bands of the $^{1}B_1 - ^{1}A_1$ transition was recorded, including $^{1}B_1(1, v, 0) - ^{1}A_1(0, 0, 0)$ progression, with $v = 0–3$. The germanium isotopic splitting was observed for most of the bands. A number of new rotational lines were revealed in the $^{1}B_1(0, 0, 0) - ^{1}A_1(0, 0, 0)$ band, including a few very weak lines in the $^1R_0$ and $^1Q_0$ branches, terminating on upper state levels involving $K_a' = 1$. It allowed one to determine the ground and the excited state rotational constants and effective ($r_0$) molecular structure of GeH$_2$ in both states for the first time. The measured fluorescence lifetimes$^{26}$ have been found to be in good agreement with the previous data$^{25}$ for lower vibronic levels and noticeably longer for higher levels. The reason of this discrepancy is...
related to a revealed sensitivity of the observed fluorescence lifetimes to the experimental conditions\textsuperscript{26}, and the recently measured lifetimes\textsuperscript{26} are in much better agreement with the theoretically predicted ones than those reported previously\textsuperscript{25}. The mechanisms of predissociation processes have been discussed in detail on the basis of the experimental results and CAS SCF calculations\textsuperscript{26}.

A small part of the rotationally resolved absorption spectrum of GeH\textsubscript{2} at room temperature in the region of the $^{1}B_1(0,1,0)-^{1}A_1(0,0,0)$ transition has been recorded by a laser resonance absorption flash kinetic spectroscopy (LRAFKS)\textsuperscript{27}. The most intensive (not assigned) lines (17118.67 and 17111.31 cm\textsuperscript{-1}) have been used further for kinetic studies\textsuperscript{27,28}. Later, the room temperature absorption spectrum of GeH\textsubscript{2} (produced in a continuous flow discharge of GeH\textsubscript{4} diluted with argon) was recorded by the intracavity laser absorption spectroscopy (ICLAS) in a wider region (17090–17135 cm\textsuperscript{-1}), corresponding to the central part of the same $^{1}B_1(0,1,0)-^{1}A_1(0,0,0)$ transition\textsuperscript{29}. The rotational constants for all five germanium isotopomers in the excited state have been obtained from analysis of the observed rotational structure, and the equilibrium geometry, $r_e$, of GeH\textsubscript{2} in the $^{1}B_1$ state has been estimated\textsuperscript{29}. Recently, laser optogalvanic spectroscopy was used to investigate the central part of the $^{1}B_1(0,0,0)-^{1}A_1(0,0,0)$ band of GeH\textsubscript{2} generated from GeH\textsubscript{4} by rf discharge at room temperature\textsuperscript{30}. Analysis of the rotational structure of these spectra as well as in LIF spectra of jet-cooled GeD\textsubscript{2} has yielded improved ground and excited state rotational constants for a number of germanium and hydrogen isotopomers of germylene. It allowed us to obtain more accurate $r_0$ geometries for the ground and the excited states and approximate equilibrium structures for both states of the germylene\textsuperscript{30}. Additional $^{1}B_1(1,v,0)-^{1}A_1(0,0,0)$ progression, with $v = 0–3$, was observed in LIF spectra of jet-cooled GeD\textsubscript{2}, which gave the $\nu_1$ fundamental frequency for the $^{1}B_1$ state of this molecule. The ground state $\nu''_1$ and $\nu''_2$ vibrational frequencies have also been obtained from dispersed fluorescence spectra of GeH\textsubscript{2} and GeD\textsubscript{2}\textsuperscript{30}.

Electronic spectra of the prototype stannylene, SnH\textsubscript{2}, and plumbylene, PbH\textsubscript{2}, have not been reported so far.

### B. EHal\textsubscript{2} Molecules

The first low-resolution ultraviolet absorption spectrum of GeF\textsubscript{2} was reported by Hauge and coworkers\textsuperscript{31}. GeF\textsubscript{2} was generated by interaction of GeF\textsubscript{4} with germanium metal at 250 °C and by evaporation of germanium difluoride (GeF\textsubscript{2})\textsubscript{x} at 150 °C. The spectrum consisted of $(0,v',0)-(0,v'',0)$ progressions in the region 240–220 nm and was attributed to $^{1}B_1-^{1}A_1$ transition. LIF spectrum of jet-cooled GeF\textsubscript{2} produced by reaction of Ge with F\textsubscript{2} at 450 °C was reported later\textsuperscript{32}. It represents a poorly resolved band system extending from 231 to 224 nm, corresponding to the same electronic transition\textsuperscript{32}. Progressions including both bending and symmetric stretching vibrational modes of the upper state, terminating on some lowest ground state bending mode levels, have been revealed. The vibronic structure was accompanied by a background due to a $^{1}B_1$ state dissociation process with onset near 225 nm\textsuperscript{32}. An unresolved emission band of $^{1}B_1-^{1}A_1$ transition in GeF\textsubscript{2}, peaking at 235 nm and spanning 265–215 nm, has been observed by irradiation of GeF\textsubscript{4} with synchrotron radiation (SR) with energy above 14 eV\textsuperscript{33}. The lifetime of the GeF\textsubscript{2}$^{1}B_1$ state measured at 235 nm has been found to be 9.3 ± 0.1 ns\textsuperscript{33}.

A structureless absorption band with maximum at 146.3 nm, assigned to $^{1}B_2-^{1}A_1$ transition in GeF\textsubscript{2} (produced by pyrolysis of GeF\textsubscript{4}) was reported by Cole and coworkers\textsuperscript{34}.

The $^{3}B_1-^{3}A_1$ transition in GeF\textsubscript{2} in the 370–325 nm region was first observed using emission spectroscopy\textsuperscript{35}. GeF\textsubscript{2} was generated by microwave discharge in GeF\textsubscript{4} vapor. The vibronic structure of this band was analyzed. Emission from the $^{3}B_1$ state of GeF\textsubscript{2} has
also been reported by other groups for GeF$_2$ produced by rf glow discharge in GeH$_4$, H$_2$ and CF$_4$ or C$_2$F$_6$ mixtures$^{36,37}$ and in GeF$_4$ vapor$^{38}$. All the results$^{35–38}$ agree well with one another. An unresolved broad chemiluminescence band, spanning 490–270 nm and peaking at 407 nm, was detected in the reaction of Ge with CIF$_3$ or SF$_4$ and has also been ascribed to this transition in GeF$_2$$^{39}$. In the course of studying vacuum-UV fluorescence spectroscopy of GeF$_4$, an unresolved emission band was observed in the 380–300 nm region with a maximum at 340 nm, corresponding to $^3B_1$–$^1A_1$ transition in GeF$_2$ (produced by GeF$_4$ dissociation at a radiation energy of ca 14 eV)$^{33}$. The lifetime of the $^3B_1$ state has been estimated from decay measurements at the band maximum; it was found to be greater than 500 ns$^{33}$. Analysis of the high resolution laser-induced phosphorescence (LIP) spectra of jet-cooled GeF$_2$ (produced by reaction of Ge with F$_2$) in the 331–305 nm region$^{32}$ has resulted in the correction of the previous$^{35}$ assignments of the bands in the vibronic structure of this transition and in a more precise definition of the $T_{00}$ value. Besides, in addition to progressions involving activities of bending modes of both states, two new weaker progressions have been revealed$^{32}$. The first corresponds to $^3B_1(1, v′, 0)$–$^1A_1(0, 0, 0)$ transitions. The second progression should involve the ground state symmetric stretching frequency, but such an assignment should imply an increase in the previous$^{40}$ value of this frequency from 692 cm$^{-1}$ to 721 cm$^{-1}$$^{32}$. At the same time no alternative way of assignment of all the observed progressions has been found$^{32}$.

Vibrationally resolved chemiluminescent emission spectrum of GeCl$_2$ in the 490–410 nm region has been obtained by burning GeCl$_4$ in potassium vapor$^{41}$. From analysis of the vibrational structure, bending and symmetric stretching frequencies were obtained for both the ground and excited states of GeCl$_2$$^{41}$. The energy $T_{00}$ was also measured, but the nature of the excited state was left unknown$^{41}$. Later$^{42}$, this emission was attributed to the $^3B_1$–$^1A_1$ transition. The absorption spectrum of GeCl$_2$, generated by evaporation of polymeric germanium dichloride or by interaction of GeCl$_4$ with Ge, with resolved vibrational structure due to bending and symmetric stretching modes in the upper state, was recorded in the 330–300 nm region and assigned to the $^1B_1$–$^1A_1$ transition using extended Hückel calculations$^{42}$. The continuous absorption starting at about 310 nm was suggested to be due to predissociation of the Ge–Cl bond. In the corresponding emission spectrum, obtained by microwave discharge in GeCl$_4$ vapor, the vibrational structure was not resolved$^{42}$. Unresolved emission bands corresponding to both $^3B_1$–$^1A_1$ and $^1B_1$–$^1A_1$ transitions in GeCl$_2$ were observed during the reaction of a high temperature Ge beam with ICl$^{43}$ and in the vacuum ultraviolet (VUV) photolysis of Me$_n$GeCl$_4$–$_n$ ($n = 0–2$)$^{44}$ and GeCl$_2$$^{45,46}$. In the case of Me$_n$GeCl$_4$–$_n$ photolysis the band in the 560–390 nm region ($^3B_1$–$^1A_1$) was more intensive than the band in the 370–310 nm region ($^1B_1$–$^1A_1$), which forced the authors to reassign the longer wavelength band to $^1B_1$–$^1A_1$ transition in GeCl$_2$, while the shorter wavelength band was attributed to $^1A_2$–$^1A_1$ transition$^{44}$. However, the proposed$^{44}$ assignment did not find further support later$^{46,47}$. The measured$^{44}$ lifetime of the upper state responsible for the shorter wavelength band was found to equal ca 90 ns, while the longer wavelength band showed a pressure-dependent biexponential decay with zero-pressure components of 17.4 and 101 µs. Such values of lifetimes are typical for the excited singlet and triplet states, respectively.

High resolution laser-induced emission excitation spectra in both regions of GeCl$_2$ transitions (450–400 and 320–300 nm) have been recorded using the supersonic jet technique$^{47}$. GeCl$_2$ was produced by pyrolysis of HGeCl$_3$ at 200°C. This study represents the first direct LIP detection of the excited triplet state of any carbene or carbene analogs. More accurate definitions have been given to the band origins ($T_{00}$) and fully symmetric vibration frequencies in all the involved electronic states of GeCl$_2$. In spite of small rotational constants of the molecule under consideration and overlapping of the
lines due to different germanium and chlorine isotopomers, the authors have succeeded in observing poorly resolved rotational band contours for a number of bands of shorter-wavelength band systems. It has also been shown that the part of the spectrum below 316 nm was mainly caused by emission of GeCl, a product of a predissociative process for GeCl₂, rather than by GeCl₂ itself. All the assignments made have been supported by \textit{ab initio} calculations\cite{47}.

Interaction of K or Na vapor with GeCl₄ is accompanied by a very weak chemiluminescence in the even longer wavelength region (666–560 nm)\cite{48}. Its emitter has been proposed to be GeCl₂, because two frequencies obtained from analysis of the vibrational structure of the band coincided with fundamental frequencies of the full-symmetric (stretching and bending) modes of the ground state of GeCl₂. However, further attempts to observe this emission system failed\cite{43,47}, and the nature of this band remains unknown.

Reactions of Ge atoms (in both the ground $^3P_J$ and metastable $^1D_2$ states) with Br₂ and I₂ produced structureless emission bands with maxima at ca 480, 380 and 600, 500 nm respectively, which have been assigned to $^3B_1→^1A_1$ (longer wavelength bands) and $^1B_1→^1A_1$ (shorter wavelength bands) transitions in GeBr₂ and GeI₂, respectively\cite{43}.

The low resolution absorption spectrum of GeI₂ vapors contains bands with maxima at 575, 475, 360 and 225 nm\cite{49,50}.

Only low resolution absorption spectra have been recorded for SnF₂ (in the 246–237 nm region) and PbF₂ (band maximum at 243.5 nm) in the region of $^1B_1→^1A_1$ transitions\cite{51}.

Monomeric SnF₂ and PbF₂ were produced by evaporation of the corresponding difluorides (EF₂)x at ca 700 and ca 800 K, respectively. An analysis of the vibronic structure observed only on the longer wavelength side of the SnF₂ band gave values for the bending frequencies in the ground and in the excited states and the $T_{00}$ value. The band of PbF₂ was not resolved vibrationally, but the $T_{00}$ value has been estimated, assuming an analogy in relative positions of the band maxima and the (0,0,0)→(0,0,0) transitions for EF₂, E = Ge, Sn, Pb. A broad emission band with maximum at ca 400 nm observed in beam reactions of Sn($^3P$) atoms with ClF₃, SF₄ and SF₆ was attributed to the $^3B_1→^1A_1$ transition in SnF₂\cite{39}.

$^3B_1→^1A_1$ transition in SnCl₂ (generated by electric discharge in SnCl₄ vapor) has been detected in the 500–400 nm region as an emission band with clear vibronic structure\cite{8} and as chemiluminescence (produced in reactions of SnCl₄ with nitrogen or hydrogen atoms\cite{52} or by burning of SnCl₄ in potassium vapor\cite{53}). An unresolved absorption band of SnCl₂ (as a vapor over the molten salt at about 570 K) with maximum at 322 nm has been assigned to the $^1B_1→^1A_1$ transition\cite{42}. A weak emission band due to this transition was recorded in the course of the reaction of Sn atoms in the $^1D_2$ state with Cl₂\cite{43}.

Beam-gas reactions of Sn atoms in the ground $^3P_J$ and in the metastable $^1D_2$ states with ICl result in the appearance of two intensive chemiluminescence bands peaking at 350 and 425 nm, which correspond to $^1B_1→^1A_1$ and $^3B_1→^1A_1$ transitions, respectively\cite{43}.

Structureless absorption bands with maxima at 245 and 195 nm were also observed for SnCl₂ vapors\cite{42,54}. These absorptions and an absorption below 320 nm within the region of the $^1B_1→^1A_1$ transition lead to dissociation of SnCl₂ with the formation of SnCl and Cl in the ground and excited states\cite{42,54–56}.

Beam-gas reaction of Sn atoms (in the $^3P_J$ state) with Br₂ and I₂ results in chemiluminescence continuous bands peaking at 470 and 553 nm respectively, attributed to $^3B_1→^1A_1$ transitions in SnHal₂ (Hal = Br, I) molecules\cite{39}. Excitation of SnBr₂ vapors with N₂($A^3Σ^+_u$) also produces luminescence in the visible region (in the range of 550–440 nm) with a maximum at 505 nm\cite{57}. Low resolution absorption spectra recorded for SnBr₂ (at 608–749 K) and SnI₂ (at 593–920 K) vapors revealed bands peaking at ca 480, 365, 285, 245 and 200 nm for SnBr₂\cite{49,54} and at 550, 458, 358, 225 and below...
TABLE 1. Energies, geometries and fundamental frequencies of triatomic carbene analogs of EX₂ type in ground and excited states.\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Electronic state</th>
<th>Region of transition from or to the ground state (nm)</th>
<th>$T_{00}$ (cm⁻¹)</th>
<th>$ν_1$ (cm⁻¹)</th>
<th>$ν_2$ (cm⁻¹)</th>
<th>Bond length, $r_0$ (Å)</th>
<th>Bond angle, $θ_0$ (deg)</th>
<th>Reference</th>
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<tr>
<td>SiH₂ $^1A_1$</td>
<td>—</td>
<td>0</td>
<td>1009</td>
<td></td>
<td>1.51402\textsuperscript{c}</td>
<td>91.9830\textsuperscript{c}</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>$^3B_1$</td>
<td>4800</td>
<td>6300 or 7300</td>
<td></td>
<td>1.515</td>
<td>92.12</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>$^1B_1$</td>
<td>650–460</td>
<td>15 547.7730</td>
<td>1 990</td>
<td>1.48532\textsuperscript{c}</td>
<td>122.4416\textsuperscript{c}</td>
<td>63</td>
</tr>
<tr>
<td>SiD₂ $^1A_1$</td>
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<td>0</td>
<td>731</td>
<td></td>
<td></td>
<td></td>
<td>62</td>
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<td>15 539.8751</td>
<td>616</td>
<td>1.483</td>
<td>123.2</td>
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<td>30 582.7</td>
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<td>22 315.0</td>
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<td>440–340</td>
<td>23 000</td>
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(continued overleaf)
### TABLE 1. (continued)

<table>
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<tr>
<th>Electronic state</th>
<th>Region of transition from or to the ground state (nm)</th>
<th>( T_{00} ) (cm(^{-1}))</th>
<th>( v_1 ) (cm(^{-1}))</th>
<th>( v_2 ) (cm(^{-1}))</th>
<th>Bond length, ( r_0 ) (Å)</th>
<th>Bond angle, ( \theta_0 ) (deg)</th>
<th>Reference</th>
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</thead>
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<td>GeI(_2)</td>
<td>( ^1A_1 ) — 0</td>
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<td>550–450 ( \sim 18,000^d )</td>
<td>43, 49</td>
<td>43, 49</td>
<td>43, 49</td>
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<tr>
<td>SnF(_2)</td>
<td>( ^1A_1 ) — 0</td>
<td>500–300 ( \sim 20,000^d )</td>
<td>350–120</td>
<td>39</td>
<td>39</td>
<td>39</td>
<td></td>
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<td>SnCl(_2)</td>
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<td>240</td>
<td>80</td>
<td>53</td>
<td>39</td>
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<tr>
<td>SnBr(_2)</td>
<td>( ^1A_1 ) — 0</td>
<td>550–370 ( \sim 18,000^d )</td>
<td>350–120</td>
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<td>39</td>
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</tr>
<tr>
<td>SnI(_2)</td>
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<td>600–520 ( \sim 17,000^d )</td>
<td>350–120</td>
<td>39</td>
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<td>39</td>
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<td>PbF(_2)</td>
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<td>~243.5 ( \sim 40,500 )</td>
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<td>149</td>
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<td>PbI(_2)</td>
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<td>20200</td>
<td>20200</td>
<td>149</td>
<td>60</td>
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</table>

\(^a\) The data correspond to isotopomers, containing the most abundant isotopes, or represent the average values if the isotopic structure has not been observed.

\(^b\) The number of the significant digits in the values exhibited corresponds to that presented in the original publications.

\(^c\) Equilibrium geometry (\(r_e, \theta_e\)).

\(^d\) A rough estimate from the longer wavelength limit of the band.

\(^e\) Tentative value.

200 nm for SnI\(_2\)\(^{49,54,58,59}\). Thermal luminescence for SnI\(_2\) (in the 1125–1423 K range) consisted of bands with maxima at 615, 570 and 500 nm\(^{59}\). Tentative interpretations of the observed spectra have been proposed\(^{49,59}\); in particular the longest wavelength absorption bands have been assigned to the \( ^1B_1 \rightarrow ^1A_1 \) transition. Interpretation of the absorption spectra of SnHal\(_2\) (and PbHal\(_2\)) taking into account dissociation processes was first conducted by Samuel\(^{56}\). The ultraviolet absorption cross sections of SnHal\(_2\) (Hal = Cl, Br, I) in the 400–200 nm region were measured and ways of photodissociation of these molecules depending on the absorbed light wavelength in this region were considered\(^{54}\).

In the absorption spectra of PbCl\(_2\) vapors three continuous bands peaking at 360, 320 and below 291.6 nm have been observed\(^{9,10,42}\). The first band has been attributed to \( ^1B_1 \rightarrow ^1A_1 \) transition and the others to dissociation continuum\(^{9,10,42,56}\). A number of structureless bands with maxima at about 450, 330 and 230 nm and at about 530, 430, 300 and 200 nm have been found in the low resolution absorption spectra of PbBr\(_2\) and PbI\(_2\) vapors, respectively\(^{49}\); the first bands were tentatively (and obviously erroneously) attributed to \( ^1B_1 \rightarrow ^1A_1 \) transitions.

Vibrationally resolved LIP and dispersed fluorescence spectra in the 525–475 nm region have been recorded for the heaviest triatomic plumbylene PbI\(_2\) in the 670–1170 K temperature interval\(^{60}\). The observed band system was assigned to the \( ^3B_1 \rightarrow ^1A_1 \) transition, based on SCF-X\(\alpha\)-SW calculations. The frequencies of the bending mode of the ground state and the symmetric stretching modes of both the ground and the excited states of
PbI₂ have been obtained from vibronic structure analysis together with the \( T_{00} \) value\(^{60} \). Eight well-resolved emission bands in the 710–395 nm region have been observed under photoexcitation of PbI₂\(^{61} \). Some of them can belong to vibrational progressions of the \(^3B_1 - ^1A_1 \) transition in PbI₂.

C. EHHal Molecules

Electronic transitions in triatomic CAs of the EXY type have been reported only for monohalorgermynes and monohalosilylenes. The latter are beyond the scope of the current review. The \(^1A'' - ^1A' \) transition in GeHCl and GeDCI was first detected in the 520–445 nm region as chemiluminescence, produced by interaction of GeH₄ or GeD₄ with Cl₂\(^{75} \). An analysis of the vibronic structure of the band has been carried out and the bending and Ge−Cl stretching frequencies in the ground and in the excited states have been determined. The electronic spectra of HGeCl\(^{76} \) and HGeBr\(^{77} \) produced at ambient temperatures by the reaction of GeH₄ with chlorine and bromine atoms have been reported in LIF studies. The spectra represented progressions of the bending modes in the \(^1A'' \) excited state and indicated activity of the bending mode in the ground \(^1A' \) state in the case of HGeBr. From the analysis of the observed rotational structure the bond angles in both states have been estimated for HGeCl as well as HGeBr.

The LIF spectra of jet-cooled HGeCl, HGeBr, HGeI and their deuterium isotopomers in the region of the \(^1A'' - ^1A' \) transition have been recorded using the pulsed discharge of the corresponding monohalogermaines\(^{78,79} \). All three excited state vibrational frequencies have been measured for each molecule. Analysis of the rotational structure of the (0,0,0)–(0,0,0) transition gave the rotational constants for both the states of all the molecules. However, direct determination of the geometrical parameters from the rotational constants appeared to be impossible due to the large correlation found between the Ge–H bond lengths and the bond angles. Finally, the approximate \( r_0 \) structures for both states of HGeHal molecules have been obtained when the bond angles were constrained to previous \textit{ab initio} values\(^{80} \). The lifetimes of the \(^1A'' \) states of HGeHal and DGeHal were found to equal 548 ns for GeHCl, 527 ns for GeDCI, 736 ns for GeHBr and 733 ns for GeDBr\(^{78} \) and to be dependent on the rovibronic state for HGeI and DGeI and lying within 1.5–2.3 \( \mu \)s for the vibrationally unexcited and monoexcited levels of the \(^1A'' \) state\(^{79} \), which implies existence of some nonradiative processes for the latter germynes. Comparison of the lifetimes of \(^1A'' \) states of the analogous silylenes\(^{81–83} \) and germynes shows that the lifetimes increase with increasing mass of both the central atom and the halogen atom\(^{78,79} \).

Attempts to detect HGeF in the reaction of GeH₄ with fluorine atoms or in a pulsed discharge of H₄GeF using the LIF technique were unsuccessful\(^{78} \) and it has been concluded that HGeF either cannot be obtained by these methods or does not fluoresce in the excited state\(^{78} \).

D. Comparison of the Molecular Constants of the Triatomic Carbene Analogs

In accordance with the data of Tables 1 and 2 the parent dihydrides EH₂ (E = Si, Ge) have the lowest energy of transition to the first excited singlet state among the triatomic CAs. Consecutive introduction of halogen substituents into a molecule of CA results in the gradual increase of this energy, which is obviously associated with lowering the energy of the HOMO in the ground state due to admixing halogen p atomic orbitals. Apparently, this conclusion is also valid for transitions to the first excited triplet state. The same mechanism is responsible for variations of the singlet–triplet splitting in triatomic carbenes\(^{88} \). In both series of mono- and dihalogenides the \( S_1 - S_0 \) and \( T_1 - S_0 \) energy gaps decrease with increasing mass of the halogen atoms, i.e., on decreasing the substituent electronegativity,
TABLE 2. Energies, geometries and fundamental frequencies of triatomic carbene analogs of EXY type in ground and excited states\textsuperscript{a,b}

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<th>Electronic state</th>
<th>Region of the transition (nm)</th>
<th>$T_{00}$ (cm$^{-1}$)</th>
<th>$\nu_1$ (cm$^{-1}$)</th>
<th>$\nu_2$ (cm$^{-1}$)</th>
<th>$\nu_3$ (cm$^{-1}$)</th>
<th>$r_0$(E-H) (Å)</th>
<th>$r_0$(E-X) (Å)</th>
<th>Bond angle $\theta_0$ (deg$^\circ$)</th>
<th>Reference</th>
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<td>$^1A''$</td>
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<td>324.8</td>
<td>1.515</td>
<td>2.436</td>
<td>114.9</td>
</tr>
</tbody>
</table>

$a$ The data correspond to isotopomers, containing the most abundant isotopes, or represent the average values if the isotopic structure has not been observed.

$b$ The number of the significant digits in the values exhibited corresponds to that presented in the original publications.

$c$ The bond angles given in parentheses were taken from quantum-chemical calculations and were used in calculations of the bond lengths from the rotational constants.

$d$ Equilibrium geometry $(r_e, \theta_e)$. 

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which is in accord with a qualitative theory\textsuperscript{89}. The effect of the central atom on the energy separation is not obvious, perhaps partly due to the lack of reliable data.

Geometries of some triatomic CAs in both the ground and excited states have been obtained from the rotational constants determined from analysis of the rotational structure of the electronic bands (see Tables 1 and 2). The ground state geometries will be considered in Section VIII. Due to lack of experimental data it is difficult to find any trend in the central atom or substituent effects on the bond angles or bond lengths in the triatomic CAs in the excited states. However, it is clear that these effects are less pronounced in the excited states than in the ground state. Comparison of structural parameters for the triatomic CAs in the ground and excited states shows that, in general, electronic excitation results in slight contraction of valence bonds (except for the E–H bonds in EHHal) and in significant increase of bond angle, with the latter trend being in agreement with electrostatic force theory\textsuperscript{90,91}.

In accordance with the selection rules, only excitation of full-symmetric vibrational modes can accompany the electronic transitions. One can conclude that the vibrational progressions for electronic transitions in the triatomic CAs more often result from excitation of bending modes. It is caused by significant change in the bond angle at the excitation.

As can be seen from Tables 1 and 2, electronic excitation is usually accompanied by lowering of the fundamental frequencies, with the fundamental frequencies in the first excited singlet state being lower than those in the first triplet state. Apparently, diminution of the bending frequencies is related to the increase of bond angle in the excited states, whereas lowering the stretching frequencies reflects weakening of the bonds in spite of their shortening.

E. Intrinsic Defects in Solid Silicon and Germanium Dioxides

In the final part of the treatment of the electronic spectra of triatomic germynes, silylenes and stannylenes it is worth mentioning studies of intrinsic defects on the surface and in the bulk of solid SiO\textsubscript{2} and GeO\textsubscript{2}, which have been discussed in detail in a review\textsuperscript{92}. Among the different types of defects, active centers, containing two coordinated silicon and germanium, have been revealed. The reactivity of these centers closely resembles that of dihalosilylenes and dihalogermylenes. The optical properties of such unusual silylenes and germynes have also been found to be similar to those of difluorosilylene and difluorogermylene. Indeed, the absorption maxima of silylene- and germylene-type defects on the surface lie at 243–234 nm and at ca 230 nm respectively, whereas the emission maxima are at ca 460 nm (T\textsubscript{1} – S\textsubscript{0} transition, the lifetime of the upper state is 19 ms) and 285 nm (S\textsubscript{1} – S\textsubscript{0} transition, the lifetime of the upper state is 5.1 ns) for the silylene\textsuperscript{93–97} and at 390 nm (T\textsubscript{1} – S\textsubscript{0} transition, the lifetime of the upper state is 145 μs) and at 290 nm (T\textsubscript{1} – S\textsubscript{0} transition) for the germylene\textsuperscript{92}. The absorption maxima of the silylene and germylene defects in the bulk are at 248 and 243 nm, respectively, and the emission maxima are at 459 (T\textsubscript{1} – S\textsubscript{0} transition, the lifetime of the upper state is ca 10 ms) and 282 nm (S\textsubscript{1} – S\textsubscript{0} transition) for the silylene and at 400 (T\textsubscript{1} – S\textsubscript{0} transition, the lifetime of the upper state is ca 100 μs) and 288 nm for the germylene\textsuperscript{98}. Both emission bands of these silylenes and germynes arise under their excitation into the S\textsubscript{1} state, which suggests the existence of nonradiative S\textsubscript{1} – T\textsubscript{1} transition. This transition has an activation barrier because, depending on the temperature, the major luminescence channel can be either S\textsubscript{1} – S\textsubscript{0} or T\textsubscript{1} – S\textsubscript{0} transition. A plausible mechanism for the S\textsubscript{1} – T\textsubscript{1} conversion has been suggested\textsuperscript{92}; it involves the second triplet state and explains the existence of the activation barrier by the necessity of linearization of the carbene analogs in the course of the conversion.
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<td>1.1022</td>
<td>115.05</td>
<td>101</td>
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</tbody>
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$^a$C–H stretching; $^b$CH$_2$ scissoring; $^c$E–C stretching; $^d$Out-of-plane bending; $^e$CH$_2$ rocking.
F. Tetraatomic Carbene Analogs: Germylidene and Silylidene

The first observation of 1-germavinylidene or germylidene, H$_2$C=Ge, and its deuteriated derivative, D$_2$C=Ge, have been reported in 1997$^{99}$. Both were produced in a pulsed electric discharge jet using GeMe$_4$ and Ge(CD$_3$)$_2$ as precursors. An attempt to obtain stannylidene by using the same method was unsuccessful$^{99}$. The identification of the germylidenes was based on both the detailed analysis of their LIF spectra, recorded in the 367–345 nm region, and comparison of the observed spectral features with those predicted by quantum-chemical calculations$^{99}$. The observed band system has been assigned to the allowed transition from the second excited singlet electronic state $\tilde{B}^1B_2$ [with the $\ldots(11a_1)^1(4b_1)^2(5b_2)^1$ electron configuration, where $11a_1$ MO is the lone electron pair on the Ge atom, $4b_1$ MO is the Ge–C $\pi$-bonding orbital and $5b_2$ MO is essentially the in-plane $p_y$ orbital on Ge$^{100}$] to the ground $\tilde{X}^1A_1$ singlet state [with the $\ldots(11a_1)^2(4b_1)^2$ electron configuration]. The $^1A_2^1A_1$ transition from the first excited singlet state $\tilde{A}^1A_2$ [$\ldots(11a_1)^2(4b_1)^1(5b_2)^1$] is forbidden by the selection rules. Further study of germylidenes enriched with the $^{74}$Ge isotope$^{101}$ allowed one to analyze in detail the rotational structure of the vibronic subband, corresponding to the transition between vibrationally unexcited levels of the electronic states, and to obtain geometries of the germylidene in the ground and in the excited states. The molecule has been found to be planar and to have $C_{2v}$ symmetry, as expected. Some characteristics of the germylidene and its silicon analog obtained from analysis of their LIF spectra are compared in Table 3. As can be seen from Table 3, the $T_{00}$ energy for germylidene is lower than that for silylidene, which is in agreement with the results of quantum-chemical calculations$^{99,100}$. The structures of germylidene and silylidene closely resemble each other in both the ground and excited states. Electronic excitation results in elongation of the E=C double bond and in a slight contraction of the C–H bonds and opening of the CH$_2$ angle. The lifetime of the vibrationally unexcited level of the upper state of germylidene has been measured to be ca 2 $\mu$s and depends on the rotational level$^{101}$. Many rovibronic levels of germylidene reveal quantum beats in their fluorescence decays, originating from interaction of the excited state with some other states, mainly with the ground state. The same effect has been found for almost all rovibronic levels of the upper state of silylidene$^{102}$.

IV. ELECTRONIC SPECTRA OF POLYATOMIC GERMYLENES, STANNYLENES AND PLUMBYLENES

This section is devoted to the electronic spectra of germylenes, stannylenes and plumbylenes carrying polyatomic substituents. The available data on the absorption maxima of these species are collected in Table 4, from which it can be seen that only stable polyatomic stannylenes and plumbylenes have been characterized by UV spectroscopy.

A. Detection and Identification

Most of the short-lived germylenes were generated by photolysis of suitable precursors in low-temperature (77 K) hydrocarbon glasses or by flash photolysis in solutions at room temperature and characterized by low-resolution absorption UV spectroscopy, using a fast response probe technique in the last case. With rare exception, their UV spectra consisted of a single broad absorption band. Because the position of this band is the only measured quantity which can be obtained from the low-resolution UV spectrum, and it is not sufficient for unequivocal identification of the absorbing species, these studies are usually accompanied by experiments on chemical trapping of the germylenes. Chemical trapping experiments were carried out under photolysis of the same precursor in solutions
in the presence of suitable scavengers to prove predominant formation of the germylene upon photodecomposition of the chosen precursor, and also after melting the hydrocarbon glasses doped with a trapping agent to prove the presence of the germylene in the glass. Thus, the assignment of the observed band to the particular species was mostly based on the stoichiometry of the precursor photodecomposition (from analysis of stable end products) and a chemical proof of the intermediacy of the germylene. Besides that, in some studies several different precursors were used for generation of the same germylene.

UV spectra of the two germylenes, dimethylgermylene, GeMe₂₁⁰³,₁⁰⁴ and 1-germacyclopent-3-en-1-ylidene¹⁰⁵, were recorded in low-temperature (11–21 K) Ar matrices. Their UV detection was supplemented by studying IR bands of these germylenes in the same matrices¹⁰⁴,₁⁰⁵ (see Section VI), which significantly enhanced the reliability of the UV identification. Reversible phototransformations of the 1-germacyclopent-3-enylidene into the isomeric 1-germacyclopent-2,4-diene (germole) and 1-germacyclopent-1,3- and 1,4-diienes have also been observed¹⁰⁵. This allowed one to establish unambiguously the correspondence of the UV and IR bands assigned to the germylene by observing simultaneous changes in their intensities.

The gas-phase UV spectrum of GeMe₂ generated from two different precursors has been recorded by laser resonance absorption flash kinetic spectroscopy¹⁰⁶. The identity of the germylene was supported by chemical trapping experiment and by analysis of the stable end products of the decomposition of the chosen precursors.

Most of the direct UV detection of germylenes in the liquid phase as well as the detection of GeMe₂ in the gas phase were followed by kinetic studies of the germylene reactions. Unfortunately, the obtained liquid-phase rate constants show a large scatter and differ appreciably from those obtained in the gas phase. Thus, the rate constants of the germylene reactions can hardly be used to confirm the identity of the germylene in the liquid phase.

UV spectra of stable germylenes, stannylenes and plumbylenes were recorded in solutions or in the solid phase under inert atmosphere in order to prevent access of oxygen and moisture. Thermochromic transitions have been revealed for many stable solid germylenes, stannylenes and plumbylenes. Their nature has not been studied.

**B. Complications**

Generation of short-lived germylenes is often accompanied by formation of other short-lived species. Germyl radicals with absorption maxima in the 300–350 nm region were identified upon photodecomposition of trigermanes¹⁰⁷,¹⁰⁸, linear oligogermanes Me(Me₂Ge)₅Me¹⁰⁹ and polygermanes (R₂Ge)₂, n = 10–100¹¹⁰, phenyl-substituted digermanes¹¹¹ and germatrisilacyclobutanes¹¹². A short wavelength band detected besides the GePh₂ band¹¹³ upon photolysis of (Me₃Si)₂GePh₂ was also attributed to a radical species¹⁰⁷. In general, the presence of aromatic substituents in the precursor molecule seems to favor the formation of germanium centered radicals¹¹⁴,¹¹⁵. A similar effect of aromatic substituents has been also noted for silylene precursors¹¹⁶,¹¹⁷. A check of the presence of radical species in hydrocarbon glasses by ESR spectroscopy has been used in some studies¹⁰⁳,¹⁰⁹,¹¹⁸–¹²⁰. Germylene generation from arylgermanes can be accompanied by formation of germaethenes (germenes)¹¹⁴,¹¹⁵,¹²¹. In the course of photolysis of 7,7-dimethyl-1,2,3,4-tetraphenyl-6,6-benzo-7-germanorbornadiene, a known photochemical precursor of GeMe₂, another labile product has been detected and tentatively identified as the corresponding germanorcaradiene¹²², a product of isomerization of the precursor. Dimerization of germylenes leading to formation of digermenes is a process often observed in solutions and upon annealing of hydrocarbon glasses. The list of labile by-products which accompany formation of short-lived germylenes, stannylenes...
and plumbylenes will probably be expanded in the future. The presence of such species in the systems under investigation represents the most seriously interfering factor in detection and identification of UV absorptions of polyatomic germynes, stannylenes and plumbylenes.

The majority of the studies cited here have produced forcible arguments for the performed assignment of the detected absorption to the particular short-lived germylene. However, the absorption maxima observed for the same germylene formed from different precursors differ remarkably from each other (Table 4). The largest scatter in the reported absorption maxima (from 380 to 506 nm) exists for GeMe₂, which UV spectrum has been studied in the greatest number of studies. Such discrepancies can partly be explained by low precision in determination of the maximum for typically broad bands of low intensity belonging to short lived germynes (for stable germynes, stannylenes and plumbylenes the extinction coefficient is usually <1000–2000 M⁻¹ cm⁻¹) and also by medium effects. In the case of low-temperature hydrocarbon glasses, the influence of the by-products of precursor photodecomposition, which remain in the same cage of the hydrocarbon matrix, can be the main factor determining the band shift. A special type of such influence, which can affect the UV band position in both liquid and solid phases, is the formation of a CA complex with by-products (and precursors) possessing Lewis basicity. The effect of complexation on the UV absorptions of germynes, stannylenes and plumbylenes will be considered in detail in Section V. A series of labile complexes of germynes, stannylenes and plumbylenes has also been detected by IR spectroscopy and they will be considered in Section VII. The important conclusions which can be drawn from these considerations, are that (i) UV absorptions of germynes, stannylenes and plumbylenes seem to be very sensitive to complexation, (ii) complexation usually results in a blue shift of the UV absorption, and (iii) many classes of organic compounds (aromatics, unsaturated organic compounds, organic derivatives of the Group 15, 16 and 17 elements etc.) could form complexes with CAs. Thus, complex formation is expected to be a very common reaction accompanying generation of short-lived polyatomic germynes. The reasons mentioned above can explain qualitatively most disagreements in the reported UV band positions of short-lived germynes, but not all of them. For example, it can hardly be understood in the framework of these reasons why the absorption of GeMe₂, generated from cyclo-(GeMe₂)₅ should be strongly red-shifted relative to its absorption upon its generation from cyclo-(GeMe₂)₆ or Me(GeMe₂)₅Me under the same conditions (Table 4). Obviously, the reasons for the discrepancy in the UV band positions of short-lived polyatomic germynes and the differences in their reaction kinetics, which were mentioned above, are of the same nature, and these reasons are not yet completely understood.

C. Nature of Electronic Transitions in Polyatomic Germynes, Stannylenes and Plumbylenes

It follows from numerous theoretical studies that the ground electronic state of all CAs (except those with very peculiar substituents, like Li atoms or extra-bulky t-Bu₃Si groups ) is the singlet state, in which the HOMO is typically a lone pair of the divalent atom E (E = Si, Ge, Sn, Pb) and the LUMO is essentially a p orbital of the same atom. The promotion of the lone electron pair to the empty p orbital corresponds to the first allowed electronic transition. The absorption maxima (presented in Table 4) of germynes, stannylenes and plumbylenes (the longest wavelength absorption maxima for those possessing more than one absorption band in the near UV-vis region) with alkyl, aryl and silyl substituents lie in the usual region for such n → p transitions and therefore can surely be assigned to this transition. For series of polyatomic silylenes and
It will be seen in Section IX that in the case of germynes, stannylenes and plumbylenes bearing two amino-substituents there are three high-lying occupied MOs which are close in energy. The lone pair of the divalent germanium, tin or lead atom lies in energy between two MOs, which represent a nitrogen lone-pair antibonding orbital (HOMO) and bonding combinations. A similar order of the highest occupied MOs has also been noted for GeCl(N(SiMe3)2)134. Thus, one can expect that for such germynes, stannylenes and plumbylenes (Table 4) the second band from the red edge of the spectrum corresponds to the excitation of an electron from the lone pair of the divalent atom of the Group 14 element. In the case of 1,3-dineopentylpyrido[6,1b]-1,3,2αλ2-diazasilole, -germolene and -stannolene only the third MO corresponds to the divalent atom lone pair135. Two higher-lying MOs represent combinations of nitrogen atom lone pairs and the π orbital of the aromatic ring. Calculations at the CIS level with ECP DZ basis of the MO structure of diphasphanyl- and diarsanyl-substituted germynes, stannylenes and plumbylenes has shown that the three highest occupied MOs in these molecules represent combinations of lone-pair orbitals of the divalent germanium, tin or lead atom and phosphorus or arsenic atoms with some admixture of p-AO of the divalent atom of the Group 14 element, while the LUMO corresponds to the π orbital of the divalent atom136. Therefore, two or three observed UV bands for experimentally studied diphasphanyl- and diarsanyl-substituted germynes, stannylenes and plumbylenes (Table 4) have been assigned to electronic transitions from these MOs of mixed character to the p orbital136.

To the best of our knowledge there are no published studies of the MO structure of CAs of E(XR)2 type, where X = O, S, Se, Te. Consequently, the assignment of UV bands of these molecules is not clear, but it is usually assumed that the HOMO of such CAs is the lone pair of the divalent atom of the Group 14 element. By analogy with silylenes128, one can expect that the HOMO of germynes, stannylenes and plumbylenes containing only one substituent with a lone pair at the α-atom (which belongs to the Group 15, 16 or 17 elements) is the lone pair of divalent germanium, tin or lead atom, and the longest wavelength electronic transition in these species is the n → p transition.

D. Effects of Substituents on the Position of the Electronic Transition Band

The nature of substituent effects on the position of absorption maxima corresponding to n → p transition in polyatomic silylenes have been considered in detail in theoretical studies of Apeloig and coworkers126,128. Unfortunately, there is no similar study for germynes, stannylenes or plumbylenes. However, the available experimental data show that the main conclusions obtained by Apeloig and coworkers are also applicable to polyatomic germynes, stannylenes and plumbylenes.

Substituent effects can be divided into two types: electronic and steric. The steric effect results from steric repulsion of bulky substituents, and destabilizes the ground electronic state and simultaneously results in an increasing bond angle at the divalent atom of the Group 14 element. Because the bond angle in the first excited singlet state is much larger for CAs (see experimental data for triatomic systems in Section III and the theoretical data for GeMe2 by Barthelat and coworkers129), the repulsion of bulky substituents will destabilize this state to a much lower extent. Therefore, the energy of the n → p electronic transition is expected to decrease on increasing the ground state bond angle for a series of CAs bearing substituents with similar electronic properties at the same divalent atom E (E = Si, Ge, Sn, Pb). Assuming essential resemblance of the potential energy curves for the first excited singlet states for such CAs, one can expect that the red shift of the
experimentally observed vertical electronic transitions will be even more pronounced. Simple MO consideration leads to the same conclusion. Increasing the bond angle in the ground electronic state of a CA results in an increase of the degree of hybridization of the divalent atom of the Group 14 element and therefore in a rise of the HOMO (the divalent atom lone pair) energy and lowering of the LUMO (p orbital of this divalent atom) energy in accordance with Bent’s rule\textsuperscript{137} and thereby lowering the energy of the corresponding electronic transition.

Dependence of the absorption maximum on the bond angle can be illustrated by data on stable germylenes, stannylenes and plumbylenes containing alkyl and aryl substituents (Table 5). It is noteworthy that according to the X-ray analysis, the aromatic rings in the aryl-substituted germylenes, stannylenes and plumbylenes presented in Table 5 are rotated out of the plane of the carbene center. This excludes conjugation effects and allows one to consider alkyl- and aryl-substituted compounds together. It can be seen that there is a clear parallel between the values of the bond angles and the positions of the UV bands for these stable species. Variations in band positions depending on the bond angle are most prominent in the case of germylenes. Observation of the absorption bands of (2,4,6-(CF\textsubscript{3})\textsubscript{3}C\textsubscript{6}H\textsubscript{2})\textsubscript{2}E (E = Ge, Sn) at unexpectedly low wavelengths is explained by intramolecular coordination of the germanium and tin atoms to fluorine atoms of the \(\sigma\)-CF\textsubscript{3} groups, which has been established by X-ray analysis\textsuperscript{138,139}. The extra-high value of the absorption maximum of ((Me\textsubscript{3}Si)\textsubscript{3}Si)\textsubscript{2}Pb reflects the strong \(\sigma\)-donor effect of the (Me\textsubscript{3}Si)\textsubscript{3}Si group.

Besides the absorption spectra, the fluorescence spectra were recorded for GeMe\textsubscript{2}\textsuperscript{118,119}, GeMePh\textsuperscript{119} and GePh\textsubscript{2}\textsuperscript{119} (Table 4). The slightly larger Stokes shift (difference between maxima of the fluorescence and absorption bands) found for GeMe\textsubscript{2} can also be attributed to a slightly larger change in the C—Ge—C bond angle upon excitation for this germylene compared to GeMePh and GePh\textsubscript{2}. This suggests some increase in the ground state bond angle at the Ge atom upon introduction of the bulkier phenyl group.

The nature of the electronic effects of a number of substituents has been elucidated in the course of theoretical studies of the \(n\rightarrow p\) electronic transitions in silylenes\textsuperscript{126,128}. \(\sigma\)-Acceptor substituents increase and \(\sigma\)-donor substituents (like Me\textsubscript{3}Si) reduce the singlet–singlet energy gap in accordance with Bent’s rule\textsuperscript{137} due to change in the hybridization of the divalent atom of the Group 14 element. Thus, the steric effect of bulky substituents is equivalent to the weak \(\sigma\)-donor effect. \(\pi\)-Donors affect the p orbital of the divalent atom of the Group 14 element, raising its energy, which increases the energy of the \(n\rightarrow p\) transition. Substituents like Hal, NR\textsubscript{2}, OR or SR show both \(\sigma\)-acceptor and \(\pi\)-donor properties, affecting the transition energy in the same direction. \(\alpha\)-Unsaturated organic substituents (aryl, vinyl, ethynyl) have two orbitals which can interact with the p orbital of the divalent atom of the Group 14 element. Those are occupied \(\pi\) and empty low-lying \(\pi^*\) orbitals. Interaction with the \(\pi\) orbital results in raising the p orbital energy, while interaction with the \(\pi^*\) orbital results in lowering its energy. It has been found\textsuperscript{126} that in the case of silylenes, the latter interaction prevails over the former for aryl and vinyl groups, whereas for ethynyl group the situation is the reverse. Substitution of an H atom by a Me group slightly increases the transition energy. Thus, the Me group acts as a weak \(\sigma\)-acceptor. In the case of silylenes, increasing the transition energy by an Me group is stronger than that by the ethynyl group. Experimental data on absorption maxima of the corresponding silylenes\textsuperscript{140,141} are in excellent agreement with the transition energies calculated in the course of these studies\textsuperscript{126,128}. The available data on absorption maxima of germylenes, stannylenes and plumbylenes (Table 4) are also in qualitative agreement with these predictions\textsuperscript{142}.

The energy of the 0–0 transition in GeH\textsubscript{2} is 16320 cm\textsuperscript{-1} (613 nm, see Section III). The corresponding energy for GeMe\textsubscript{2} can be roughly estimated as an average of the
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<tr>
<td>Me&lt;sub&gt;2&lt;/sub&gt;Ge</td>
<td>Me&lt;sub&gt;2&lt;/sub&gt;Ge(N&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>( h \nu, 3\text{-MP}, 77 \text{ K} )</td>
<td>( ca ) 405</td>
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<td>Me&lt;sub&gt;2&lt;/sub&gt;Ge</td>
<td>7-germanorbornadiene&lt;sup&gt;d&lt;/sup&gt;</td>
<td>( h \nu, 3\text{-MP}, 77 \text{ K} )</td>
<td>( 416 (620) )</td>
<td>119</td>
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<tr>
<td>Me&lt;sub&gt;2&lt;/sub&gt;Ge</td>
<td>Me&lt;sub&gt;2&lt;/sub&gt;Ge(SePh)&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>Me&lt;sub&gt;2&lt;/sub&gt;Ge</td>
<td>7-germanorbornadiene&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>( 420 )</td>
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<td>7-germanorbornadiene&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>( 420 )</td>
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<td>Me&lt;sub&gt;2&lt;/sub&gt;Ge</td>
<td>(PhMe&lt;sub&gt;2&lt;/sub&gt;Ge)GeMe&lt;sub&gt;2&lt;/sub&gt;</td>
<td>( h \nu, 3\text{-MP}, 77 \text{ K} )</td>
<td>( 422 (623) )</td>
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<td>( h \nu, 3\text{-MP}, 77 \text{ K} )</td>
<td>( 430 (650) )</td>
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<td>c-(Me&lt;sub&gt;2&lt;/sub&gt;Ge)&lt;sub&gt;6&lt;/sub&gt;</td>
<td>( h \nu, 3\text{-MP}, 77 \text{ K} )</td>
<td>( 430 (630) )</td>
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<td>Me(Me&lt;sub&gt;2&lt;/sub&gt;Ge)&lt;sub&gt;5&lt;/sub&gt;Me</td>
<td>( h \nu, 3\text{-MP}, 77 \text{ K} )</td>
<td>436 (628)</td>
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<td>( h \nu, \text{THF, r.t.} )</td>
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<td>Me&lt;sub&gt;2&lt;/sub&gt;Ge(SePh)&lt;sub&gt;2&lt;/sub&gt;</td>
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(continued overleaf)
TABLE 4. (continued)

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<th>Precursor</th>
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<th>λ&lt;sub&gt;max&lt;/sub&gt;</th>
<th>Reference</th>
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<td>Et&lt;sub&gt;2&lt;/sub&gt;Ge(SePh)&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>7-germanorbornadiene&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>440</td>
<td>142, 144</td>
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<td>(Et&lt;sub&gt;2&lt;/sub&gt;Ge)&lt;sub&gt;n&lt;/sub&gt;, n = 10–100</td>
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<td>c-Pr&lt;sub&gt;2&lt;/sub&gt;Ge(SePh)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>hν, 3-MP, 77 K</td>
<td>542</td>
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<td>c-(i-Pr&lt;sub&gt;2&lt;/sub&gt;Ge)&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>Bu&lt;sub&gt;2&lt;/sub&gt;Ge(SePh)&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>148</td>
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<td>7-germanorbornadiene&lt;sup&gt;d&lt;/sup&gt;</td>
<td>hν, 3-MP, 77 K</td>
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<td>142</td>
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<td>(Bu&lt;sub&gt;2&lt;/sub&gt;Ge)&lt;sub&gt;n&lt;/sub&gt;, n = 10–100</td>
<td>hν, C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;, r.t.</td>
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<td>(Hex&lt;sub&gt;2&lt;/sub&gt;Ge)&lt;sub&gt;n&lt;/sub&gt;, n = 10–100</td>
<td>hν, C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;, r.t.</td>
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<td>Ge(N&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>hν, Ar matrix</td>
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<td><strong>PhMeGe</strong></td>
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<td>hν, 3-MP, 77 K</td>
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<td>(Me&lt;sub&gt;3&lt;/sub&gt;Si)&lt;sub&gt;2&lt;/sub&gt;GeMePh</td>
<td>hν, 3-MP, 77 K</td>
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<td>107, 108</td>
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<td>PhMeGe</td>
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<td>Ph(Me&lt;sub&gt;3&lt;/sub&gt;Si)&lt;sub&gt;n&lt;/sub&gt;, n = 10–100</td>
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<td>107, 108</td>
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<td>Ph(Me&lt;sub&gt;3&lt;/sub&gt;Si)</td>
<td>hν, 3-MP, 77 K</td>
<td>610</td>
<td>154</td>
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<sup>a</sup> Carbene analogs.

<sup>b</sup> Conditions of generation and spectrum recording.

<sup>c</sup> λ<sub>max</sub> values are given in nm.

<sup>d</sup> Data from references not provided in the table.
<table>
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<tr>
<th>Compound</th>
<th>Formula</th>
<th>Conditions</th>
<th>λ (nm)</th>
<th>Δ (°C)</th>
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<td>Mes(t-Bu)Ge(SiMe₃)₂</td>
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<tr>
<td>Ph₂Ge</td>
<td>Ph₂Ge(GeMe₃)₂</td>
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<td>462 (651)</td>
<td>107, 108, 119</td>
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<td>Ph₂Ge(SiMe₃)₂</td>
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<td>Ph₂Ge(SiMe₃)₂</td>
<td>hν, 3-MP, 77 K</td>
<td>466</td>
<td>142, 144</td>
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<td>7-germanorbordiene&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>142, 144</td>
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<td>Ph₂Ge(GeMe₃)₂</td>
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<td>(Ph₃Ge)₂</td>
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<td>Mes₂Ge</td>
<td>Mes₂Ge(SiMe₃)₂</td>
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<td>142, 144, 145</td>
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<td>(2,6-Me₂C₆H₃)₂Ge</td>
<td>(2,6-Me₂C₆H₃)₂Ge(SiMe₃)₂</td>
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<td>solvent is not reported, r.t.</td>
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<sup>d</sup> CA is stable solvent is not reported, r.t.
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<th>Conditions of generation and spectrum recording(^b)</th>
<th>(\lambda_{\text{max}})</th>
<th>Reference</th>
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<td>((t\text{-Bu})_2N)(_2)Ge</td>
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<td>445, 310, 227</td>
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<td>(C_6H_{14}), r.t.</td>
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<td>(i)-(C_6H_{14}), r.t.</td>
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<td>(C_6H_{14}), r.t.</td>
<td>484, 370, 280, 247</td>
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<td>(C_6H_{14}), r.t.</td>
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<td>(C_6H_{14}), r.t.</td>
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</tr>
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<td>((2-t\text{-Bu}-4,5,6\text{-Me}_3\text{C}_6\text{H}_2))(((\text{Me}_3\text{Si})_2)(_2)Si)Sn</td>
<td>CA is stable</td>
<td>(C_6H_{14}), r.t.</td>
<td>586</td>
<td>171</td>
</tr>
<tr>
<td>((2-t\text{-Bu}-4,5,6\text{-Me}_3\text{C}_6\text{H}_2))(((\text{Me}_3\text{Si})_2)(_2)Si)Sn</td>
<td>CA is stable</td>
<td>(C_6H_{14}), r.t.</td>
<td>563</td>
<td>171</td>
</tr>
<tr>
<td>((2,4,6-(\text{CF}_3)_3\text{C}_6\text{H}_2))(((\text{Me}_3\text{Si})_2)(_2)Si)Sn</td>
<td>CA is stable</td>
<td>(C_6H_{14}), r.t.</td>
<td>476</td>
<td>172</td>
</tr>
<tr>
<td>((2,4,6-(\text{CF}_3)_3\text{C}_6\text{H}_2))(((\text{Me}_3\text{Si})_2)(_2)Si)Sn</td>
<td>CA is stable</td>
<td>(C_6H_{12}), r.t.</td>
<td>479</td>
<td>173</td>
</tr>
<tr>
<td>((2,4,6-(\text{CF}_3)_3\text{C}_6\text{H}_2))(((\text{Me}_3\text{Si})_2)(_2)Si)Sn</td>
<td>CA is stable</td>
<td>solid, r.t.</td>
<td>345</td>
<td>139</td>
</tr>
<tr>
<td>((2,4,6-(\text{CF}_3)_3\text{C}_6\text{H}_2))(((\text{Me}_3\text{Si})_2)(_2)Si)Sn</td>
<td>CA is stable</td>
<td>(c)-(C_6H_{12}), r.t.</td>
<td>372</td>
<td>143</td>
</tr>
<tr>
<td>((2,4,6-(\text{CF}_3)_3\text{C}_6\text{H}_2))(((\text{Me}_3\text{Si})_2)(_2)Si)Sn</td>
<td>CA is stable</td>
<td>solid, r.t.</td>
<td>466</td>
<td>174</td>
</tr>
<tr>
<td>Compound</td>
<td>Stability</td>
<td>Temperature</td>
<td>References</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>-----------</td>
<td>-------------</td>
<td>------------</td>
<td></td>
</tr>
<tr>
<td>(2,4,6-t-Bu₃C₆H₂C(S)S)_₂Sn</td>
<td>CA is stable</td>
<td>solid, r.t.</td>
<td>464, 364, 174</td>
<td></td>
</tr>
<tr>
<td>(t-Bu(Me₃Si)N)_2Sn</td>
<td>CA is stable</td>
<td>C₆H₁₄, r.t.</td>
<td>433, 330, 305, 236, 132</td>
<td></td>
</tr>
<tr>
<td>((Me₃Si)₂N)_2Sn</td>
<td>CA is stable</td>
<td>C₆H₁₄, r.t.</td>
<td>487, 389, 287, 230, 131, 132</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>387, 175</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₆H₁₄, r.t.</td>
<td>475, 222, 164</td>
<td></td>
</tr>
<tr>
<td>((Tip(t-Bu)FSi)(i-Pr₃Si)P)_₂Sn</td>
<td>CA is stable</td>
<td>C₆H₁₄, r.t.</td>
<td>579, 438, 136</td>
<td></td>
</tr>
<tr>
<td>((Tip₂FSi)(i-Pr₃Si)P)_₂Sn</td>
<td>CA is stable</td>
<td>C₆H₁₄, r.t.</td>
<td>644, 433, 384, 136</td>
<td></td>
</tr>
<tr>
<td>((Tip(t-Bu)FSi)(i-Pr₃Si)As)_₂Sn</td>
<td>CA is stable</td>
<td>C₆H₁₄, r.t.</td>
<td>641, 459, 136</td>
<td></td>
</tr>
<tr>
<td>(2,6-Tip₂C₆H₃)ISn</td>
<td>CA is stable</td>
<td>C₆H₁₄, r.t.</td>
<td>428, 165</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₆H₁₄, r.t.</td>
<td>610, 385, 176</td>
<td></td>
</tr>
<tr>
<td>((Me₃Si)_₃Si)_₂Pb</td>
<td>CA is stable</td>
<td>not reported</td>
<td>1056, 578, 167</td>
<td></td>
</tr>
<tr>
<td>(2,6-Tip₂C₆H₃)MePb</td>
<td>CA is stable</td>
<td>C₆H₁₄, r.t.</td>
<td>466, 332, 177</td>
<td></td>
</tr>
<tr>
<td>(2,6-Tip₂C₆H₃)(t-Bu)Pb</td>
<td>CA is stable</td>
<td>C₆H₁₄, r.t.</td>
<td>470, 177</td>
<td></td>
</tr>
<tr>
<td>(3,5-(t-Bu)₂C₆H₃CMe₂CH₂)(2,4,6-(t-Bu)₂C₆H₃)Pb</td>
<td>CA is stable</td>
<td>solid, r.t.</td>
<td>406, 178</td>
<td></td>
</tr>
<tr>
<td>((Me₃Si)₂CH)TbtPb</td>
<td>CA is stable</td>
<td>C₆H₁₄, r.t.</td>
<td>531, 179, 180</td>
<td></td>
</tr>
<tr>
<td>((Me₃Si)₃Si)(2,3,4-Me₃-6-t-BuC₆H)Pb</td>
<td>CA is stable</td>
<td>solvent is not reported, r.t.</td>
<td>610, 341, 303, 178</td>
<td></td>
</tr>
<tr>
<td>((Me₃Si)₃Si)(2,4,6-(CF₃)₃C₆H₂)Pb</td>
<td>CA is stable</td>
<td>C₆H₁₂, r.t.</td>
<td>1025, 586, 168</td>
<td></td>
</tr>
<tr>
<td>Tbt₂Pb</td>
<td>CA is stable</td>
<td>C₆H₁₄, r.t.</td>
<td>610, 179, 180</td>
<td></td>
</tr>
<tr>
<td>TmtTbtPb</td>
<td>CA is stable</td>
<td>C₆H₁₄, r.t.</td>
<td>560, 179, 180</td>
<td></td>
</tr>
<tr>
<td>TipTbtPb</td>
<td>CA is stable</td>
<td>C₆H₁₄, r.t.</td>
<td>550, 179, 180</td>
<td></td>
</tr>
</tbody>
</table>

(continued overleaf)
<table>
<thead>
<tr>
<th>Carbene analog (^a)</th>
<th>Precursor</th>
<th>Conditions of generation and spectrum recording (^b)</th>
<th>(\lambda_{\text{max}})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tip2Pb</td>
<td>CA is stable</td>
<td>(\text{C}<em>6\text{H}</em>{14}, \text{r.t.})</td>
<td>541, 385, 321</td>
<td>181</td>
</tr>
<tr>
<td>((2,3,4-\text{Me}_3, 6-\text{t-BuC}_6\text{H}_2)\text{Pb})</td>
<td>CA is stable</td>
<td>solid, r.t.</td>
<td>490</td>
<td>178</td>
</tr>
<tr>
<td>((2,6-\text{Mes}_2\text{C}_6\text{H}_3)\text{Pb})</td>
<td>CA is stable</td>
<td>(\text{Et}_2\text{O}, \text{r.t.})</td>
<td>526</td>
<td>158</td>
</tr>
<tr>
<td>((2,6-\text{Tip}_2\text{C}_6\text{H}_3)\text{Pb})</td>
<td>CA is stable</td>
<td>(\text{C}<em>6\text{H}</em>{14}, \text{r.t.})</td>
<td>460</td>
<td>177</td>
</tr>
<tr>
<td>((2,4,6-\text{Me}(\text{NCH}_2)_3\text{C}_6\text{H}_2\text{O})_2\text{Pb})</td>
<td>CA is stable</td>
<td>(\text{c-C}<em>6\text{H}</em>{12}, \text{r.t.})</td>
<td>360</td>
<td>143</td>
</tr>
<tr>
<td>Tbt(TbtS)Pb</td>
<td>CA is stable</td>
<td>toluene, r.t.</td>
<td>540</td>
<td>182</td>
</tr>
<tr>
<td>((\text{Tip}(\text{t-Bu})\text{FSi})(\text{i-Pr}_3\text{Si})\text{P})_2\text{Pb})</td>
<td>CA is stable</td>
<td>(\text{C}<em>6\text{H}</em>{14}, \text{r.t.})</td>
<td>645, 465, 346</td>
<td>136</td>
</tr>
</tbody>
</table>

\(^a\) Tbt = 2,4,6-\((\text{Me}_3\text{Si})_2\text{CH})_3\text{C}_6\text{H}_2\); Tip = 2,4,6-(\text{i-Pr})_3\text{C}_6\text{H}_2\); Ttm = 2,4,6-\((\text{Me}_3\text{SiCH}_2)_3\text{C}_6\text{H}_2\); Np = neopentyl; Tcp = 2,4,6-(\text{c-C}_6\text{H}_{11})_3\text{C}_6\text{H}_2\); Tpp = 2,4,6-tris(1-ethylpropyl)phenyl.

\(^b\) 3-MP = 3-methylpentane, IP = isopentane.

\(^c\) The fluorescence maxima are shown in parentheses.

\(^d\) 7-germanorbornadiene = 7,7-disubstituted 1,2,3,4-tetraphenyl-5,6-benzo-7-germanorbornadiene; substituents at Ge atom correspond to those in the gemylene generated from this 7-germanorbornadiene.
TABLE 5. The long-wavelength absorption maxima and bond angles at divalent germanium, tin and lead atoms for stable carbene analogs

<table>
<thead>
<tr>
<th>Carbene analog</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Reference</th>
<th>Bond angle (deg) (method)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2,6-Mes$_2$C$_6$H$_3$)$_2$Ge</td>
<td>578</td>
<td>158</td>
<td>114.2 (X-ray)</td>
<td>158</td>
</tr>
<tr>
<td>(2,4,6-t-Bu$_3$C$_6$H$_2$)$_2$Ge</td>
<td>430, 405$^b$</td>
<td>156</td>
<td>108.0 (X-ray)</td>
<td>156</td>
</tr>
<tr>
<td>((Me$_3$Si)$_2$CH)$_2$Ge</td>
<td>414</td>
<td>152, 153</td>
<td>107 (ED)</td>
<td>185</td>
</tr>
<tr>
<td>Me$_3$Si</td>
<td>450</td>
<td>150</td>
<td>90.97 (X-ray)</td>
<td>150</td>
</tr>
<tr>
<td>Me$_3$Si</td>
<td>484</td>
<td>166</td>
<td>86.7 (X-ray)</td>
<td>166</td>
</tr>
<tr>
<td>(2,4,6-(CF$_3$)$_3$C$_6$H$_2$)$_2$Ge</td>
<td>374</td>
<td>138</td>
<td>99.95 (X-ray)</td>
<td>138</td>
</tr>
<tr>
<td>(2,6-Mes$_2$C$_6$H$_3$)$_2$Sn</td>
<td>553</td>
<td>158</td>
<td>114.7 (X-ray)</td>
<td>158</td>
</tr>
<tr>
<td>(2,4,6-t-Bu$_3$C$_6$H$_2$)$_2$Sn</td>
<td>476</td>
<td>172</td>
<td>103.6 (X-ray)</td>
<td>172</td>
</tr>
<tr>
<td>((Me$_3$Si)$_2$CH)$_2$Sn</td>
<td>495</td>
<td>152</td>
<td>97 (ED)</td>
<td>185</td>
</tr>
<tr>
<td>C(SiMe$_3$)$_2$</td>
<td>450</td>
<td>150</td>
<td>90.97 (X-ray)</td>
<td>150</td>
</tr>
<tr>
<td>C(SiMe$_3$)$_2$</td>
<td>484</td>
<td>166</td>
<td>86.7 (X-ray)</td>
<td>166</td>
</tr>
<tr>
<td>(2,4,6-(CF$_3$)$_3$C$_6$H$_2$)$_2$Sn</td>
<td>345</td>
<td>139</td>
<td>98.3 (X-ray)</td>
<td>139</td>
</tr>
<tr>
<td>((Me$_3$Si)$_3$Si)$_2$Pb</td>
<td>1056</td>
<td>167</td>
<td>113.56 (X-ray)</td>
<td>167</td>
</tr>
<tr>
<td>Me$_3$Si</td>
<td>610</td>
<td>176</td>
<td>117.1 (X-ray)</td>
<td>176</td>
</tr>
<tr>
<td>Me$_3$Si</td>
<td>610</td>
<td>179, 180</td>
<td>116.3 (X-ray)</td>
<td>179, 180</td>
</tr>
<tr>
<td>(2,6-Mes$_2$C$_6$H$_3$)$_2$Pb</td>
<td>526</td>
<td>158</td>
<td>114.5 (X-ray)</td>
<td>158</td>
</tr>
<tr>
<td>(2,3,4-Me$_3$-6-t-BuC$_6$H$_2$)$_2$Pb</td>
<td>490$^b$</td>
<td>178</td>
<td>103.04 (X-ray)</td>
<td>178</td>
</tr>
<tr>
<td>(2,6-Tip$_2$C$_6$H$_3$)MePb</td>
<td>466</td>
<td>177</td>
<td>101.4 (X-ray)</td>
<td>177</td>
</tr>
<tr>
<td>(2,6-Tip$_2$C$_6$H$_3$)(t-Bu)Pb</td>
<td>470</td>
<td>177</td>
<td>100.5 (X-ray)</td>
<td>177</td>
</tr>
<tr>
<td>(2,6-Tip$_2$C$_6$H$_3$)PhPb$^c$</td>
<td>460</td>
<td>177</td>
<td>95.64 (X-ray)</td>
<td>177</td>
</tr>
<tr>
<td>(3,5-(t-Bu)$_2$C$_6$H$_3$CMe$_2$CH$_2$)PbR, R = 2,4,6-(t-Bu)$_3$C$_6$H$_2$</td>
<td>406$^b$</td>
<td>178</td>
<td>94.8 (X-ray)</td>
<td>178</td>
</tr>
<tr>
<td>(t-Bu)$_2$N</td>
<td>460</td>
<td>162</td>
<td>97.5 (X-ray)</td>
<td>162</td>
</tr>
<tr>
<td>RN</td>
<td>460</td>
<td>162</td>
<td>97.5 (X-ray)</td>
<td>162</td>
</tr>
<tr>
<td>(2,6-Tip$_2$C$_6$H$_3$)ClGe</td>
<td>393</td>
<td>165</td>
<td>101.31 (X-ray)</td>
<td>165</td>
</tr>
<tr>
<td>(2,6-Tip$_2$C$_6$H$_3$)ISn</td>
<td>428</td>
<td>165</td>
<td>102.6 (X-ray)</td>
<td>165</td>
</tr>
<tr>
<td>Tbt(TbtS)Pb</td>
<td>540$^d$</td>
<td>182</td>
<td>100.2 (X-ray)</td>
<td>182</td>
</tr>
</tbody>
</table>

(continued overleaf)
TABLE 5. (continued)

<table>
<thead>
<tr>
<th>Carbene analog</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Reference Bond angle (deg) (method$^a$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NG}_2$</td>
<td>426, 250, 217</td>
<td>164</td>
<td>111.4 (X-ray)</td>
</tr>
<tr>
<td>$(\text{Me}_3\text{Si})_2\text{N}_2\text{Ge}$</td>
<td>364, 300, 228</td>
<td>132</td>
<td>101 (ED)</td>
</tr>
<tr>
<td>$(\text{Me}_3\text{Si})_2\text{N}_2\text{Sn}$</td>
<td>487, 389, 287</td>
<td>131, 132</td>
<td>96.0 (ED)</td>
</tr>
<tr>
<td>$(\text{Tip}(t\text{-Bu})\text{FSi})(i\text{-Pr}_3\text{Si})\text{P}_2\text{Sn}$</td>
<td>579, 438</td>
<td>136</td>
<td>98.78 (X-ray)</td>
</tr>
<tr>
<td>$(\text{Tip}(t\text{-Bu})\text{FSi})(i\text{-Pr}_3\text{Si})\text{As}_2\text{Sn}$</td>
<td>641, 459</td>
<td>136</td>
<td>94.64 (X-ray)</td>
</tr>
<tr>
<td>$(\text{Tip}(t\text{-Bu})\text{FSi})(i\text{-Pr}_3\text{Si})\text{P}_2\text{Pb}$</td>
<td>645, 465, 346</td>
<td>136</td>
<td>97.88 (X-ray)</td>
</tr>
</tbody>
</table>

$^a$X-ray = X-ray analysis, ED = electron diffraction.

$^b$Absorption in solid phase.

$^c$The plane of the Ph ring almost coincides with the plane of the plumbylene center.

$^d$This absorption probably belongs to a complex of this plumbylene with solvent (toluene).

Absorption and the fluorescence band maxima. This gives ca 19000 cm$^{-1}$ (520 nm) using the data of Mochida and coworkers.$^{119}$ Thus, Me groups seem to reduce the energy of the n $\rightarrow$ p transition in the germylene series as they did in the silylene series. Lengthening of the alkyl chain does not affect much the absorption maximum position for germynes, which can be seen from comparison of the data for GeMe$_2$, GeEt$_2$, and GeBu$_2$ (Table 4).

A small bathochromic shift of the absorption band (relative to the band of GeMe$_2$) upon introduction of isopropyl or hexyl substituents is caused by steric rather than by electronic factors. Consecutive substitution of the Me groups in GeMe$_2$ by Ph groups results in red shift of the absorption bands. This shift can be caused by both steric and electronic effects of the phenyl groups. A rough estimation of the 0$\rightarrow$0 transition energy in GePh$_2$ using the data of Mochida and coworkers$^{119}$ gives ca 16500 cm$^{-1}$ (605 nm), which is close to that for GeH$_2$. However, because the latter value is too approximate, it is not clear whether the n$\rightarrow$π* interaction is stronger than the n$\rightarrow$π interaction for phenyl-substituted germynes or not. The lowest energies of the vertical electronic transition which have been measured for germynes, stannylenes and plumbynes are 610 nm (Ge(SiMe$_3$)Ph), 838 nm (Sn(Si(SiMe$_3$)$_3$)$_2$) and 1056 nm for (Pb(Si(SiMe$_3$)$_3$)$_2$) (Table 4). Obviously, the σ-donor effect of the SiMe$_3$ group is responsible for the long-wavelength absorption of these compounds. Introduction of Cl, OR, NR$_2$ or PR$_2$ groups shifts the bands of the n$\rightarrow$p transition in germynes, stannylenes and plumbynes to lower wavelengths (Table 4) in accordance with the electronic effects of these substituents. In the case of (2,4,6-(Me$_2$NCH$_2$)$_3$C$_6$H$_2$O)$_2$E (E = Ge, Sn, Pb)$^{143}$ the additional hypsochromic shift of the absorption band is due to intramolecular coordination of the germanium, tin or lead atom by the nitrogen atoms of $o$-Me$_2$NCH$_2$ groups.

E. Effect of the Nature of the Element E in R$_2$E Species on the Position of their Electronic Transition Band

Similarly to the case of the triatomic species (Section III), comparison of absorption maxima of stable germynes, stannylenes and plumbynes bearing the same substituents at different divalent atoms of the Group 14 elements (Table 4) does not reveal any
firm trends. In the series of ETbtTip, E(2,6-Mes₂C₆H₃)₂, ETip₂, E(Si(Me₃Si)₃)(2₉-Bu-4,5,6-Me₃C₆H) the absorption bands exhibit slight hypsochromic shift on going from Ge to Pb, although the complete series are available only for the first two types of compounds. In the series of the (2,4,6-(Me₂NCH₂)₃C₆H₂O)₂E, (2,4,6-(CF₃)₃C₆H₂)₂E compounds, additionally stabilized by intramolecular coordination of the divalent atom E with the N and F atoms of the ortho-substituents, the absorption bands shift to the blue region on passing from Ge to Pb too. The slight bathochromic shift of the UV bands along the same row of divalent atoms of the Group 14 elements is observed for the following series: E(CH(SiMe₃)₂)₂, E(Si(SiMe₃)₃)₂, E(2,4,6-₉-Bu₃C₆H₂)₂, E(2-₉-Bu-4,5,6-Me₃C₆H)₂, E(Si(SiMe₃)₃)(2,4,6-(CF₃)₃C₆H₂), E(NR₂)₂, E(PR₂)₂. None of these series is complete. Obviously, the same substituents reveal their effects to a different extent, depending on the nature of the divalent atom. Unfortunately, there are no UV data on labile stannylenes and plumbylenes with relatively simple substituents.

V. ELECTRONIC SPECTRA OF INTERMOLECULAR COMPLEXES OF GERMYLENES, STANNYLENES AND PLUMBYLENES WITH LEWIS BASES

Owing to the presence of an empty p-MO, the carbene analogs can form donor–acceptor complexes with Lewis bases. Formation of such molecular complexes has been repeatedly suggested as the first step of many reactions of CAs (see, e.g. References 3–5). Complexation stabilizes the CAs and leads to changes in their reactivity and spectral properties. In this section the electronic spectra of intermolecular complexes of germylenes, stannylenes and plumbylenes with n-donor agents are considered. The available data are collected in Table 6. As one can see, they include, with a single exception, only germylene complexes. The data on spectral properties of silylene complexes have recently been reviewed by Gaspar and West3.

The stronger the interaction of the lone electron pair of the n-donor agent with an empty p-MO of CA, the more stable is the complex, the higher is the energy of the LUMO of a complex, and the larger is the hypsochromic shift of the absorption maximum of a CA. Such a qualitative assessment of the strength of donor–acceptor complexes of CAs is widely used5. Based on this approach it was suggested188 that the strength of silylene complexes decreases in the following series of n-donor agents: amines > phosphines > ethers > disulfides > halogenides. Experimentally observed shifts in absorption maxima of complexes of germylenes agree in general with this tendency (Table 6). However, the nature of substituents in CA and in an n-donor agent affects the strength of the complex formed. Typically, the hypsochromic shift has a magnitude of 100–150 nm. However, it is still unclear why the absorption maxima of Me₂Ge, MePhGe and Ph₂Ge recorded in hydrocarbon solutions and in coordinating solvents (THF) at room temperature (Table 4) are the same111,114. The absorption maxima of the stable germylene (2,4,6-₉-Bu₃C₆H₂)₂Ge in cyclohexane and THF solutions coincide156. In this case a steric hindrance at the germylene center156 hampers a complexation. For the same reason the spectra of (2,6-Mes₂C₆H₃)₂E (E = Ge, Sn, Pb) recorded in diethyl ether158 correspond to free CAs, but not to their complexes with the solvent molecules.

Quantum-chemical studies showed that the ability to form complexes with Lewis bases decreases on going from silylenes to stannylenes and increases in the following series of n-donor agents: amines < phosphines < arsines < stibines189. This series somewhat differs from that proposed based on experimental data188. Calculations were successfully used to predict the absorption maxima shifts on complexation of silylenes with amines190.

Whereas coordination of a CA to a lone electron pair of a heteroatom containing only single bonds typically results in a hypsochromic shift of the CA absorption maxima, upon complexation of germylenes with S atoms of thiocarbonyl compounds (and also
TABLE 6. Absorption maxima of germylene and stannylene complexes with n-donor agents

<table>
<thead>
<tr>
<th>Complex</th>
<th>Conditions of observation of the complex$^a$</th>
<th>$\lambda_{\text{max}}$ of the complex</th>
<th>$\lambda_{\text{max}}$ of the free CA$^b$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$_2$Ge · PPh$_3$</td>
<td>C$<em>6$H$</em>{14}$, (−8) + 62 °C</td>
<td>233.8</td>
<td>310</td>
<td>198</td>
</tr>
<tr>
<td>Me$_2$Ge · PPh$_3$</td>
<td>C$<em>7$H$</em>{16}$, r.t.</td>
<td>370</td>
<td>380</td>
<td>199</td>
</tr>
<tr>
<td>Me$_2$Ge · ClPh</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>392</td>
<td>420</td>
<td>142, 145</td>
</tr>
<tr>
<td>Me$_2$Ge · (C$<em>6$H$</em>{11}$Cl-c)</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>341</td>
<td>420</td>
<td>142, 145</td>
</tr>
<tr>
<td>Me$_2$Ge · S=C=C(Bu-t)$_2$</td>
<td>3-MP/IP (1 : 4), 77 K</td>
<td>595</td>
<td>420</td>
<td>192</td>
</tr>
<tr>
<td>Me$_2$Ge · PhH</td>
<td>3-MP/IP (4 : 1), 77 K</td>
<td>436–423</td>
<td>436</td>
<td>119</td>
</tr>
<tr>
<td>Ph$_2$Ge · (2-MeTHF)</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>325</td>
<td>463</td>
<td>142, 145</td>
</tr>
<tr>
<td>Ph$_2$Ge · OH(Et)</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>320</td>
<td>466</td>
<td>142</td>
</tr>
<tr>
<td>Ph$_2$Ge · OH(i-Pr)</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>324</td>
<td>466</td>
<td>142</td>
</tr>
<tr>
<td>Ph$_2$Ge · OH(Bu-t)</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>325</td>
<td>466</td>
<td>142</td>
</tr>
<tr>
<td>Ph$_2$Ge · OH(Bu-t)</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>332</td>
<td>466</td>
<td>142</td>
</tr>
<tr>
<td>Ph$_2$Ge · S</td>
<td>3-MP/IP (3 : 7), 77 K</td>
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<td>463</td>
<td>142, 145</td>
</tr>
<tr>
<td>Ph$_2$Ge · SMe$_2$</td>
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<td>142, 145</td>
</tr>
<tr>
<td>Ph$_2$Ge · N</td>
<td>3-MP/IP (3 : 7), 77 K</td>
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<td>463</td>
<td>142, 145</td>
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<tr>
<td>Ph$_2$Ge · (C$<em>6$H$</em>{11}$Cl-c)</td>
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<td>Ph$_2$Ge · ClPh</td>
<td>3-MP/IP (3 : 7), 77 K</td>
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<td>Ph$_2$Ge · S=C=C(Bu-t)$_2$</td>
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<td>192</td>
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<tr>
<td>Me$_2$Ge · (2-MeTHF)</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>360</td>
<td>550</td>
<td>145</td>
</tr>
<tr>
<td>Me$_2$Ge · OH(Et)</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>373</td>
<td>550</td>
<td>145</td>
</tr>
<tr>
<td>Me$_2$Ge · OH(i-Pr)</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>339</td>
<td>550</td>
<td>142</td>
</tr>
<tr>
<td>Me$_2$Ge · OH(Bu-t)</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>359</td>
<td>550</td>
<td>142</td>
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<tr>
<td>Me$_2$Ge · OH(Bu-t)</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>362</td>
<td>550</td>
<td>142</td>
</tr>
<tr>
<td>Mes$_2$Ge · S</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>352</td>
<td>550</td>
<td>142, 145</td>
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<tr>
<td>Mes$_2$Ge · SMe$_2$</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>348</td>
<td>550</td>
<td>142, 145</td>
</tr>
<tr>
<td>Mes$_2$Ge · S(Et)CH$_2$CH=CH$_2$</td>
<td>3-MP/IP (4 : 6), 77 K</td>
<td>380</td>
<td>550</td>
<td>142, 145</td>
</tr>
<tr>
<td>Mes$_2$Ge · N</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>349</td>
<td>550</td>
<td>142, 145</td>
</tr>
<tr>
<td>Mes$_2$Ge · NEt$_3$</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>414</td>
<td>550</td>
<td>142</td>
</tr>
<tr>
<td>Mes$_2$Ge · PBu$_3$</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>306</td>
<td>550</td>
<td>142, 145</td>
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<tr>
<td>Mes$_2$Ge · (C$<em>6$H$</em>{11}$Cl-c)</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>495</td>
<td>550</td>
<td>142, 145</td>
</tr>
<tr>
<td>Mes$_2$Ge · ClPh</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>538</td>
<td>550</td>
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</tr>
<tr>
<td>Mes$_2$Ge · CICH$_2$CH=CH$_2$</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>530</td>
<td>550</td>
<td>142, 145</td>
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<tr>
<td>Mes$_2$Ge · CICH$_2$CH=CHCH$_3$</td>
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<td>550</td>
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<td>Mes$_2$Ge · S=C=C(Bu-t)$_2$</td>
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<td>580</td>
<td>550</td>
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<td>Mes$_2$Ge · S=(Ad-2)</td>
<td>3-MP, 77 K</td>
<td>582</td>
<td>550</td>
<td>192</td>
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<tr>
<td>(2,6-Et$_2$C$_6$H$_3$)$_2$Ge · (2-MeTHF)</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>369</td>
<td>544</td>
<td>145</td>
</tr>
<tr>
<td>(2,6-Et$_2$C$_6$H$_3$)$_2$Ge · OH(Et)</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>332</td>
<td>544</td>
<td>142</td>
</tr>
<tr>
<td>(2,6-Et$_2$C$_6$H$_3$)$_2$Ge · OH(i-Pr)</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>341</td>
<td>544</td>
<td>142</td>
</tr>
<tr>
<td>(2,6-Et$_2$C$_6$H$_3$)$_2$Ge · OH(Bu-t)</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>343</td>
<td>544</td>
<td>142</td>
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TABLE 6. (continued)

<table>
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<th>Complex</th>
<th>Conditions of observation of the complex&lt;sup&gt;a&lt;/sup&gt;</th>
<th>( \lambda_{\text{max}} ) of the complex</th>
<th>( \lambda_{\text{max}} ) of the free CA&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Reference</th>
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<tr>
<td>(2,6-Et&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Ge · OH(Bu-t)</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>367</td>
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<td>142, 145</td>
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<td>3-MP/IP (3 : 7), 77 K</td>
<td>359</td>
<td>544</td>
<td>142, 145</td>
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<td>544</td>
<td>142, 145</td>
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<td>(2,6-Et&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Ge · PBu&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>314</td>
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<td>3-MP/IP (3 : 7), 77 K</td>
<td>508</td>
<td>544</td>
<td>142, 145</td>
</tr>
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<td>544</td>
<td>142, 145</td>
</tr>
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<td>3-MP/IP (3 : 7), 77 K</td>
<td>376</td>
<td>558</td>
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<td>357</td>
<td>558</td>
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<td>(2,4,6-i-Pr&lt;sub&gt;3&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Ge · S</td>
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<td>3-MP/IP (3 : 7), 77 K</td>
<td>445</td>
<td>558</td>
<td>142</td>
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<tr>
<td>(2,4,6-i-Pr&lt;sub&gt;3&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Ge · N</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>363</td>
<td>558</td>
<td>142, 145</td>
</tr>
<tr>
<td>(2,4,6-i-Pr&lt;sub&gt;3&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Ge · PBu&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>334</td>
<td>558</td>
<td>142, 145</td>
</tr>
<tr>
<td>(2,4,6-i-Pr&lt;sub&gt;3&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Ge · (C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;Cl-c)</td>
<td>3-MP/IP (3 : 7), 77 K</td>
<td>544</td>
<td>558</td>
<td>142, 145</td>
</tr>
<tr>
<td>(2,4,6-i-Pr&lt;sub&gt;3&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Ge · ClPh</td>
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<td>553</td>
<td>558</td>
<td>142, 145</td>
</tr>
<tr>
<td>TbtTipGe · THF</td>
<td>THF, r.t.</td>
<td>430</td>
<td>580</td>
<td>159</td>
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<tr>
<td>((Me&lt;sub&gt;3&lt;/sub&gt;Si&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Sn · S=C=C(Bu-t)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3-MP, 77 K</td>
<td>600</td>
<td>495</td>
<td>194</td>
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</tbody>
</table>

<sup>a</sup> 3-MP = 3-methylpentane, IP = isopentane.

<sup>b</sup> Absorption maximum of the corresponding CA recorded under the same conditions without donor substrate.

of silylenes with both carbonyl and thiocarbonyl compounds<sup>191</sup>) a bathochromic shift has been observed<sup>192–194</sup>. The nature of this effect was not discussed. Complexation of Me<sub>2</sub>Si with the N atom of MeCN has been shown to result in a hypsochromic shift<sup>195</sup>.

There are several examples when molecular complexes of CAs with Lewis bases obtained in hydrocarbon glasses transformed into insertion or cycloaddition products upon annealing or melting the matrices. Namely, the transformation of complexes of allyl chloride and allyl mercaptan with Mes<sub>2</sub>Ge into insertion products of Mes<sub>2</sub>Ge into the C−Cl or S−H bond has been described<sup>145</sup>. Similarly, intermediate complexes of germylenes<sup>142</sup> and silylenes<sup>196</sup> with alcohols were found to isomerize into O−H bond insertion products. Formation of thia(oxa)siliranes was observed upon annealing (and also upon irradiation at a suitable wavelength) of matrices containing complexes of silylenes with ketones and thioketones<sup>191</sup>. These facts represent a compelling argument for intermediate formation of such CA complexes in these and similar reactions under other conditions.

Complexation of germylenes with such weak Lewis bases as aromatics was suggested<sup>119</sup>. The authors observed hypsochromic shifts of the absorption maximum of Me<sub>2</sub>Ge if its precursors contained aromatic substituents. Moreover, the absorption maximum of
Me$_2$Ge generated in the presence of benzene from precursors containing no aromatic moieties was found to shift hypsochromically, with the shift increasing with an increase in benzene concentration (up to ca. 20 nm)$^{119}$. At the same time, the existence of a complex of Me$_2$Ge with benzene as a discrete compound was not established. Complexation of Me$_2$Ge with aromatics can be a reason for the large scatter of its reported absorption maxima (see Table 4). Similarly, the absorption spectrum of the stable Tbt(TbtS)Pb in toluene solution could in fact be due to its complex with the solvent$^{182}$. At the same time, the position of the absorption band of (2,4,6-(CF$_3$)$_3$C$_6$H$_2$)$_2$Sn observed in toluene at very low wavelengths is determined by intramolecular coordination of the tin atom by the fluorine atoms of o-CF$_3$ groups but not by interaction with the solvent$^{139}$. Complexation of CAs with dinitrogen will be discussed in Section VII. Here, we just note that such complexation is probably responsible for large shifts in the UV absorption maxima of MeClSi, MeHSi and Me$_2$Si on going from noble gas matrices to nitrogen matrices$^{197}$. The UV spectra of germeylenes, stannylenes or plumbylenes in nitrogen matrices were not reported.

VI. VIBRATIONAL SPECTRA OF GERMYLENES, STANNYLENES AND PLUMBYLENES

Vibrational spectra of labile CAs were recorded using matrix IR and Raman spectroscopy and, in the case of some triatomic CAs, using IR and Raman spectroscopy in the gas phase. The gas phase spectra are often complicated by the decomposition of CAs at the temperatures required to obtain adequate vapor pressures, besides that the gas phase Raman spectra are often complicated by laser-induced resonance fluorescence, which is the greatest interfering factor in the Raman spectroscopy of gases$^{200}$. The full-symmetric fundamental frequencies for the ground electronic state of a molecule can also be obtained from high resolution electronic spectra. The reported frequencies of CAs measured in the course of electronic spectroscopy studies are also included and discussed in this section. IR spectra of stable germeylenes, stannylenes and plumbylenes considered below have been recorded in Nujol mull, in the liquid phase or in thin films. The vibrational spectra of stable dihalides of germanium, tin and lead, (EHal$_2$)$_x$, in the solid phase are not considered in this section, because the crystal structure of solid (EHal$_2$)$_x$ contains no EHal$_2$ units, as is well known.

The general approaches used in the studies considered below for assignment of the observed vibrational bands to the short-lived molecules are analogous to those described in Sections III and IV. The assignment of the revealed bands to normal, or fundamental, vibrational modes has been based on taking into account selection rules, observations of the bands in characteristic regions, observations of isotopic shifts, results of depolarization measurements in the Raman spectra and results of normal coordinate analysis. (It is noteworthy that Raman depolarization measurements can be conducted for matrix isolated species as well; see Reference$^{200}$ and references cited therein.) Lately, quantum-chemical calculations of vibrational spectra have become an important tool for both identification of CAs and assignment of their vibrational spectra.

Frequencies assigned to the fundamental vibrations of the triatomic germeylenes, stannylenes and plumbylenes are collected in Table 7 together with corresponding data on triatomic silylenes for comparison. The vibrational frequencies are sensitive to the environment of the molecule. Therefore, the most precise frequency values measured under each type of condition used (in the gas phase and in different low-temperature inert matrices) by different spectroscopic methods are shown in the table for each of the CAs. Nonfundamental frequencies of triatomic and observed frequencies of polyatomic germeylenes, stannylenes and plumbylenes are listed in the text.
A. Prototype EH₂ Molecules

The data on vibrational frequencies of the prototype germylene, GeH₂, are ambiguous. Several reactive species were produced by the vacuum-ultraviolet (VUV) photolysis (by H₂ and Xe microwave discharge lamps) of GeHₙD₁₋ₙ, n = 0–4, isolated in an Ar matrix at 4–23 K²⁰¹. Two series of IR absorptions at 1839, 1813, 928, 850 cm⁻¹ and at 1887, 1864, 920 cm⁻¹ were tentatively attributed to germyl radical, GeH₃, and germylene, GeH₂, respectively on the basis of a normal coordinate analysis, taking into account the observed deuteration shifts. A similar mixture of the reactive products was formed from multipole dc discharge of GeH₄ and detected in low temperature Ar matrices by IR spectroscopy²⁰². In disagreement with previous conclusions²⁰¹ it has clearly been observed that the intensity of the 928 cm⁻¹ band correlated with that of the 1870 cm⁻¹ (1864 cm⁻¹ in Reference²⁰¹) band upon annealing of the matrices, whereas the intensity of the 913 cm⁻¹ band correlated with the intensity of the 1814 cm⁻¹ (1813 cm⁻¹ in Reference²⁰¹) band. Thus the bands at 1890, 1870 and 928 cm⁻¹ have been attributed to the symmetric stretching (ν₁), antisymmetric stretching (ν₃) and bending (ν₂) modes of GeH₂, respectively. (This numbering of the fundamental frequencies of symmetric triatomic CAs will be used below.) Doping the matrices with hydrogen, passed through discharge plasma, resulted in a faster decrease of the intensities of the GeH₂ bands in comparison with those of GeH₃ bands upon annealing, indicating that the reaction of GeH₂ with hydrogen atoms is faster than the reaction of GeH₃²⁰².

Another assignment of the vibrational bands observed in the 1800–1900 cm⁻¹ region upon the VUV photolysis of GeH₄²⁰¹ was proposed later²⁰³. It was suggested that the bands attributed²⁰¹ to GeH₂ actually belong to GeH₃ and vice versa, and also that ν₃ > ν₁ for GeH₂. This suggestion was based on the similarity of the germanium and silicon analogs. For the latter it had been shown theoretically²⁰³,²⁰⁴ that the Si–H stretching frequencies decrease in the series SiH₄, SiH₃, SiH₂, SiH, and the corresponding order of stretching frequencies, ν₃ > ν₁, had been found both experimentally²⁰⁵ and theoretically²⁰³ for SiH₂. The proposed²⁰³ order of stretching frequencies of GeH₂ was later supported by ab initio calculations²⁰⁶. Positions of IR bands attributed to matrix isolated complexes of GeH₂ and GeD₂ with one and two molecules of HF²⁰³ were well understood based on this new assignment of the GeH₂ bands, keeping the initial²⁰¹ assignment of GeD₂ bands without change.

At the same time the value 1856 cm⁻¹ obtained for the ν₁ frequency of GeH₂ in the ground electronic state from the analysis of the vibronic structure of the ¹B₁−¹A₁ transition³⁰ is closer to the 1864 cm⁻¹ frequency, which was initially²⁰¹ attributed to the matrix isolated GeH₂, but assigned to the ν₃ mode. Thus, the initial²⁰¹ identification of the GeH₂ bands can be correct, but requires changes in assignment of the Ge–H stretching frequencies to symmetric and antisymmetric modes in accordance with the requirement that ν₃ > ν₁.

The studies of vibrational spectra of GeH₂ paralleled those of SiH₂. The VUV photolysis of SiH₄ in Ar matrices also resulted in the formation of several reactive species, detected by IR spectroscopy²⁰⁷. Two of them were identified as SiH₂ and SiH₃²⁰⁷. However, it has recently been argued that the observed sets of bands attributed²⁰⁷ to SiH₂ and SiH₃ can belong to SiH₂ molecules occupying different matrix sites²⁰⁸. Using the same arguments one can conclude that both sets of bands observed upon the VUV photolysis of GeH₄ in Ar matrices²⁰¹, except the band at 850 cm⁻¹, can also be attributed to GeH₂ occupying different matrix sites.

The vibrational spectra of SnH₂ and PbH₂ have not been reported so far.
IR spectra of GeF$_2$ in the region of Ge–F stretching frequencies have been recorded both in the gas phase$^{40}$ and in solid Ne$^{40}$ and Ar matrices$^{40,209}$. Monomeric GeF$_2$ was produced by evaporation of a (GeF$_2$)$_x$ sample at temperatures up to ca 425 K$^{40}$ or by reaction of GeF$_4$ vapor with metallic Ge at 570–620 K$^{209}$. The first process was accompanied by production of dimeric species in a significant amount, but the dimer absorption, fortunately, did not overlap the bands of the monomer$^{40}$. Two bands of monomeric GeF$_2$ were observed in all the cases. The germanium isotopic structure of these bands (at 685 and 655 cm$^{-1}$) was well resolved in the Ne matrix. Using the known relation$^{210}$ between bond angle and antisymmetric stretching frequencies ($v_3$) of isotopomers, the bond angle in GeF$_2$ was calculated for two possible assignments of the observed bands to symmetric and antisymmetric stretching modes$^{40}$. Assuming that the lower frequency was $v_3$, the bond angle was found to be 94 ± 2°, whereas assignment of the higher frequency to $v_3$ gave an angle of only 82 ± 3°. The latter value is unreasonably small. Thus, the higher of the observed frequencies has been assigned to the $v_1$ mode, while the lower frequency has been assigned to $v_3$. This assignment was confirmed later by observing the fluorine spin weight effects on the intensities of the rotational lines in the microwave spectra of GeF$_2$ in the first excited vibrational state$^{211}$. The value 97.148° for the GeF$_2$ bond angle determined from the microwave spectrum$^{211}$ has also turned out to be very close to that calculated from the isotopic structure of the $v_3$ band.

Raman spectra of GeF$_2$ (generated by reaction of GeF$_4$ vapor with Ge metal) isolated in N$_2$ and Ar matrices were also recorded only in the Ge–F stretching vibration region$^{209}$. The Raman spectra in N$_2$ matrices were of a higher quality than those in Ar matrices. Among the number of bands observed in N$_2$ matrices only the bands at 702 and 653 cm$^{-1}$ could be attributed to monomeric GeF$_2$; the other bands were assigned to GeF$_2$ oligomers on the basis of warm-up experiments. Raman depolarization measurements showed that the strong band at 653 cm$^{-1}$ was clearly polarized and therefore corresponds to a $v_1$ mode, in disagreement with the previous$^{40}$ assignment. The polarization of the band at 702 cm$^{-1}$ was not measured because of its low intensity, it is noteworthy that the use of dinitrogen as a matrix gas is not favorable for the matrix studies of CAs, because N$_2$ is a weak Lewis base whereas CAs exhibit Lewis acid properties (see Sections V and VII). Although possible complexation with dinitrogen can hardly be expected to significantly affect the depolarization measurements, nevertheless it would be of interest to obtain results of such measurements for GeF$_2$ in Ar matrices. Unfortunately, the depolarization measurements in the Ar matrices were not carried out$^{209}$. The Raman spectra of GeF$_2$ in Ar matrices contained only three bands at 705, 689 and 659 cm$^{-1}$. The strong band at 659 cm$^{-1}$ was assigned to a $v_1$ vibration of monomeric GeF$_2$ by analogy with the assignment in the N$_2$ matrix spectrum. The assignment of the 689 cm$^{-1}$ band, whose position is closest to that of one of the IR bands of GeF$_2$ observed in Ar matrices, has not been reported$^{209}$.

Ab initio calculations of fundamental frequencies of GeF$_2$ at different levels of theory predict the $v_1$ frequency to be higher than the $v_3$ frequency$^{32}$, in support of the initial assignment$^{40}$ of the GeF$_2$ stretching vibrations. In the LIF spectrum of GeF$_2$ in the region of the $^1B_1 - ^1A_1$ transition (see Section III) a minor progression was revealed, which can be assigned only on the assumption that the gas-phase $v_1$ frequency of GeF$_2$ in the ground state is equal to ca 721 cm$^{-1}$. This value is much higher than that obtained from the gas-phase IR spectrum$^{40}$. However, the GeF$_2$ ground state fundamental frequencies obtained from ab initio calculations$^{32}$ rather agree with the IR data, so the question as to the assignment of these progressions remains open. Thus, there is apparent disagreement in
the assignments of the stretching frequencies of GeF$_2$ and experimental reexamination of its IR and Raman spectra both in the gas phase and in inert low-temperature matrices is desired. The frequency of the bending vibration ($\nu_2$) of GeF$_2$ has only been obtained from analysis of the vibronic structure of the $^1B_1-^1A_1^{31,32}$ and $^3B_1-^1A_1^{32,35-38}$ electronic transitions in this molecule.

IR spectra of GeCl$_2$ were recorded in the region of the Ge–Cl stretching vibrations in Ar matrices$^{212-215}$. Monomeric GeCl$_2$ was produced by VUV photolysis of GeH$_n$Cl$_4-n, n = 0-2^{212,215}$ or by evaporation of (GeCl$_2$)$_x$ polymers$^{213,214}$. The stretching frequencies observed in all the studies are in good agreement. Both germanium and chlorine isotopic patterns of the stretching vibration bands were almost completely resolved in the spectra obtained by Maltsev and coworkers$^{214}$. A bond angle equal to $99 \pm 4^\circ$ has been computed using the measured $\nu_3$ frequencies for different isotopomers$^{214}$. This value is in excellent agreement with the values obtained by other methods (see Section VIII).

Raman spectra of GeCl$_2$ were recorded in the gas phase$^{216,217}$ and in N$_2$ matrices$^{200}$. GeCl$_2$ was generated by evaporation of polymeric (GeCl$_2$)$_x$ at 600–800 K$^{216}$, by reaction of GeCl$_4$ with metallic Ge$^{200}$ or by reaction of gaseous GeCl$_4$ with solid GeAs at temperatures above 700 K$^{217}$. All three bands due to fundamental vibrations have been observed$^{200,217}$. Depolarization measurements performed in the gas phase and in the N$_2$ matrices in the region of stretching vibrations$^{200,216,217}$ indicate that the $\nu_1$ frequency is higher than $\nu_3$, in agreement with the tentative assignment made earlier$^{213}$.

Monomeric GeBr$_2$ was produced by UV photolysis of H$_2$GeBr$_2$,$^{204,218}$ by evaporation of polymeric (GeBr$_2$)$_x$,$^{218}$ or by reaction of gaseous GeBr$_4$ with solid GeAs at temperatures above 700 K$^{217}$ and detected by IR spectroscopy in Ar matrices$^{204,218}$ or by Raman spectroscopy in the gas phase$^{217}$. The initial tentative assignment of stretching frequencies to symmetric and antisymmetric modes was based on the fact that in IR spectra the $\nu_3$ bands of dihalides of the Group 14 elements are usually more intensive than the $\nu_1$ bands, and also on normal coordinate analysis performed taking into account isotopic splitting pattern of these bands$^{218}$. This assignment was supported later by the Raman depolarization measurements$^{217}$.

Raman spectra of GeI$_2$ were recorded in the gas phase$^{217,219,220}$ and its IR spectra were obtained in the gas phase and in Ar matrices$^{50}$. Assignment of the GeI$_2$ stretching frequencies to $\nu_1$ and $\nu_3$ modes was based on the Raman depolarization measurements$^{217,219}$. The bond angle calculated from the observed $\nu_3$ frequency isotopic shifts has been found to be equal to $ca 105^\circ$.$^{50}$ This value is close to that of $102^\circ$ obtained from electron diffraction measurements.$^{221}$ Besides the fundamental frequencies, a series of overtones and differential and combinational frequencies were observed in the gas-phase Raman spectra of GeI$_2$ at elevated temperatures$^{219}$.

In the studies considered below dihalostannylenes and dihaloplumbylenes were typically generated by evaporation of the corresponding salts at appropriate temperatures.

IR spectra of SnF$_2$,$^{222}$ and PbF$_2$,$^{222,223}$ were recorded in Ar$^{222,223}$ and Ne$^{222}$ matrices, both in the E–F (E = Sn, Pb) stretching and bending vibration regions. Interaction of SnF$_4$ with Sn metal was also used to produce SnF$_2$.$^{222}$ Besides monomeric species, their dimers (EF$_2$)$_2$$^{222,223}$ and products of interaction of the monomers or dimers with the metal atoms were detected in the matrices$^{222}$. Assignment of the observed bands of EF$_2$ to fundamental modes in the stretching vibration region has been based on assumptions that the intensity of the band of the antisymmetric vibration is higher than that of the symmetric one$^{222}$ and that the order of stretching frequencies of EF$_2$ is the same as for the corresponding dichlorides (see Table 7)$^{222}$. The F–Sn–F bond angle calculated from the isotopic structure of the $\nu_3$ band is equal to $94 \pm 5^\circ$; calculation of the bond angle
assuming an alternative assignment of the SnF₂ bands in the stretching vibration region also gave a reasonable value, 90 ± 5°. No other measurement of the bond angle in SnF₂ has so far been reported. Raman spectra of SnF₂ and PbF₂ have not been reported.

Three bands of SnCl₂ were identified in the gas-phase Raman spectra. Their assignment to the fundamental modes was performed based on the depolarization measurements. In the Raman spectra of SnCl₂ isolated in N₂ matrix all SnCl₂ fundamental frequencies were also observed, whereas in Ar matrix the bending vibration region was not recorded. Depolarization measurements were not carried out for matrix isolated SnCl₂. IR spectra of SnCl₂ isolated in Ar matrices were recorded in the stretching vibration region only. Both observed bands showed splitting due to chlorine isotopes. Assignment of these bands to fundamental modes ν₁ and ν₃ was initially conducted by taking into account the gas-phase value for ν₁ known from the analysis of the vibronic structure of the 3B₁ – 1A₁ electronic transition. This assignment is in agreement with the Raman data discussed above. VUV photolysis of SnCl₄ was also used to generate SnCl₂. This process is accompanied by formation of an SnCl₃ radical and a number of ionic species.

The Raman spectrum of PbCl₂ in the gas phase has been obtained at 1270 K in the presence of Cl₂ to suppress its decomposition to PbCl₂. Only two bands assigned to ν₁ and ν₂ modes on the basis of depolarization measurements have been observed. The band corresponding to the ν₃ mode has not been observed, apparently due to its low intensity. Three fundamental frequencies of PbCl₂ have been obtained from the Raman spectra in N₂ and Ar matrices. In the Ar matrices, the chlorine isotopic splitting of the PbCl₂ bands was well resolved. Depolarization measurements were only carried for the species isolated in the Ar matrices. IR spectra of PbCl₂ isolated in Ar and N₂ matrices were recorded in the stretching vibration region. The chlorine isotopic structure of the bands was much better resolved in Ar matrices. From the measured ν₃ frequency values for different isotopomers, the ClPbCl bond angle was computed to be 96 ± 3°.

Only Raman spectra have been reported for SnBr₂ and PbBr₂. The gas-phase Raman spectrum of PbBr₂ has been recorded in the presence of Br₂. Only two bands corresponding to ν₁ and ν₂ modes according to the Raman depolarization measurements were observed. The spectrum was complicated by laser-induced resonance fluorescence processes. The strong laser-induced (514.5 nm) resonance fluorescence precluded one from recording the gas-phase SnBr₂ Raman spectrum. However, the bending frequency of SnBr₂ was obtained from the separation of the vibronic bands in the observed resonance fluorescence spectrum. Raman spectra of SnBr₂ isolated in both Ar and N₂ matrices and PbBr₂ isolated in N₂ matrices have been recorded. The bending frequency for PbBr₂ has not been observed because of its appearance in a region difficult for detection. Depolarization measurements carried out in the E – Br stretching vibration region allowed one to distinguish ν₁ and ν₃ frequencies of SnBr₂ and PbBr₂.

Attempts to record the gas-phase Raman spectra of SnI₂ and PbI₂ failed. It was impossible to obtain any information on vibrational frequencies from the PbI₂ spectrum due to resonance fluorescence and emissions by products of PbI₂ decomposition. In the case of SnI₂, only strong resonance fluorescence has been observed. From the separation of vibronic bands in this fluorescence spectrum, the ν₂ frequency of SnI₂ has been determined. IR spectra of monomeric SnI₂ and PbI₂ were recorded in Ar and Xe matrices in the stretching vibration region and in the gas phase at elevated temperatures in the bending vibration region. Thus, three bands corresponding to three fundamental modes were detected for each of the diiodides. In addition to monomeric SnI₂, an oligomeric species, probably (SnI₂)₂, has also been detected in the matrices. Its single
band was distinguished from the bands of the monomer by warm-up experiments. The matrix IR spectra of PbI$_2$ were not complicated by the presence of oligomers. The same bands of PbI$_2$ in Ar matrices were obtained upon matrix reaction of Pb atoms with I$_2$. Assignment of the SnI$_2$ and PbI$_2$ bands observed in the stretching region to the symmetric and antisymmetric modes was based on the assumption that the $\nu_3$ bands are usually more intensive than the $\nu_1$ bands in the IR spectra of dihalides of the Group 14 elements. The $\nu_1$ frequency of PbI$_2$ obtained from the IR spectrum is close to that obtained from the vibronic structure of the $^3B_1-^1A_1$ electronic transition in this molecule$^{60}$.

C. Mixed EXY Molecules

VUV and UV photolysis of GeH$_3$Cl in Ar matrices resulted in formation of a GeH$_2$Cl radical and a minor neutral labile product, containing only one hydrogen atom and characterized by a single IR band in the Ge–H stretching vibration region, which shows typical deuterium shift by use of GeD$_3$Cl as precursor$^{228}$. This product was tentatively identified as monochlorogermylene, GeHCl, which can be formed by secondary photolysis of the GeH$_3$Cl radical. Similarly, the minor products of UV photolysis of GeH$_3$Br and GeD$_3$Br in Ar matrices were GeHBr and GeDBr, respectively$^{229}$. Each of these germylenes was characterized by three bands, corresponding to the three fundamental vibrations. The bands corresponding to Ge–H(D) stretching and bending modes were split due to different trapping sites. The bending and Ge–Br stretching frequencies of GeHBr obtained from the IR spectra are in excellent agreement with those determined from the vibronic structure of the $^1A'^{\prime}\rightarrow^1A^{\prime}$ electronic transition in this molecule$^{77,78}$.

Evaporation of the mixtures of SnCl$_2$ with SnBr$_2$ (2 : 1) and PbCl$_2$ with PbBr$_2$ (2 : 1) at 500 K and 740 K, respectively, resulted in formation of SnClBr and PbClBr species detected by Raman spectroscopy in N$_2$ matrices$^{200}$. The spectra were recorded only in the E–Hal stretching vibration region. It was noted that the E–Hal stretching frequencies of the mixed halides lay between the symmetric and antisymmetric E–Hal stretching frequencies of the corresponding EHal$_2$, isolated in N$_2$ matrices. This fact has been explained by simple force field analysis. In the gas-phase Raman spectrum of SnClBr produced by the same method, two of three bands corresponding to the bending and Sn–Br stretching fundamental vibrations were found$^{216}$. The third band corresponding to the Sn–Cl stretching vibration of SnClBr was believed to coincide with the strong $\nu_1$ band of SnCl$_2$, which was also present in the vapor phase. The values of the Sn–Br vibration frequency of SnClBr measured in both studies$^{200,216}$ are in good agreement. Strong resonance fluorescence was observed during an attempt to obtain the Raman spectrum of SnClI generated by the evaporation of a mixture of SnCl$_2$ and SnI$_2$ (20 : 1)$^{216}$. From the separation of vibronic bands in this fluorescence spectrum, the bending frequency of SnClI was determined.

D. Some Conclusive Remarks on the Vibrational Spectra of the Triatomic Carbene Analogs

As discussed above, some discrepancies still remain in the identification and assignment of the bands of GeH$_2$ and GeF$_2$ (and also of SiH$_2$$^{205,207,208,230}$, SiCl$_2$ and SiBr$_2$$^{71,217,231,232}$; see Table 7). The complete sets of the fundamental frequencies have been established for other germynes, stannylenes and plumbylenes. Although different fundamental frequencies were often measured under different conditions, the frequency shifts are usually not large on going from the gas phase to inert matrices. It can be seen from the data of Table 7 that with a rare exception, the frequencies of triatomic CAs decrease on going from the gas phase to matrices and decrease in matrices formed by
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</table>

ᵃThe fundamental frequencies correspond to isotopomers, containing the most abundant isotopes, or represent the effective values if the isotopic structure has not been observed.
ᵇν₁, ν₃ are stretching frequencies, symmetric and antisymmetric, respectively, in the case of symmetric EX₂ molecules; ν₂ are bending frequencies.
ᶜIRDLs = infrared diode laser spectroscopy; ES = electronic spectroscopy, spectra with resolved vibrational structure; MW = microwave spectroscopy; force field calculations denote harmonic frequencies obtained on the basis of combined analysis of electron diffraction and vibrational spectroscopy data.
ᵈThe bands are split due to different trapping sites in the matrix.
ᵉThe frequencies correspond to the more stable trapping site in the matrix.
ᶠExcitation at 457.9 nm.
ᵍExcitation at 480 nm.
ʰExcitation at 514.5 nm.
iValues calculated from data in this reference.
different matrix gases in the following order: Ne > Ar > Xe and N$_2$. The bending frequency is the least sensitive to the environment. Such a matrix effect is quite usual for different types of compounds; however, it is worth emphasizing here that in nitrogen matrices the matrix shift of CA frequencies can be determined predominantly by specific donor–acceptor interaction (by complexation) with dinitrogen molecules (see below). The order of the fundamental frequencies remains the same in both the gas phase and matrices for all CAs, with the possible exception of SiH$_2$\textsuperscript{230}. The observation of two IR active stretching vibrations for some of the symmetric germynes, stannynes and plumbynes was historically the first firm experimental evidence of their bent structure. Besides the fundamental frequencies, those of other types have been observed for GeI$_2$ (a set of overtones, differential and combinational frequencies)\textsuperscript{219} and for SiH$_2$ ($\nu_1/2\nu_2$ Fermi and $2\nu_1/2\nu_3$ Darling-Dennison resonances)\textsuperscript{205,230,233}. In some studies the recorded matrix spectra of CAs were complicated by band splittings due to trapping the molecules in different matrix sites. Such matrix splittings can be a source of contradictions in the identification of the bands of matrix isolated SiH$_2$\textsuperscript{205,207,208} and GeH$_2$\textsuperscript{201–203}.

The relative intensities of the stretching vibration bands of the symmetric triatomic CAs seem to be very characteristic: in all cases when the symmetric and antisymmetric frequencies were identified unambiguously (SiF$_2$, GeCl$_2$, GeI$_2$, SnCl$_2$, SnBr$_2$, PbCl$_2$, PbBr$_2$) the $\nu_1$ Raman band was much more intensive than the $\nu_3$ one, while the intensity of the $\nu_1$ IR band was lower than that of the $\nu_3$ IR band. This observation has been used for assignments of stretching vibration bands of some other triatomic CAs (GeBr$_2$, SnF$_2$, SnI$_2$, PbF$_2$, PbI$_2$). Based on the observed isotopic splitting of the $\nu_3$ bands of SiF$_2$\textsuperscript{234}, SiCl$_2$\textsuperscript{232,235,236}, SiBr$_2$\textsuperscript{232}, GeF$_2$\textsuperscript{40}, GeCl$_2$\textsuperscript{214}, GeI$_2$\textsuperscript{50}, SnF$_2$\textsuperscript{222} and PbCl$_2$\textsuperscript{226}, bond angles were computed for these molecules. For SnF$_2$ there is no other experimental measurement of the bond angle. The obtained values for other molecules are in good agreement with more precise values determined in microwave and electron diffraction studies (presented in Section VIII).

The stretching (and also bending) frequencies of EX$_2$ and EXY decrease in the series in the order Si > Ge > Sn > Pb and F > Cl > Br > I (except for the Si–H stretching frequencies of HSiHal, which increase with increasing halogen weight). This reflects not only the increase in the weights of the composing atoms, but also a real weakening of the bonds, seen by comparing the stretching force constants reported in most of the studies performed. Initially, this conclusion was reached by Andrews and Frederick who compared stretching frequencies of dichlorides\textsuperscript{213}. It has also been noted that dichlorides have smaller stretching force constants than the tetrachlorides, due to more p character of the E–Hal bonds in the former compounds\textsuperscript{213}. This is also valid for other pairs of EX$_2$ and EX$_4$ molecules\textsuperscript{11}.

### E. Polyatomic Germynes, Stannynes and Plumbynes

The number of polyatomic germynes, stannynes and plumbynes characterized by their vibrational spectra is still very limited. Only IR spectroscopy was used for this purpose. Unstable molecules were studied in low-temperature inert matrices. The stable germynes, stannynes and plumbynes were treated by standard means.

Hydroxygermylene, HGeOH, was first produced in Ar matrix at 15 K upon photoinduced (340–300 nm) intramolecular insertion of Ge atom into the OH bond of H$_2$O submolecule in a Ge·OH$_2$ complex, formed by co-deposition of Ge atoms and water with excess Ar\textsuperscript{240}. Three observed IR bands at 1741.3, 661.3 and 566.2 cm$^{-1}$ were assigned to Ge·OH stretching, Ge–O stretching and torsion vibrational modes. Later, HGeOH was identified as one of the products of the photochemical reaction of GeH$_4$ with O$_3$ in Ar matrices\textsuperscript{241}. All the fundamental frequencies of this molecule \[\nu_1 (\text{OH}) = 3652.0,\]
\( \nu_2(\text{HGe}) = 1741.1 \) (being in Fermi resonance with the overtone \( 2\nu_3 \) observed as a weak band at \( 1757.6 \text{ cm}^{-1} \)), \( \nu_3(\text{GeOH}) = 885.2, \nu_4(\text{HGeO}) = 708.7, \nu_5(\text{GeO}) = 661.0 \) (shows characteristic Ge isotope splitting) and \( \nu_6(\text{torsion}) = 566.0 \text{ cm}^{-1} \) were observed in its IR spectrum. These frequencies were assigned to the normal vibrational modes by observing isotopic shifts, when deuterium-substituted germane and ozone containing \(^{16}\text{O} \) and \(^{18}\text{O} \) isotopes were used in this reaction. The complete set of fundamental frequencies was also obtained for HGe\(^{18}\text{OH}, \text{DGe}^{16}\text{OD} \) and DGe\(^{18}\text{OD}, \) whereas HGe\(^{16}\text{OD} \) and HGe\(^{18}\text{OD} \) were characterized by \( \nu(\text{HGe}) \) frequency only. Similarly to HGe\(^{16}\text{OH}, \) Fermi resonance between \( \nu_2 \) and \( 2\nu_3 \) was revealed in the case of HGe\(^{18}\text{OH}. \) Unlike hydroxysilylene\(^{242,243} \), the bands of only one conformer were present in the IR spectrum of hydroxygermylene\(^{241} \). Taking into account results of \textit{ab initio} calculations\(^{244} \), which showed that the \( s\text{-cis} \) conformer of HGeOH is lower in energy than the \( s\text{-trans} \) conformer, the authors\(^{241} \) concluded that the observed conformer is the \( s\text{-cis} \) one. Quantum-chemical calculations at a higher level of theory have confirmed that the \( s\text{-cis} \) conformer is the more stable of the two conformers, but the difference in their energies is very small (\(<0.4 \text{ kcal mol}^{-1}\))\(^{245} \). Thus, quantum-chemical calculations do not allow one to identify the observed\(^{240,241} \) conformer of HGeOH unequivocally.

Similarly to Ge atoms (and Si atoms\(^{240} \)) co-condensation of Sn atoms with water molecules results in the formation of the Sn·OH\(_2\) complex, stabilized and observed in Ar matrices\(^{240} \). Upon UV irradiation (340–300 nm) this complex transforms into HSnOH. The hydroxystannylene molecule has been characterized by five IR bands: \( \nu_2 \) (HSn) as doublet at 1608.0 and 1597.7 cm\(^{-1} \) (the source of this splitting is not clear), \( \nu_3 \) (SnOH) at 782.6, \( \nu_5 \) (SnO) at 569.3 and \( \nu_6 \) (torsion) at 475.5 cm\(^{-1} \)\(^{240} \).

Methylgermylene, GeHMe, has been detected in the course of a matrix (Ar matrices, 12 K) FTIR spectroscopy study of vacuum pyrolysis of 1,1-dimethyl-1-germa-3-thietane and 1,1,3,3-tetramethyl-1-germacyclobutane (equation 1)\(^{246} \).

\[
\text{Me}_2\text{Ge} + \text{S} \rightarrow \begin{array}{c}
\text{Me}_2\text{Ge} \equiv \text{CH}_2 \\
\text{Me}_2\text{Ge} \equiv \text{CH}_2
\end{array}
\]

(1)

Methylgermylene has been shown to result from thermal decomposition of an intermediate 1,1-dimethyl-1-germene, Me\(_2\)Ge=CH\(_2\). Five of the twelve IR bands of this germylene have been observed and assigned to normal vibrational modes, based on results of B3LYP calculations. The most intensive band at 1798.6 cm\(^{-1} \), which undoubtedly corresponds to stretching vibration of the Ge–H bond, is slightly lower than the Ge–H stretching frequencies of GeH\(_2\), GeHHal and slightly higher than that of GeHOH (see above). The band at 535.6 cm\(^{-1} \), which exhibited a clear quadruplet structure due to natural Ge isotope content, was identified as the Ge–C stretching vibration band. Other observed frequencies at 2891.6, 1201.2 and 868.8 cm\(^{-1} \) were attributed to C–H stretching mode and rocking modes of the methyl group.

Three other weak bands at 528.0, 554.8 and 783.6 cm\(^{-1} \) revealed in these experiments\(^{246} \) were tentatively attributed to ethylmethylgermylene, GeMeEt, which is believed to be an intermediate product of decomposition of Me\(_2\)Ge=CH\(_2\) to GeHMe (equation 1).
In accordance with the B3LYP calculations, these frequencies have been assigned to Ge–C stretching vibrations of the Ge–CH$_2$ and Ge–CH$_3$ groups and to CH$_3$ rocking mode, respectively.

Dimethylgermylene, GeMe$_2$, dimethylstannylene, SnMe$_2$, and its perdeuteriated derivative, Sn(CD$_3$)$_2$, were produced by the reactions shown in equation 2$^{104}$ and equations 3–5$^{247}$ and stabilized in low-temperature Ar matrices.

\[
\begin{align*}
\text{Ar, 12–18 K} \\
\text{Me}_2\text{Ge(N}_3\text{)}_2 \xrightarrow{h\nu, 248 \text{ or } 254 \text{ nm}} \text{GeMe}_2 + 3\text{N}_2
\end{align*}
\]

\[
\begin{align*}
\text{Ar, 5 K} \\
c-(\text{Me}_2\text{Sn})_6 \xrightarrow{400 \text{ K}} \text{SnMe}_2 + c-(\text{Me}_2\text{Sn})_5
\end{align*}
\]

\[
\begin{align*}
\text{Me}_2\text{SnH}_2 + \text{Ar}^* \longrightarrow \text{SnMe}_2 + \text{H}_2
\end{align*}
\]

\[
\begin{align*}
\text{c-}((\text{CD}_3)_2\text{Sn})_6 \xrightarrow{400 \text{ K}} \text{Sn(CD}_3)_2 + c-((\text{CD}_3)_2\text{Sn})_5
\end{align*}
\]

Frequencies obtained from matrix IR spectra of GeMe$_2$, SnMe$_2$ and SiMe$_2$ and their assignments are shown in Table 8. It is noteworthy that the close similarity of the IR spectra observed for these species is an additional argument for correct identification of these CAS. *Ab initio* calculated fundamental frequencies of SiMe$_2$ and GeMe$_2$, and the results of normal coordinate analysis of the SnMe$_2$ spectrum are also presented in Table 8. The theoretically predicted and experimentally observed frequencies are in good agreement.

Matrix IR spectra of 1-germacyclopent-3-enylidene and its d$_6$ analogue were obtained during a study of the photochemical interconversions shown in equation 6$^{105}$.

Each of the species has been characterized by a large number of IR bands and by its UV absorption. Full vibrational assignment in the IR spectra of these molecules has been performed on the basis of RHF/DZ+d calculations for both non-deuteriated and deuteriated analogs. The bands of 1-germacyclopent-3-enylidene at 508 and 478 (438 for
TABLE 8. Experimentally observed and calculated fundamental frequencies (cm$^{-1}$) of Me$_2$Si, Me$_2$Ge and Me$_2$Sn$^a$

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<th>Type of vibration $^{247}$</th>
<th>Me$_2$Si exp.$^{250,251}$</th>
<th>Me$_2$Si calc.$^{b,c,127}$</th>
<th>Me$_2$Ge exp.$^{104}$</th>
<th>Me$_2$Ge calc.$^{d,129}$</th>
<th>Me$_2$Sn exp.$^{247}$</th>
<th>Me$_2$Sn calc.$^{e,247}$</th>
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<td>$\nu$(C–H)</td>
<td>3261 (15.7)</td>
<td>2987 w.</td>
<td>2990 m.</td>
<td>3008</td>
<td>2900 m.</td>
<td>2924 m.</td>
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<td>$\nu$(C–H)</td>
<td>3261 (39.0)</td>
<td>2974 s.</td>
<td>2924 m.</td>
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<td>$\nu$(C–H)</td>
<td>3227 (56.9)</td>
<td>2957 s.</td>
<td>2897 w.</td>
<td>2875</td>
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<td></td>
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<tr>
<td>$\nu$(C–H)</td>
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<tr>
<td>$\delta$(CH$_3$)</td>
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<td>1600 (26.2)</td>
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<tr>
<td>$\delta$(CH$_3$)</td>
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<tr>
<td>$\delta$(CH$_3$)</td>
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<td>1234 m.</td>
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<td>$\delta$(CH$_3$)</td>
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<tr>
<td>$\delta$(CH$_3$)</td>
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<td>$\delta$(CH$_3$)</td>
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<td>1426 (23.8)</td>
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<td>1182 sh.</td>
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<tr>
<td>$\rho$(CH$_3$)</td>
<td>850 s.</td>
<td>958 (49.1)</td>
<td>882 m.</td>
<td>874 s.</td>
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<tr>
<td>$\rho$(CH$_3$)</td>
<td>806 v.s.</td>
<td>803 (14.8)</td>
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<tr>
<td>$\rho$(CH$_3$)</td>
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<td>$\nu$(E–C), sym.</td>
<td>690 m.</td>
<td>697 (12.6)</td>
<td>541 w.</td>
<td>560</td>
<td>504 s.</td>
<td>509</td>
</tr>
<tr>
<td>$\nu$(E–C), asym.</td>
<td>735 m.</td>
<td>690 (49.4)</td>
<td>527 v.s.</td>
<td>497</td>
<td>518 s.</td>
<td>522</td>
</tr>
<tr>
<td>$\delta$ (CEC)</td>
<td>266 (3.5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\tau$(E–CH$_3$)</td>
<td>124 (0.0)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\tau$(E–CH$_3$)</td>
<td>55 (0.0)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ w. = weak, m. = medium, s. = strong, v.s. = very strong, sh. = shoulder.
$^b$ SCF/DZP calculations.
$^c$ Calculated intensities (km mol$^{-1}$) are presented in parentheses.
$^d$ SCF/ECP DZP calculations.
$^e$ Force field calculations.
$^f$ Tentative assignment to SiMe$_2$.

1-germacyclopent-3-enylidene-d$_6$ cm$^{-1}$ were attributed to the symmetric and antisymmetric Ge–C stretching vibrations, respectively. Analogous study of the similar silicon-containing systems was published earlier$^{248,249}$. The symmetric and antisymmetric Si–C stretching frequencies of 1-silacyclopent-3-enylidene are at 616 and 741 cm$^{-1}$, whereas those of 3,4-dimethyl-1-silacyclopent-3-enylidene are at 626 and 775 cm$^{-1}$, respectively.

The IR spectrum of the stable Sn(CH(SiMe$_3$)$_2$)$_2$ has been recorded in hexane solution$^{152}$. Assignment of the observed bands was carried out by analogy with the spectra of related compounds; the bands corresponding to the stretching vibrations of Sn–C bonds have not been revealed.

The IR spectra of stable cyclic Me$_2$Si(t-BuN)$_2$E(E = Ge, Sn) have been obtained in films$^{252}$. The IR spectrum of their labile silicon analog, Me$_2$Si(t-BuN)$_2$Si, generated by photolysis of the diazide Me$_2$Si(t-BuN)$_2$Si(N$_3$)$_2$ in Ar matrix, has been recorded too$^{252}$. All spectra are similar to each other. The bands of the silylene, the germylene and the stannylene, at 781, 771 and 764 cm$^{-1}$ respectively, were tentatively assigned to $\nu$(E–N), those at 830, 814 and 811 cm$^{-1}$ to $\nu$(Si–C) and those at 883, 853 and 845 cm$^{-1}$ to $\rho$(Me$_2$Si). Assignment of the other bands has not been reported.

The IR spectra of a series of stable symmetric diaminogermylenes, diaminostannylenes and diaminoplumbylenes [(t-Bu(Me$_3$Si)N)$_2$E, ((Me$_3$Si)$_2$N)$_2$E, E = Ge, Sn, Pb; (t-Bu$_2$N)$_2$E, ((Et$_3$Si)$_2$N)$_2$E, ((Me$_3$Ge)$_2$N)$_2$E, ((Et$_3$Ge)$_2$N)$_2$E, ((Ph$_3$Ge)$_2$N)$_2$E, E = Ge,
The frequencies of antisymmetric stretching vibrations of the E−N bonds in these CAs have been identified in the 430−380 cm$^{-1}$ region. Some decrease in the frequencies on passing from germylenes through to stannylenes with the same substituents has been observed. IR frequencies of the stretching Sn−N vibrations have also been reported for a series of cyclic diaminostannylenes (Me$_3$Si)N-(CH$_2$)$_n$-N(SiMe$_3$)-Sn, $n = 2$−4$^{175}$. The frequencies were found in the 400−355 cm$^{-1}$ region. Their position clearly depends on the strain in the cycle, decreasing with its increase.

The apparent disagreement in the identification of the $\nu$(E−N) vibrations in the cited studies$^{132,163,175,252}$ clearly indicates that more careful analysis of the vibrational spectra of these CAs is needed.

The stretching frequency of the Ge−O bond in Ge(OC$_6$H$_2$(CH$_2$NMe$_2$)$_3$·2,4,6)$_2$ recorded in benzene solution, has been reported to lie at 1040 cm$^{-1}$. However, this germyle is additionally stabilized by intramolecular coordination of the Ge center by the N atoms of two dimethylaminomethyl groups attached to different benzene rings in the ortho-positions and in fact can be considered as an intramolecular donor−acceptor complex$^{143}$.

Several other stable germylenes$^{138,156,158,184,253−260}$, stannylenes$^{158,184,254,261−271}$ and plumbylenes$^{158,184,271,272}$ were characterized by their IR spectra. The assignments of the observed bands in these studies were restricted to identification of a number of characteristic frequencies of the substituents only.

**VII. VIBRATIONAL SPECTRA OF COMPLEXES OF GERMYLENES, STANNYLENES AND PLUMBYLENES WITH LEWIS BASES**

A number of complexes of CAs with Lewis bases ($X_2E$·$B_n$) were studied by matrix IR spectroscopy. Their absorptions are collected in Table 9. Data for complexes of silylenes are included in the table for comparison.

Weak complexes H$_2$Si·HF and H$_2$Si·(HF)$_2$ and also cyclic SiHF·HF with coordination of both the H and F atoms of HF to the F and H atoms of SiHF, respectively, were produced in Ar matrices (at 13 K) by interaction of silane (and its deuteriated analog) with F$_2$ upon codeposition, followed by UV photolysis$^{203}$. Identification of these complexes was based on results of HF/DZP calculations$^{203}$. Similar reaction of GeH$_4$ and GeD$_4$ with F$_2$ were used to generate the corresponding complexes H$_2$Ge·HF, H$_2$Ge·(HF)$_2$, their deuteriated analogs as well as complexes GeHF(GeDF)···HF(DF) in Ar matrices$^{203}$. In this case both cyclic and open [with coordination of the H(D) atom of HF(DF) to the F atom of HGeF] complexes between GeHF(GeDF) and HF(DF) have been observed.

In the donor−acceptor complex H$_2$Ge·OH$_2$ was obtained by photochemical reaction of germane and ozone in solid argon at 14−18 K$^{273}$. Isotopic substitution provided a basis for assignment of the IR absorptions observed and the suggestion that in the H$_2$Ge·OH$_2$ complex a H$_2$Ge submolecule has inequivalent hydrogen atoms, while the hydrogen atoms of the H$_2$O submolecule are equivalent. Later, quantum-chemical calculations at different levels of theory supported this suggestion$^{274}$. Complexes H(OH)Si·OH$_2$ and H(OH)Ge·OH$_2$ were detected by IR spectroscopy in the reaction of Si and Ge (in this case under UV photolysis) atoms with excess of water in Ar matrices$^{240}$. Under similar conditions complex H(OH)Sn·OH$_2$ was not observed$^{240}$.

1 : 1 Complex formation of SnCl$_2$, PbF$_2$, PbCl$_2$, PbBr$_2$ and PbI$_2$ with CO, as well as SnCl$_2$ and PbF$_2$ with NO and N$_2$ in Ar matrices was studied with IR spectroscopy by
### TABLE 9. Infrared absorptions (cm$^{-1}$) of complexes ($X_2E \cdot B_n$) of carbene analogs ($EX_2$) with Lewis bases ($B$)

<table>
<thead>
<tr>
<th>$X_2E \cdot B_n$</th>
<th>Frequencies (cm$^{-1}$) of $EX_2$ moiety and assignments</th>
<th>Frequencies (cm$^{-1}$) of $B_n$ moiety and assignments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{Si} \cdot \text{HF}$</td>
<td>1985.7 $\nu_{as}(\text{Si–H})$</td>
<td>3828.1 $\nu(\text{H–F})$</td>
<td>203</td>
</tr>
<tr>
<td>$\text{D}_2\text{Si} \cdot \text{DF}$</td>
<td>1448.3 $\nu_{as}(\text{Si–D})$</td>
<td>2798 $\nu(\text{D–F})$</td>
<td>203</td>
</tr>
<tr>
<td>$\text{H}_2\text{Si} \cdot (\text{HF})_2$</td>
<td>1942.8 $\nu_{as}(\text{Si–H})$</td>
<td></td>
<td>203</td>
</tr>
<tr>
<td>$\text{D}_2\text{Si} \cdot (\text{DF})_2$</td>
<td>1424.7 $\nu_{as}(\text{Si–D})$</td>
<td></td>
<td>203</td>
</tr>
<tr>
<td>cyclic-$\text{SiHF} \cdot \text{HF}$</td>
<td>1908.0 $\nu(\text{Si–H})$</td>
<td>3796 $\nu(\text{H–F})$</td>
<td>203</td>
</tr>
<tr>
<td></td>
<td>865.5 $\nu(\text{Si–F})$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>751.6 $\delta(\text{F–Si–H})$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cyclic-$\text{SiDF} \cdot \text{DF}$</td>
<td>1385.4 $\nu(\text{Si–D})$</td>
<td>2784 $\nu(\text{D–F})$</td>
<td>203</td>
</tr>
<tr>
<td>$\text{H(OH)Si} \cdot \text{OH}_2$</td>
<td>1929.4 $\nu(\text{Si–H})$</td>
<td></td>
<td>240</td>
</tr>
<tr>
<td></td>
<td>778.5 $\nu(\text{Si–O})$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{Ge} \cdot \text{HF}$</td>
<td>1870.7 $\nu_{as}(\text{Ge–H})$</td>
<td>3730.6 $\nu(\text{H–F})$</td>
<td>203</td>
</tr>
<tr>
<td>$\text{D}_2\text{Ge} \cdot \text{DF}$</td>
<td>1846.8 $\nu_{as}(\text{Ge–D})$</td>
<td>2739 $\nu(\text{D–F})$</td>
<td>203</td>
</tr>
<tr>
<td>$\text{H}_2\text{Ge} \cdot (\text{HF})_2$</td>
<td>1819.0 $\nu_{as}(\text{Ge–H})$</td>
<td></td>
<td>203</td>
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<tr>
<td>$\text{D}_2\text{Ge} \cdot (\text{DF})_2$</td>
<td>1312.5 $\nu_{as}(\text{Ge–D})$</td>
<td></td>
<td>203</td>
</tr>
<tr>
<td>$\text{H}_2\text{Ge} \cdot ^{16}\text{OH}_2$</td>
<td>1813.6 $\nu(\text{Ge–H})$</td>
<td>3686.0 $\nu_{as}(\text{O–H})$</td>
<td>273</td>
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<tr>
<td></td>
<td>1777.2 $\nu(\text{Ge–H})$</td>
<td>3597.4 $\nu_{as}(\text{O–H})$</td>
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<td></td>
<td>1794.4 $2\delta(\text{H–Ge–H})$</td>
<td>1586.1 $\delta(\text{H–O–H})$</td>
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<tr>
<td>$\text{H}_2\text{Ge} \cdot ^{18}\text{OH}_2$</td>
<td>1813.6 $\nu(\text{Ge–H})$</td>
<td>3672.5 $\nu_{as}(\text{O–H})$</td>
<td>273</td>
</tr>
<tr>
<td></td>
<td>1777.2 $\nu(\text{Ge–H})$</td>
<td>3590.3 $\nu_{as}(\text{O–H})$</td>
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</tr>
<tr>
<td></td>
<td>1794.4 $2\delta(\text{H–Ge–H})$</td>
<td>1580.1 $\delta(\text{H–O–H})$</td>
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<tr>
<td>$\text{HDGe} \cdot ^{16}\text{OHD}$</td>
<td>1811.6 $\nu(\text{Ge–H})$</td>
<td>3637.3 $\nu(\text{O–H})$</td>
<td>273</td>
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<tr>
<td></td>
<td>1782.0 $\nu(\text{Ge–H})$</td>
<td>2682.3 $\nu(\text{O–D})$</td>
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<td></td>
<td>1307.4 $\nu(\text{Ge–D})$</td>
<td>1398.4 $\delta(\text{H–O–D})$</td>
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</tr>
<tr>
<td>$\text{HDGe} \cdot ^{18}\text{OHD}$</td>
<td>1811.6 $\nu(\text{Ge–H})$</td>
<td>3626.3 $\nu(\text{O–H})$</td>
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<td>2667.6 $\nu(\text{O–D})$</td>
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<td>1307.4 $\nu(\text{Ge–D})$</td>
<td>1390.9 $\delta(\text{H–O–D})$</td>
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<tr>
<td>$\text{D}_2\text{Ge} \cdot ^{16}\text{OD}_2$</td>
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<td>2738.5 $\nu_{as}(\text{O–D})$</td>
<td>273</td>
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<tr>
<td></td>
<td>1281.6 $\nu(\text{Ge–D})$</td>
<td>2627.8 $\nu_{as}(\text{O–D})$</td>
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</tr>
<tr>
<td></td>
<td>1293.3 $2\delta(\text{D–Ge–D})$</td>
<td>1173.6 $\delta(\text{D–O–D})$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>646.4 $\delta(\text{D–Ge–D})$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{D}_2\text{Ge} \cdot ^{18}\text{OD}_2$</td>
<td>1308.9 $\nu(\text{Ge–D})$</td>
<td>2718.3 $\nu_{as}(\text{O–D})$</td>
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<td></td>
<td>1281.6 $\nu(\text{Ge–D})$</td>
<td>2617.2 $\nu_{as}(\text{O–D})$</td>
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<td>1164.8 $\delta(\text{D–O–D})$</td>
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<td></td>
<td>646.4 $\delta(\text{D–Ge–D})$</td>
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<tr>
<td>cyclic-$\text{GeHF} \cdot \text{HF}$</td>
<td>1784.6 $\nu(\text{Ge–H})$</td>
<td>3662.1 $\nu(\text{H–F})$</td>
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<td>cyclic-$\text{GeDF} \cdot \text{DF}$</td>
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<tr>
<td>linear-$\text{HGeF} \cdot \text{HF}$</td>
<td>1795.2 $\nu(\text{Ge–H})$</td>
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<td>203</td>
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<tr>
<td>linear-$\text{DGeF} \cdot \text{DF}$</td>
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<td>2732.1 $\nu(\text{D–F})$</td>
<td>203</td>
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<tr>
<td>$\text{H(OH)Ge} \cdot \text{OH}_2$</td>
<td>1763.1 $\nu(\text{Ge–H})$</td>
<td>3609.1 $\nu(\text{Ge–O})$</td>
<td>240</td>
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<tr>
<td>$\text{Cl}_2\text{Ge} \cdot \text{PPh}_3$</td>
<td>328 $\nu(\text{P–GeCl}_2)$</td>
<td></td>
<td>282</td>
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<tr>
<td></td>
<td>313 $\nu(\text{P–GeCl}_2)$</td>
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<tr>
<td></td>
<td>300 $\nu(\text{P–GeCl}_2)$</td>
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</tr>
<tr>
<td>$\text{Cl}_2\text{Ge} \cdot \text{P(Bu-}r)_3$</td>
<td>322 $\nu(\text{P–GeCl}_2)$</td>
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</tr>
<tr>
<td></td>
<td>298 $\nu(\text{P–GeCl}_2)$</td>
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</tr>
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</table>

(continued overleaf)
<table>
<thead>
<tr>
<th>X₂E · Bₙ</th>
<th>Frequencies (cm⁻¹) of EX₂ moiety and assignments</th>
<th>Frequencies (cm⁻¹) of Bₙ moieties and assignments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br₂Ge · PPh₃</td>
<td>242 ν(P–GeBr₂)</td>
<td>227 ν(P–GeBr₂)</td>
<td>205 ν(P–GeBr₂)</td>
</tr>
<tr>
<td>F₂Sn · N₂</td>
<td>588 ν₄(Sn–F)</td>
<td>565 ν₃a(Sn–F)</td>
<td>583 ν₄(Sn–F)</td>
</tr>
<tr>
<td>F₂Sn · (N₂)₂</td>
<td>551.5 ν₄(Sn–F)</td>
<td>537.5 ν₃a(Sn–F)</td>
<td>588 ν₄(Sn–F)</td>
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<tr>
<td>F₂Sn · C₂H₄</td>
<td>565 ν₄(Sn–F)</td>
<td>540 ν₃a(Sn–F)</td>
<td>3 256 ν(≡C–H)</td>
</tr>
<tr>
<td>F₂Sn · PhH</td>
<td>564 ν₄(Sn–F)</td>
<td>542 ν₃a(Sn–F)</td>
<td>696 δ(C–H)</td>
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<td>F₂Sn · (PhH)₂</td>
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<td>538 ν₃a(Sn–F)</td>
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<td>F₂Sn · PhCl</td>
<td>566 ν₄(Sn–F)</td>
<td>549 ν₃a(Sn–F)</td>
<td>740 δ(C–H)</td>
</tr>
<tr>
<td>F₂Sn · PhMe</td>
<td>563 ν₄(Sn–F)</td>
<td>536 ν₃a(Sn–F)</td>
<td>280</td>
</tr>
<tr>
<td>F₂Sn · ClMe</td>
<td>567 ν₄(Sn–F)</td>
<td>543 ν₃a(Sn–F)</td>
<td>281</td>
</tr>
<tr>
<td>Cl₂Sn · ¹² CO</td>
<td>324.3 ν₃a(Sn–Cl in Sn³⁵Cl₂)</td>
<td>319.9 ν₃a(Sn–Cl in Sn³⁵³⁷Cl)</td>
<td>2175.5 ν(C–O)</td>
</tr>
<tr>
<td>Cl₂Sn · ¹³ CO</td>
<td>324.3 ν₃a(Sn–Cl in Sn³⁵³⁷Cl)</td>
<td>319.9 ν₃a(Sn–Cl in Sn³⁵³⁷Cl)</td>
<td>2127.8 ν(C–O)</td>
</tr>
<tr>
<td>Cl₂Sn · NO</td>
<td>326.9 ν₃a(Sn–Cl in Sn³⁵³⁷Cl)</td>
<td>323 ν₃a(Sn–Cl in Sn³⁵³⁷Cl)</td>
<td>1891.7 ν(N–O)</td>
</tr>
<tr>
<td>Cl₂Sn · N₂</td>
<td>329.8 ν₃a(Sn–Cl in Sn³⁵³⁷Cl)</td>
<td>326.7 ν₃a(Sn–Cl in Sn³⁵³⁷Cl)</td>
<td>223</td>
</tr>
<tr>
<td>Cl₂Sn · (N₂)₂</td>
<td>326.1 ν₃a(Sn–Cl in Sn³⁵³⁷Cl)</td>
<td>322.3 ν₃a(Sn–Cl in Sn³⁵³⁷Cl)</td>
<td>223</td>
</tr>
<tr>
<td>Cl₂Sn · P(Bu-t)₃</td>
<td>290 ν(P–SnCl₂)</td>
<td>250 ν(P–SnCl₂)</td>
<td>282</td>
</tr>
<tr>
<td>Br₂Sn · P(Bu-t)₃</td>
<td>204 ν(P–SnBr₂)</td>
<td>192 ν(P–SnBr₂)</td>
<td>282</td>
</tr>
<tr>
<td>F₂Pb · CO</td>
<td>520.6 ν₄(Pb–F)</td>
<td>496.3 ν₄(Pb–F)</td>
<td>2176.4 ν(C–O)</td>
</tr>
<tr>
<td>F₂Pb · NO</td>
<td>522.6 ν₄(Pb–F)</td>
<td>498.7 ν₄(Pb–F)</td>
<td>1891.4 ν(N–O)</td>
</tr>
<tr>
<td>F₂Pb · N₂</td>
<td>526.6 ν₄(Pb–F)</td>
<td>502.2 ν₄(Pb–F)</td>
<td>223</td>
</tr>
<tr>
<td>Cl₂Pb · ¹² CO</td>
<td>315.2 ν₄(Pb–Cl)</td>
<td>292.6 ν₄(Pb–Cl)</td>
<td>2174.5 ν(C–O)</td>
</tr>
<tr>
<td>Cl₂Pb · ¹³ CO</td>
<td>315.2 ν₄(Pb–Cl)</td>
<td>292.6 ν₄(Pb–Cl)</td>
<td>2126 ν(C–O)</td>
</tr>
<tr>
<td>Br₂Pb · CO</td>
<td>2161.2 ν(C–O)</td>
<td>223</td>
<td></td>
</tr>
</tbody>
</table>
Tevault and Nakamoto. It was found that the bands of CO and NO shift to higher (up to 2%) frequencies whereas CA bands shift to lower (up to 10%) frequencies by complex formation. No band assignable to the N₂ stretching mode was observed, evidently due to weak interaction between SnCl₂(PbF₂) and N₂. When the N₂ concentration reached 4% in Ar the new bands corresponding to the SnCl₂·(N₂)₂ complex were detected (Table 9).

The magnitude of the observed shifts upon complexation was used as a measure of the extent of σ donation from the ligand to the metal center of the carbene analogs, i.e. as a measure of the strength of the complexes. The effect of changing the ligand has been elucidated in the SnCl₂·B and PbF₂·B series. The magnitude of the negative shifts of the EX₂ stretching bands follows the order CO > NO > N₂. The effect of changing the halogen was studied in the PbX₂·CO series. The CO stretching frequencies of these complexes follow the order: PbF₂ > PbCl₂ > PbBr₂ > PbI₂. Thus, the strength of the complexes decreases from CO to N₂ and from fluorides to iodides.

Recently, complex formation between SnF₂ and N₂ was studied by matrix IR spectroscopy. Complexes of SnF₂ with one and two molecules of N₂ were detected. Based on the magnitudes of the shifts of the EX₂ stretching bands upon complexation, it has been demonstrated that the strength of complexes of these molecules with N₂ of the same composition [1 : 1 : N₂·SnF₂, N₂·SnCl₂, N₂·PbF₂, and 1 : 2 : (N₂)₂·SnF₂, (N₂)₂·SnCl₂] is nearly identical. The structure and stability of N₂·SnF₂ and (N₂)₂·SnF₂ were studied by ab initio methods (see Section X).

The undesirability of using dinitrogen as a matrix gas in studies of CAs is one of the important conclusions of these works. The vibrational bands recorded in N₂ matrices for SiCl₂, SiBr₂, GeF₂, GeCl₂, SnCl₂, SnBr₂, SnBrCl, PbBr₂, PbBrCl, PbCl₂, MeSiCl, MeSiH, and Me₂Si which were assigned to the corresponding CAs can in fact belong to complexes of CAs with N₂ (probably of 1 : 2 composition). Complexation with N₂ results in only small shifts in the IR bands of CAs, but probably affects significantly the position of the absorption maximum in the UV-VIS spectra of the CAs (see Sections IV and V, and compare UV-spectral data of MeClSi, MeHSi and Me₂Si in different matrices).

Complexes between SnF₂ and very weak donors of electron density like ethylene, silyne, and aromatics (PhH, PhCl and PhMe) of 1 : 1 composition were formed in Ar matrices at 12 K and studied by IR spectroscopy. In addition, the complex F₂Sn·(PhH)₂ was detected (Table 9). The magnitudes of shifts of the SnF₂ stretching bands upon complexation with unsaturated compounds testify to the similar strength of these complexes. In this series a C=C double bond is found to be a slightly stronger electron density donor than a triple one. In the series of monosubstituted benzenes, an electron donor substituent (Me) increases while an electron-withdrawing substituent (Cl) decreases the strength of complexes formed.

The only example of a complex of CA with alkyl halide detected by matrix IR spectroscopy is the complex MeCl·SnF₂. Its structure and stability were studied by ab initio methods (see Section X).

The ability of SnF₂ to form labile complexes with varied electron density donors provides a better understanding of the mechanisms of action of Sn(II) salts as co-catalysts in important industrial processes.

To conclude this section we note that IR absorptions corresponding to the vibrations of P···EHal₂ (E = Ge, Sn) fragments were described for the room-temperature stable complexes Ph₃P·GeCl₂, (t-Bu)₃P·GeCl₂, Ph₃P·GeBr₂, (t-Bu)₃P·SnCl₂ and (t-Bu)₃P·SnBr₂.
VIII. MICROWAVE SPECTRA OF GERMYLENES. STRUCTURES OF SHORT-LIVED CARBENE ANALOGS

A. Rotational Transitions

Rotational transitions in the ground electronic state have been studied for only two germylenes: GeF$_2$ and GeCl$_2$. There are no microwave studies of stannylenes or plumbylenes. GeF$_2$ was produced by evaporation of germanium difluoride at 363 K or by electric discharge in GeF$_4$. GeCl$_2$ was generated in a glow discharge of GeCl$_4$ or by interaction of GeCl$_4$ with metallic Ge at 770 K.

The microwave spectrum of GeF$_2$ in the region 8–35 GHz and the millimeter-wave spectrum of GeCl$_2$ in the frequency range 108–160 GHz have been recorded for the ground (0,0,0) and vibrationally excited (1,0,0), (0,1,0), (0,0,1) and (0,2,0) states. In the case of GeF$_2$ only lines originating from molecules containing germanium isotopes with zero nuclear spin ($^{70}$Ge, $^{72}$Ge, $^{74}$Ge, $^{76}$Ge) were assigned initially, using characteristic Stark patterns and isotope shifts. Later, the lines of $^{73}$GeF$_2$ were also assigned and the quadrupole coupling constants obtained from the observed hyperfine structure due to $^{73}$Ge nuclear quadrupole. No hyperfine structure due to chlorine nuclear quadrupoles was resolved in the spectrum of GeCl$_2$.

Rotational constants obtained for both the ground and the three first excited vibrational states allowed one to derive the equilibrium molecular structures of GeF$_2$ ($r_e = 1.7321$ Å, $\theta_e = 97.148^\circ$) and GeCl$_2$ ($r_e = 2.169452$ Å, $\theta_e = 99.8825^\circ$). From measurements of the Stark effect the dipole moment of GeF$_2$ has been determined to be 2.61 Debye. The harmonic and anharmonic force constants up to the third order have been obtained for both molecules and reported too.

A further study of rotational transitions for four isotopomers of GeF$_2$ with germanium isotopes 70, 72, 74 and 76 (and also for $^{28}$SiF$_2$) using a cavity pulsed microwave Fourier transform spectrometer has allowed us to observe the $^{19}$F hyperfine structure owing to the higher resolution achieved in the spectra. Spin–spin and spin–rotation coupling constants have been obtained from the analysis of this hyperfine structure. The F–F internuclear distance has been determined from these constants. It turned out to be only slightly smaller than the distance, which can be derived from the equilibrium geometry, reported previously.

B. The Ground State Geometries of Short-lived Carbene Analogs

The ground state geometries of labile CAs obtained by different methods are collected in Table 10. There is good agreement in the results reported for each of the CAs. The bond lengths in triatomic CAs increase with increasing atomic mass of the central atom and the substituents, reflecting the increase in the covalent radii of the composing atoms. It has been noted repeatedly that the E–X bond lengths in EX$_2$ are always longer than those in EX$_4$ (E = Si, Ge, Sn, Pb; X = H, Hal)11,283,286–288. This was ascribed to a higher ionic character of the E–X bonds in EX$_2$ than in EX$_4$, and to the presence of occupied antibonding MOs in EX$_2$, which are absent in EX$_4$, resulting in lengthening and weakening of the E–X bonds in EX$_2$ (a detailed description of the valence shell MOs in triatomic germylenes, stannylenes and plumbylenes is presented in Section IX).

The bond angle in triatomic CAs with the same substituents decreases upon increasing the atomic number of the central atom, although it is worth noting that uncertainties in the determination of bond angles for plumbylenes are extremely large. In the case
TABLE 10. Geometries of labile carbene analogs in the ground electronic state

<table>
<thead>
<tr>
<th>Method</th>
<th>Bond length(s) (Å)</th>
<th>Bond angle(s) (deg)</th>
<th>Reference</th>
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</thead>
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<td>SiH₂</td>
<td>1.525⁵, 1.514⁸</td>
<td>91.8⁵, 92.0⁸</td>
<td>291</td>
</tr>
<tr>
<td>ES</td>
<td>1.5140²</td>
<td></td>
<td>63</td>
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<tr>
<td>SiHF</td>
<td>1.548⁹, 1.606⁹</td>
<td>97.0⁹</td>
<td>85</td>
</tr>
<tr>
<td>ES</td>
<td>1.528¹, 1.603¹</td>
<td>96.9⁹</td>
<td>85</td>
</tr>
<tr>
<td>SiF₂</td>
<td>1.590¹</td>
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<td>SiCl₂</td>
<td>2.0653¹⁰</td>
<td>101.32⁴⁰</td>
<td>294</td>
</tr>
<tr>
<td>ED</td>
<td>2.08³, 2.08⁹</td>
<td>102.⁸</td>
<td>295</td>
</tr>
<tr>
<td>ED</td>
<td>2.07⁶</td>
<td>104.²</td>
<td>231</td>
</tr>
<tr>
<td>ES</td>
<td>2.06⁸</td>
<td>101.⁵</td>
<td>71</td>
</tr>
<tr>
<td>SiHBr</td>
<td>1.51⁸, 2.23⁷</td>
<td>93.⁴</td>
<td>83</td>
</tr>
<tr>
<td>ES</td>
<td>1.52², 2.23³</td>
<td>95.⁹</td>
<td>83</td>
</tr>
<tr>
<td>SiBr₂</td>
<td>2.24³, 2.24⁹</td>
<td>102.⁷</td>
<td>295</td>
</tr>
<tr>
<td>ED</td>
<td>2.22⁷</td>
<td>103.¹</td>
<td>231</td>
</tr>
<tr>
<td>SiH</td>
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<td>92.⁴</td>
<td>86</td>
</tr>
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<td>GeH₂</td>
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<td>91.2⁸</td>
<td>30</td>
</tr>
<tr>
<td>ES</td>
<td>1.58⁸³</td>
<td>91.2²</td>
<td>30</td>
</tr>
<tr>
<td>GeF₂</td>
<td>1.73²³</td>
<td>97.1⁴⁰</td>
<td>211</td>
</tr>
<tr>
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<td>(94.3)³⁹, h</td>
<td>78</td>
</tr>
<tr>
<td>GeBr₂</td>
<td>2.3⁹⁰, 2.3²⁹</td>
<td>(93.⁹)³⁹, h</td>
<td>78</td>
</tr>
<tr>
<td>GeI</td>
<td>1.5⁹³, 2.5²⁵</td>
<td>(93.⁵)³⁹, h</td>
<td>79</td>
</tr>
<tr>
<td>GeI₂</td>
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<td>102.¹⁸</td>
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</tr>
<tr>
<td>SnF₂</td>
<td>2.06³</td>
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<td>SnCl₂</td>
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<td>99.¹²</td>
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<td>SnI₂</td>
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<td>300</td>
</tr>
<tr>
<td>PbBr₂</td>
<td>2.5⁹³</td>
<td>97.³</td>
<td>300</td>
</tr>
<tr>
<td>PbI₂</td>
<td>2.8⁰³</td>
<td>97.³</td>
<td>300</td>
</tr>
<tr>
<td>H₂C = Si</td>
<td>ES</td>
<td>1.1⁰⁵⁴, 1.7⁰⁶⁵</td>
<td>114.⁴⁵ (HCH)</td>
</tr>
<tr>
<td>H₂C = Ge</td>
<td>ES</td>
<td>1.1⁰²²⁴, 1.7⁰⁸⁰</td>
<td>115.⁰⁵ (HCH)</td>
</tr>
</tbody>
</table>

⁻IRDLKS = infrared diode laser kinetic spectroscopy, investigation of the rotational structure of the ν₂ band; MW = microwave spectroscopy; ED = electron diffraction; ES = electronic spectroscopy, investigation of the rovibronic structure of electronic transitions; bond angles calculated from isotopic shifts of the ν₃ bands of triatomic CAs are not presented here due to their large experimental error; these values are reported in Section VI. h The bond angles presented in parentheses have been transferred from quantum-chemical calculations and used to obtain the bond lengths presented.

of symmetric triatomic CAs the bond angle increases upon changing the substituents from H to F and then down the Group 17 elements. This can be explained in that the increasing ratio of the substituent covalent radius to the central atom covalent radius brings about increasing spatial repulsion between the two substituents. This trend is also in
agreement with predictions of valence-shell electron pair repulsion (VSEPR) theory. In accordance with Bent’s rule, the central atom's AO contribution to bonding decreases and the s character of the lone electron pair increases with the increasing difference in electronegativities of the central atom and the substituents, which leads to a decrease in the bond angle. However, a decrease in the bond angle can be seen for asymmetric triatomic CAs in the series F > Cl > Br > I. Apparently, lengthening the E–Hal bonds on passing successively from F to Br results in diminution of the spatial interaction between the halogen and hydrogen atoms in these CAs.

Besides the triatomic CAs, the molecular structures have been determined experimentally for only labile silylidene and germylidene, as shown in Table 10. At the same time most of the stable CAs have been characterized by X-ray analysis or by electron diffraction. The available structural data for some stable germynes, stannynes and plumbynes have partly been presented in Section IV. The comprehensive consideration of the geometries of stable CAs is beyond the scope of the present review.

**IX. PHOTOELECTRON SPECTRA, IONIZATION ENERGIES, ELECTRON AFFINITIES AND REDOX POTENTIALS OF GERMYLENES, STANNYLENES AND PLUMBYLENES**

Photoelectron spectroscopy is an important tool for studying the molecular orbital (MO) structure. Photoelectron spectroscopy probes the occupied molecular orbitals by measuring the ionization energies of electrons. The angle distribution of the photoelectrons gives information on the symmetry of the MOs. In accordance with Koopmans’ theorem, ionization energy (IE), or binding energy, of an electron is the negative of the energy of the corresponding molecular orbital. Thus photoelectron spectroscopy gives a set of MO energies for a molecule. However, it is noteworthy that there are some restrictions in the application of Koopmans’ theorem. At the same time no significant deviations from predictions made on the basis of Koopmans’ theorem have been revealed in photoelectron spectroscopy studies of carbene analogs (CAs). Most studies of germynes, stannynes and plumbynes were performed by means of ultraviolet photoelectron spectroscopy. Assignment of bands in photoelectron (PE) spectra is based on quantum-chemical calculations at different levels, which have been carried out in parallel with the photoelectron spectroscopy studies. Correlations with previous assignments of bands of other CAs have been taken into account too. For some germynes, stannynes and plumbynes the first adiabatic ionization energy (IE) has also been evaluated by means of mass spectrometry.

**A. Prototype EH₂ Molecules**

The upper limit for the adiabatic first IE of GeH₂ has been obtained by means of photoionization mass spectrometry in the course of photoionization studies of GeH₄ molecules, generated by abstraction of hydrogen atoms from GeH₄ by fluorine atoms. It was found to be 9.25 eV. On the basis of simple MO considerations it can be concluded that this ionization comes from HOMO, which is of the germanium atom lone-pair character. This is the only study of molecules of this simplest type.

**B. EHal₂ Molecules**

The PE spectra of EHal₂ were recorded in a molecular effusive beam. Monomeric SnHal₂ and PbHal₂ were produced by evaporating the corresponding salts (EHal₂)ₓ at temperatures above the melting point. The formation of SnF₂ in this process was accompanied by the appearance of another species (a band at 10.63 eV), which was tentatively identified as the dimer (SnF₂)₂. This is the only complication noted for the evaporation processes used. For the production of vapors of sufficiently pure monomeric GeHal₂
(Hal = F, Cl, Br, I), a solid state reaction between germanium sulfide and suitable lead dihalides at ca 570 K was used\textsuperscript{304–306}. The observed IEs, corresponding to ionizations from the valence shell MOs, are presented in Table 11.

$\text{EHal}_2$ molecules belong to the $C_{2v}$ symmetry group and have nine occupied valence MOs, four of which are of $a_1$ symmetry, three of $b_2$ symmetry, one of $b_1$ symmetry and one of $a_2$ symmetry, taking the $YZ$ plane as the molecular plane with the $Z$ axis being the $C_2$ axis.

Quantum-chemical calculations [relativistic HF/TZ, using geometrical parameters derived from experimental data for GeHal\textsubscript{2}\textsuperscript{304–306}, pseudo-potential LCAO-MO-SCF\textsuperscript{307} and Cl\textsuperscript{308} for SnCl\textsubscript{2}, as well as CNDO for SnCl\textsubscript{2} and SnBr\textsubscript{2}\textsuperscript{130}, and extended Hückel MO (EHMO) for a series of EHal\textsubscript{2}\textsuperscript{309}] predict the following sequence of the valence shell MOs.

The HOMO, $4a_1$ (only valence shell orbitals are numbered), represents a combination of halogen p AOs destabilized by an antibonding interaction with a central atom sp hybrid orbital. Thus this MO is antibonding $E$–Hal MO in nature and has quite a large contribution from a central atom valence $s$ orbital. This explains the quite low IEs observed for ionizations from $4a_1$ MO, incompatible with a lone-pair orbital mainly localized on the central atom. This MO determines the Lewis base properties of the central atom in EHal\textsubscript{2}.

The following four MOs have a predominantly halogen lone-pair character. The $3b_2$ and $1a_2$ MOs are almost completely localized on the halogen atoms. The $3b_2$ MO is formed by in-plane halogen p AOs and corresponds to antibonding halogen–halogen through space interaction. Therefore, it is slightly destabilized relative to the $1a_2$ MO, which arises from two spatially remote, slightly overlapping, out-of-plane halogen p AOs. The $1b_1$ and $3a_1$ orbitals, being also localized mainly on the halogen atoms, have some stabilizing contribution from the central atom p orbitals. The $1b_1$ MO is constructed from the halogen out-of-plane p AOs and the central atom unoccupied $p_x$ orbital, while the $3a_1$ MO corresponds to a combination of the in-plane halogen p AOs with some contribution (depending on the halogen attached) from the central atom $p_z$ orbital.

The $2b_2$ bonding MO represents an in-phase combination of the central atom $p_y$ and the radial halogen $p$ AOs. Hence this MO is of a bonding $E$–Hal nature and can be identified as $\sigma(E$–Hal). However, CNDO calculations predict that the energy of the $3a_1$ MO is lower than that of the $2b_2$ MO\textsuperscript{308}, in disagreement with $ab$ initio calculations\textsuperscript{307,308}.

The $2a_1$ MO has mainly a central atom s AO character, but is stabilized through interaction with a radial halogen p orbital combination (Hal = F, Cl, Br), and can be identified as $\sigma(E$–Hal), or it is destabilized through a halogen s orbital combination of $a_1$ symmetry (Hal = I). Some halogen s AO contribution is present in this MO, even in the case of F, Cl and Br substituents.

$1b_2$ and $1a_1$ MOs represent halogen s orbital combinations of corresponding symmetries, with $1a_1$ being stabilized through interaction with the central atom s AO in the case of iodine owing to quite high energy of the 5s AO of this atom.

The PE spectra of all EHal\textsubscript{2} molecules conform to the described sequence of MOs, although it is worth mentioning that the initial assignment\textsuperscript{310,311} of the bands of SnHal\textsubscript{2} and PbHal\textsubscript{2}, Hal = Cl, Br, based on correlations with PE bands of linear HgHal\textsubscript{2} and diatomic TlHal and InHal, differed notably from the assignment presented in Table 11.

Relative band intensity changes in the PE spectra recorded using He I and He II radiation\textsuperscript{303,307,309} or synchrotron radiation with similar photon energies (24 and 50 eV\textsuperscript{308,312}) provide experimental support to the predominant central atom orbital character of the $4a_1$ and $2a_1$ MOs, assuming that MO photoionization cross-sections are linked with those of atomic orbitals. It comes from losses in intensity of the $4a_1^{-1}$ and $2a_1^{-1}$ bands (the superscript “$-1$” means an electron detachment from this MO) relative to the...
## TABLE 11. Ionization energies (eV) for ionizations from the valence molecular orbitals of EHal$_2$ and their assignments$^{a,b}$

<table>
<thead>
<tr>
<th></th>
<th>4$a_1$</th>
<th>3$b_2$</th>
<th>1$a_2$</th>
<th>1$b_1$</th>
<th>3$a_1$</th>
<th>2$b_2$</th>
<th>2$a_1$</th>
<th>1$a_1$ + 1$b_2$</th>
<th>Exciting irradiation</th>
<th>Reference</th>
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<tr>
<td>GeF$_2$</td>
<td>11.98</td>
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<td>14.4</td>
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<td>16.2</td>
<td>18.70</td>
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<td>GeCl$_2$</td>
<td>10.55</td>
<td>11.44</td>
<td>11.70</td>
<td>12.58</td>
<td>12.69</td>
<td>13.41</td>
<td>16.73</td>
<td>He I</td>
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<tr>
<td>GeBr$_2$</td>
<td>10.02</td>
<td>10.54</td>
<td>10.86</td>
<td>11.67</td>
<td>11.82</td>
<td>12.61</td>
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<td>SnF$_2$</td>
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<td>13.61</td>
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<td>14.37</td>
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<td>11.19</td>
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$^a$Schematic MO representations are based on those shown in References 304–306 for GeHal$_2$ (Hal = F, Cl, Br, I). Only the most important contributing AOs are depicted leaving out variations, which differ for different molecules.

$^b$sh = shoulder.

$^c$The He I PE spectrum of PbI$_2$ is also shown in Reference 311.
halogen lone-pair originating bands (3b2\(^{-1}\), 1a2\(^{-1}\), 1b1\(^{-1}\) and 3a1\(^{-1}\)) in the He I PE spectra of SnHal\(_2\) and PbHal\(_2\) compared to the He II spectra. It is consistent with the lower photoionization cross-section of the halogen valence p orbitals relative to the tin and lead p and s valence orbitals with respect to the He II radiation. In spite of the predominant halogen p AOs character of the 2b2 MO, the 2b2\(^{-1}\) band of SnCl\(_2\) was found not to decrease in intensity in the He II spectrum\(^{307}\), which implies an appreciable contribution from the central atom AOs.

It has been noted repeatedly that the bands originating from ionizations from the 4a1 and 2a1 MOs are weaker than the other five observed for EHal\(_2\) in the He I PE spectra, with the 2a1\(^{-1}\) band not being observed in the PE spectrum of GeI\(_2\) and PbF\(_2\) (see Table 11). This conclusion should be treated with care, because 3b2\(^{-1}\) and 1a2\(^{-1}\) ionizations as well as those from 1b1 and 3a1 often form a single unresolved band, while 4a1\(^{-1}\) and 2a1\(^{-1}\) bands usually have no contribution from the other ionizations. Nevertheless, this fact can again be rationalized by a considerable central atom AO character of the 4a1 and 2a1 MOs and, particularly, by the predominant central atom valence s character of the 2a1 orbital (and predominant Ge 4s and I 5s character of 2a1 in GeI\(_2\)\(^{306}\)). The more intensive bands arise from MOs of mainly halogen lone-pair p character.

The predominant halogen valence-shell s character of 1b2 and 1a1 MOs, and therefore their low cross-section to He II radiation, results in extremely low intensity of the 1b2\(^{-1}\) and 1a1\(^{-1}\) bands. Actually, the band corresponding to ionizations from both MOs has been observed only for SnCl\(_2\), when intensive synchrotron radiation was used\(^{308,312}\).

IEs originating from MOs with considerable central atom character (4a1, 2a1) show smaller shifts due to exchange of halogen atoms than IEs originating from MOs with predominant halogen character (3b2, 1a2, 1b1, 3a1)\(^{305}\). This trend can be seen from the data of Table 11. It is interesting to note that such shifts for ionizations from 2b2 have an intermediate value. The general trend in decreasing IEs of EHal\(_2\) on passing from F through to I substituents parallels the IEs of the halogen atoms\(^{130,304}\).

Photoelectron spectroscopy of solid Sn(II) and Pb(II) halides, (EHal\(_2\))\(_x\), have also been recorded\(^{303,309}\). A remarkable resemblance of the solid-phase and gas-phase spectra of EHal\(_2\) (E = Sn, Pb, Hal = F, Cl, Br, I) was found, although the solid-phase bands were naturally shifted to a lower energy region and were broadened compared to the gas-phase bands. This suggests that much of the molecular orbital character of stannylenes and plumbylenes is carried over to the orbital structure of the solids, in spite of the fact that the crystal structure of solid (EHal\(_2\))\(_x\) does not include EHal\(_2\) units\(^{313,314}\).

The elements Sn and Pb have outer d-shell electrons, the ionization energy of which fall in the range normally regarded as the valence region of ionization energies (\(\leq ca\) 30 eV), although the d orbitals are essentially atomic in nature. Due to spin–orbit interaction in the final d\(^{-1}\) ion it can be formed in the \(^2D_{5/2}\) and \(^2D_{3/2}\) states, with the \(^2D_{5/2}\) state being of lower energy. Because the energy separation between these states is quite large, the features associated with d-shell ionization show characteristic \(^2D_{5/2}\)/\(^2D_{3/2}\) splittings. The d-shell orbital IEs for EHal\(_2\) are shown in Table 12. Central atom outer d-shell IEs of EHal\(_2\) show a shift to higher values with increasing halogen electronegativity\(^{307,315}\), similar to the valence-shell IEs. It has been shown that these IEs are consistent with the atomic description for the central atom outer d orbitals\(^{315,316}\). It has been found also that these IEs can be reasonably described by a simple electrostatic model\(^{315,316}\). The asymmetry parameters \(\beta\) for ionization from the 5d subshell of the metal atom in PbHal\(_2\) (as well as in HgHal\(_2\) and TlHal), Hal = F, Cl, Br, I, have been determined from He II\(_\alpha\) photoelectron spectra recorded at two angles to an unpolarized photon beam\(^{317}\).
TABLE 12. Outer d-shell ionization energies (eV) for EHal₂ (E = Sn, Pb)

<table>
<thead>
<tr>
<th></th>
<th>²D₅/₂</th>
<th>²D₃/₂</th>
<th>Exciting irradiation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnF₂</td>
<td>33.7</td>
<td>34.5</td>
<td>He IIₐ</td>
<td>303</td>
</tr>
<tr>
<td>SnCl₂</td>
<td>33.48</td>
<td>34.53</td>
<td>He IIₐ, He IIₜ</td>
<td>309, 315, 316</td>
</tr>
<tr>
<td></td>
<td>33.34</td>
<td>34.69</td>
<td>He II</td>
<td>307</td>
</tr>
<tr>
<td></td>
<td>33.48</td>
<td>34.53</td>
<td>SR</td>
<td>308, 312</td>
</tr>
<tr>
<td>SnBr₂</td>
<td>33.15</td>
<td>34.21</td>
<td>He IIₐ, He IIₜ</td>
<td>309, 315, 316</td>
</tr>
<tr>
<td>SnI₂</td>
<td>33.6</td>
<td>34.9</td>
<td>He II</td>
<td>309</td>
</tr>
<tr>
<td>PbF₂</td>
<td>27.63</td>
<td>30.34</td>
<td>He IIₐ</td>
<td>303, 317</td>
</tr>
<tr>
<td>PbCl₂</td>
<td>27.34</td>
<td>29.92</td>
<td>He IIₐ, He IIₜ</td>
<td>309, 315–317</td>
</tr>
<tr>
<td>PbBr₂</td>
<td>27.02</td>
<td>29.58</td>
<td>He IIₐ, He IIₜ</td>
<td>309, 315–317</td>
</tr>
<tr>
<td>PbI₂</td>
<td>26.48</td>
<td>29.20</td>
<td>He IIₐ, He IIₜ</td>
<td>309, 315–317</td>
</tr>
</tbody>
</table>

The most detailed photoelectron spectroscopy study has been carried out for SnCl₂ using synchrotron radiation (SR). The use of dispersed SR as an ionizing source for photoelectron spectroscopy studies has great benefit due to its features of high intensity of this radiation, continuous tunability over a wide spectral range and some others. The use of SR (21–52 eV) first allowed one to investigate the complete outer- and inner-valence shells, as well as Sn 4d subshell photoionization of SnCl₂. Some new features in the PE spectrum of SnCl₂ were revealed. On the basis of configuration interaction (CI) calculations it has been concluded that the Koopmans’ theorem assignment for the outer-valence ionizations 4⁴a⁻¹, 3b⁻¹, 1a⁻¹, 1b⁻¹, 3a⁻¹ and 2b⁻¹ has been satisfactory, whereas the spectral strength of the 2a⁻¹ main line has been considerably reduced and three new weak broad features, observed around the 2a⁻¹ band, have been mainly due to satellites of the 2a⁻¹ band. A band at 22.61 eV, corresponding to an ionization from 1a₁ + 1b₂ MOs of mainly Cl 3s character, has been detected for the first time. The quite low IE value for this ionization has been explained by high electron density on the chlorine atoms in SnCl₂ due to tin donation. For the 4d⁻¹ doublet the branching ratio (²D₅/₂ : ²D₃/₂) has been measured. The value obtained (1.39) is not far from the statistical value of 1.5. An Auger widespread band (independent of whether the radiation energy was 50 or 52 eV) due to the 4d hole decay has been observed in addition to the 4d ionization. This band corresponds to SnCl₂⁺⁺ states lying approximately within the 26.5–28.7 eV range. Records of constant ionic state spectra revealed two resonances at 25.03 and 26.11 eV, assigned to 4d → 8b₁ (LUMO) transition with spin–orbit splitting. The excitation of SnCl₂ at these energies induces intensive autoionization processes following the 4d → 8b₁ electron promotion, resulting in strongly resonant behavior of most of the bands observed.

The adiabatic first IEs for some of EHal₂ have also been determined by means of electron impact mass spectrometry (EIMS) from ionization efficiency curves. In these studies the vapor of monomeric GeF₂ was produced by reaction of CaF₂ with metallic germanium at ca 1500 K or by evaporation of melted germanium difluoride at ca 400 K. Monomeric GeCl₂ and GeBr₂ were obtained by interaction of the vapor of GeCl₄ (at 520–660 K) or GeBr₄ (at 623 K) with metallic germanium. Other monomeric species were produced by evaporation of the corresponding melted salts. The EIMS results are compared with the photoelectron spectroscopy data in Table 13. As can be seen, the EIMS and photoelectron spectroscopy data (except those for SnBr₂, PbBr₂ and some data for SnI₂) are in reasonable agreement.
C. EHalHal’ Molecules

Three molecules of this type have been studied by EIMS and their adiabatic first IEs determined\textsuperscript{322–324}. The values are given in Table 13. The EHalHal’ molecules were produced by evaporation of 1:1 mixtures of (EHal\textsubscript{2})\textsubscript{x} and (EHal\textsuperscript{′}Hal\textsubscript{2})\textsubscript{x} at Knudsen conditions\textsuperscript{322–324}. From comparison of the IE data in Table 13 it may be deduced that the available first IEs for EHalHal’ are somewhat overestimated.

D. Acyclic Organyl and Aminogermylenes, -stannylenes and -plumbylenes

The compounds ERR’ where E = Ge, Sn, Pb; R, R’ = (Me\textsubscript{3}Si)\textsubscript{2}CH, t-Bu(Me\textsubscript{3}Si)N or (Me\textsubscript{3}Si)\textsubscript{2}N, belong to the first known representatives of stable CAs. Their gas-phase PE spectra (evaporation temperature < 390 K) were reported in a series of publications\textsuperscript{130–132,153,330,331}. The IEs obtained are collected in Table 14. The assignments of PE bands of ERR\textsubscript{2}(R = (Me\textsubscript{3}Si)\textsubscript{2}CH, t-Bu(Me\textsubscript{3}Si)N and (Me\textsubscript{3}Si)\textsubscript{2}N) have been made on the basis of a comparison of the observed spectra of ERR’ with those of the parent molecules RH, as well as of ER\textsubscript{4} and also of HgR\textsubscript{2} and ZnR\textsubscript{2} (which differ from ER\textsubscript{2} by the absence of a lone-pair at the central atom), assuming a local C\textsubscript{2v} symmetry at the E atom\textsuperscript{130}.

The first bands in the PE spectra of E(CH(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{2} were assigned to the ionization from the a\textsubscript{1} HOMO, which represents a combination of sp hybrid orbitals of the divalent atom E and the carbon 2p orbitals. This MO is mainly localized on the atom E and has its lone-pair character due to a predominant contribution from s AO. Interaction of the E atom p AO with the E atom s AO lowers the energy of the resulting MO, while the interaction with $\alpha$-carbon p AOs raises it relative to the energy of the p AO of the free atom E. Both effects approximately balance out, and the resulting IE for ionization from the HOMO of ER\textsubscript{2} has been noted to be close to the atomic first IE due to ionization from p AO.

<table>
<thead>
<tr>
<th>Table 13. First ionization energies (eV) of EHal\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>EIMS</strong></td>
</tr>
<tr>
<td>adiabatic</td>
</tr>
<tr>
<td>GeF\textsubscript{2}</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>GeCl\textsubscript{2}</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>GeBr\textsubscript{2}</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>SnCl\textsubscript{2}</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>SnBr\textsubscript{2}</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>SnI\textsubscript{2}</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>PbCl\textsubscript{2}</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>PbBr\textsubscript{2}</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>SnBrCl</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Typical error for values obtained by photoelectron spectroscopy is of a few hundredths of eV.

\textsuperscript{b}Photoionization MS.
The second band in the PE spectra of E(CH(SiMe₃)₂)₂ has been assigned to ionization from the $b_2$ MO, which is antisymmetric bonding MO, localized mainly on the C₂E fragment. The next band originating from the $a_1$ symmetric bonding MO ionization has not been observed since it is obscured by the broad unresolved bands due to ionizations from the substituent’s orbitals.

In the case of E(N(SiMe₃)₂)₂ and E(N(Me₃Si)(t-Bu))₂ the first band in the PE spectra has been assigned to the ionization from the $b_2$ MO, corresponding to the nitrogen lone-pair orbital antibonding combination, whereas only the second band arises from ionization from the $a_1$ MO of the divalent atom E lone-pair character. The third band is due to ionization from nitrogen lone-pair bonding MO of $a_1$ symmetry. The fourth band, observed only for stannylenes and plumblylenes, but obscured for germlylenes by broad bands due to ionizations from the substituent’s MOs, corresponds to ionization from the $b_2$ bonding MO, $\sigma_{asym}(E-N)$.

The energy of the MO corresponding to the lone-pair of the atom E and $\sigma_{asym}(E-N)$ MO in E(N(SiMe₃)₂)₂ and E(N(SiMe₃)(t-Bu))₂ rises with increasing mass of the atom E, following the trend in the atomic first IEs of the Group 14 elements, in accordance with considerable localization of these MOs at the E atoms. The slight increase in the first IEs and the slight decrease in the third IEs on going from the germlylenes to the plumblylenes reflect the increasing spatial separation between nitrogen atoms in this series. It therefore reflects the weakening of ‘through space’ interaction between the nitrogen lone-pair AO's, resulting in that antibonding combination $(b_2)$ becoming ‘less’ antibonding, whereas the bonding combination $(a_1)$ becomes ‘less’ bonding.

Comparison of the IEs corresponding to ionization from lone-pairs of the atoms E in E(N(SiMe₃)₂)₂ and E(N(SiMe₃)(t-Bu))₂ shows that the IE values are lower in the latter case in spite of the fact that the more electronegative substituents should stabilize the HOMO, increasing its IE, and that the N(SiMe₃)₂ group is expected to be less electronegative than the N(SiMe₃)(t-Bu) group due to the presence of two electropositive trimethylsilyl substituents. This fact can be explained by a significant $p_\pi-d_\pi$ interaction between the nitrogen lone-pairs and the vacant silicon 3d orbitals, which increases the overall electronegativity of the N(SiMe₃)₂ group compared to the N(SiMe₃)(t-Bu) group. Such $p_\pi-d_\pi$ interaction lowers not only the energy level of the MO with the central atom lone-pair character, but also the energy levels of the MO representing nitrogen lone-pairs.

The proposed explanation is consistent with the reported data on the first IEs of stable E(NR₂)₂ (E = Ge, Sn; R = t-Bu or NR₂ = cyclo-NCMe₂(CH₂)₃CMc₂), bearing only β-carbon atoms in the substituents. The first IEs of these CAs are much lower than those of E(N(SiMe₃)₂)₂ and E(N(SiMe₃)(t-Bu))₂ (Table 14) due to the absence of $p_\pi(N)-d_\pi(Si)$ stabilization of their HOMO. It can be expected that the second IE, corresponding to the ionization from the divalent atom E lone-pair, is also lowered for the CAs bearing only β-carbon atoms in the substituents. These IEs have not been published, but there are indirect arguments in favor of this expectation based on easier oxidizing addition of MeI to E(NR₂)₂ (E = Ge, Sn; NR₂ = cyclo-NCMe₂(CH₂)₃CMc₂).

On the basis of the IE values for ionizations from the divalent atom E lone-pair, one can expect a decrease in the basicity of germlylenes, stannylenes and plumblylenes in the following series: E(CH(Me₃Si)₂)₂ > E(N(Me₃Si)(t-Bu))₂ > E(N(Me₃Si)₂)₂. This ordering is in agreement with available data on the chemical behavior of these molecules. At the same time it is necessary to note that EHal₂ have higher first IE (corresponding to the divalent atom E lone-pair MO), but form complexes with Lewis acids more readily than E(N(SiMe₃)₂)₂. This indicates that there are other factors which play an important role in the formation of complexes by these CAs.
TABLE 14. Valence-shell ionization energies (eV) for polyatomic ER$_2$, E = Ge, Sn, Pb

<table>
<thead>
<tr>
<th></th>
<th>$a_1$ (E:)</th>
<th>$b_2(\sigma_{asym}(E-C))$</th>
<th>$a_1$ (N:)</th>
<th>$b_2(\sigma_{asym}(E-N))$</th>
<th>Exciting irradiation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>((Me$_3$Si)$_2$CH)$_2$Ge</td>
<td>7.75</td>
<td>8.87</td>
<td></td>
<td></td>
<td>He I</td>
<td>130, 153, 331</td>
</tr>
<tr>
<td>((Me$_3$Si)$_2$CH)$_2$Sn</td>
<td>7.42</td>
<td>8.33</td>
<td></td>
<td></td>
<td>He I</td>
<td>130, 330, 331</td>
</tr>
<tr>
<td>((Me$_3$Si)$_2$CH)$_2$Pb</td>
<td>7.25</td>
<td>7.98</td>
<td></td>
<td></td>
<td>He I</td>
<td>130, 330, 331</td>
</tr>
<tr>
<td>(t-Bu(Me$_3$Si)N)$_2$Ge</td>
<td>7.24</td>
<td>8.27</td>
<td>8.61</td>
<td></td>
<td>He I</td>
<td>130–132</td>
</tr>
<tr>
<td>(t-Bu(Me$_3$Si)N)$_2$Sn</td>
<td>7.26</td>
<td>7.90</td>
<td>8.47</td>
<td>9.33</td>
<td>He I</td>
<td>130–132</td>
</tr>
<tr>
<td>(t-Bu(Me$_3$Si)N)$_2$Pb</td>
<td>7.26</td>
<td>7.69</td>
<td>8.49</td>
<td>9.00</td>
<td>He I</td>
<td>130–132</td>
</tr>
<tr>
<td>((Me$_3$Si)$_2$N)$_2$Ge</td>
<td>7.71</td>
<td>8.68</td>
<td>8.99</td>
<td></td>
<td>He I</td>
<td>130–132</td>
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<tr>
<td>((Me$_3$Si)$_2$N)$_2$Sn</td>
<td>7.75</td>
<td>8.38</td>
<td>8.85</td>
<td>9.50</td>
<td>He I</td>
<td>130–132</td>
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<tr>
<td>((Me$_3$Si)$_2$N)$_2$Pb</td>
<td>7.92</td>
<td>8.16</td>
<td>8.81</td>
<td>9.39</td>
<td>He I</td>
<td>130–132</td>
</tr>
<tr>
<td>(t-Bu$_2$N)$_2$Ge</td>
<td>6.78</td>
<td></td>
<td></td>
<td></td>
<td>He I</td>
<td>163</td>
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<tr>
<td>(t-Bu$_2$N)$_2$Sn</td>
<td>6.74</td>
<td></td>
<td></td>
<td></td>
<td>He I</td>
<td>163</td>
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<tr>
<td>((CH$_3$)$_2$C(CH$_2$)$_2$C(CH$_3$)$_2$N)$_2$Ge</td>
<td>6.90</td>
<td></td>
<td></td>
<td></td>
<td>He I</td>
<td>164</td>
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<tr>
<td>((CH$_3$)$_2$C(CH$_2$)$_2$C(CH$_3$)$_2$N)$_2$Sn</td>
<td>6.80</td>
<td>(N: + Cl:)</td>
<td>(E:)</td>
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<td>He I</td>
<td>164</td>
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<tr>
<td>GeCl(N(SiMe$_3$)$_2$)$^a$</td>
<td>9.2</td>
<td>10.0</td>
<td></td>
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<td>He I</td>
<td>134</td>
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<table>
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<tr>
<th>$\pi - 3$</th>
<th>$\sigma$-lp</th>
<th>$\pi - 2$</th>
<th>$\sigma$(Ge-N)</th>
<th>$\pi - 1^* + \sigma$(t-Bu)</th>
<th>$\sigma$</th>
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<tbody>
<tr>
<td>6.65, 6.85, 6.97</td>
<td>8.60</td>
<td>8.80</td>
<td>10.55</td>
<td>11.12</td>
<td>12.68</td>
</tr>
</tbody>
</table>

$^a$This molecule is assumed to have a local $C_s$ symmetry. For description of the MOs, see the text.

$^b$This molecule has $C_s$ symmetry. Designation of the MOs is shown in the authors' notation; for a more detailed description of the MOs, see the text.
Core levels in Sn(N(SiMe$_3$)$_2$)$_2$ have been studied by means of X-ray photoelectron spectroscopy$^{132}$. The following binding energies are observed: Sn (3d$_{5/2}$) 491.93, N (1s) 402.01, Cl (1s) 289.36 and Si (2p$_{3/2}$) 105.97 eV.

The He I PE spectrum of the labile germylene, GeCl(N(SiMe$_3$)$_2$)$_2$, has been obtained recently$^{134}$. This germylene was generated by pyrolysis of the corresponding germacyclopentene in the gas phase at 713 K, as shown in equation 7.

\[
\begin{align*}
\text{Me}_3\text{SiCl} & \rightarrow \text{GeCl(N(SiMe}_3)\text{)_2}} \\
713 \text{ K} & \rightarrow \text{GeCl(N(SiMe}_3)\text{)_2} \rightarrow \text{Ge = NSiMe}_3
\end{align*}
\]

At higher temperatures GeCl(N(SiMe$_3$)$_2$)$_2$ underwent further decomposition to trimethylsilylgermaisonitrile. The He I PE spectra of a series of germaimines and germaisonitriles, generated from similar precursors, have also been reported in this paper$^{134}$.

The assignment of the bands attributed to GeCl(N(SiMe$_3$)$_2$)$_2$ has been done with the aid of B3LYP calculations on model structures. The first band at 9.2 eV belongs to ionization from MO which represents antibonding combination of the nitrogen and chlorine lone-pair. The second band at 10.0 eV corresponds to ionization from MO of germanium atom lone-pair character. The bands around 10.7 eV are associated with a chlorine atom lone-pair and $\sigma$(Si−C) MO. Unresolved bands around 13.5 eV have also been observed.

E. Cyclic Molecules

The PE spectrum of the stable aromatic 1,3-di-tert-butyl-1,3,2-diazagermol-2-ylidene (Table 14), as well as of its carbon and silicon analogs, has been obtained using He I and He II radiation$^{133}$. Assignment of the observed bands has been carried out on the basis of DFT calculations of the compounds under consideration and Koopmans’ theorem$^{133}$. The first band of the germylene corresponds to ionization from the $\pi$-type HOMO, arising from out-of-phase mixing of the C=C $\pi$-orbital of the imidazole ring with combination of the nitrogen lone-pairs and the germanium atom p orbital. It clearly shows vibrational structure, tentatively assigned to a stretching frequency of the molecular ion in the ground state. Similarly to the stable E(NR$_2$)$_2$, considered above, the ionization from the MO of the germanium atom lone-pair character is responsible for the second band. The third band is due to ionization from MO, which is essentially the out-of-phase combination of the nitrogen lone-pairs. The fourth band corresponds to ionization from $\sigma$-MO, which mainly comprises Ge−N bonds with some contribution from tert-butyl C−C bonds. The next three bands are due to ionization from MOs with a large contribution from the tert-butyl groups.

The 1,3-di-tert-butyl-1,3,2-diazasilol-2-ylidene has been found to have similar molecular orbital structure$^{133}$. At the same time, in the case of the carbon analog, 1,3-di-tert-butylimidazol-2-ylidene, the first IE corresponds to ionization from MO of the carbene center atom lone-pair character, which suggests in the framework of Koopmans’ theorem that this compound has reverse ordering of the two highest occupied MOs$^{133}$. However, the subsequent ab initio calculations with account of electron correlation have shown that the reason for the low IE in the ionization from the carbene center atom lone-pair orbital of 1,3-di-tert-butylimidazol-2-ylidene is the large relaxation of the corresponding wave function in the cation$^{332}$. In this case Koopmans’ theorem should not be valid. The degree of aromatic stabilization in this type of carbene and carbene analogs has also been discussed in detail$^{133,332,333}$ based on the established electronic structure. The influence
of the electronic structure of these CAs on their chemical and physicochemical properties has also been considered\textsuperscript{133,332,333}.

The unoccupied molecular orbital structure of 1,3-di-tert-butylimidazol-2-ylidene and its silicon and germanium analogs, as well as of their saturated analogs, 2,5-di-tert-butyl-1-E-2,5-diazacyclopentaylidenes (E = C, Si, Ge), has been studied by means of inner-shell electron energy loss spectroscopy (ISEELS)\textsuperscript{334}. ISEELS consists in excitation of electrons from core-shell levels to the virtual levels and provides information on both the energies of the unoccupied MOs and the spatial distribution of excited electron density in those orbitals. Each of the carbenes and carbene analogs as well as a number of model compounds have been characterized by C 1s and N 1s spectra. The Ge 3p spectra have also been recorded for germylenes. The analysis of these spectra with the aid of \textit{ab initio} calculations resulted in some interesting conclusions concerning the nature of bonding in these molecules. Particularly, it has been shown that there is considerable \(\pi\)-allyl delocalization over the N−E−N fragment in all molecules and additional aromatic delocalization in the unsaturated molecules\textsuperscript{334}.

\section*{F. Electron Affinities}

Electron affinity (EA) is a measure of the ability of a molecule to attach an electron. This value is equal to an adiabatic IE of the corresponding negative ion. EAs for some EHal\(_2\) have been derived from appearance energies of the corresponding anions formed by low-energy electron dissociative resonance capture from EHal\(_4\)\textsuperscript{335–337} in the course of mass spectrometric studies. For the purpose of evaluation of the EAs, many possible processes following the electron capture were considered, but most of them were found not to fit the experiments. The EAs corresponding to appropriate processes are presented in Table 15. In the case of GeCl\(_2\) and GeBr\(_2\) the authors\textsuperscript{337} were unable to decide between two possible processes, but inclined to favor the process leading to electronically excited Hal\(_2\).

Relatively low values of IP and significant values of EA obtained experimentally for a number of CAs suggest that these species can participate in electron transfer interactions with a variety of electron acceptors/donors.

\section*{G. Electrochemistry}

One-electron electrochemical oxidation \((E_{ox})\) and reduction \((E_{red})\) potentials are quantities closely related to the first IEs and EAs, respectively. One of the main differences between the two series of quantities is that the former embrace effects of solvation of both the initial neutral precursors and the final ions. Unfortunately, the solvation energies cannot be evaluated easily, therefore it is usually difficult to correlate electrochemical

| \multicolumn{2}{c}{Assumed type of dissociative resonance capture} & Reference |
|-----------------|-----------------|-----------|
| EHal\(_4\) + e → EHal\(_2\)\(^-\) + 2Hal | EHal\(_4\) + e → EHal\(_2\)\(^-\) + Hal\(_2\)\(^*\) |
| GeF\(_2\)  | 1.3  | —  | 335 |
| GeCl\(_2\)  | 2.90 | 2.56 | 337 |
| GeBr\(_2\)  | 1.80 | 1.61 | 337 |
| SnCl\(_2\)  | —    | 1.04 | 336 |
| SnBr\(_2\)  | —    | 1.33 | 336 |
| SnI\(_2\)   | —    | 1.74 | 336 |
potentials with the IEs and EAs. Since many reactions occur in the liquid phase, the oxidation and reduction potentials are of great importance for chemists.

Data on the redox potentials of germynes, stannylenes, plumbynes and their complexes are scarce. In fact, only the electrochemistry of dihalogermylenes, dihalostannylenes and their complexes with Lewis bases as well as with chromium, molybdenum and tungsten pentacarboxylies has been studied.

Cyclic voltammetry of dihalogermylenes, dihalostannylenes and their complexes with Lewis bases revealed one reduction and one oxidation peak (both are one-electron). The \( E_{1/2} \) values are given in Table 16. Most of the reduction and oxidation waves of \( \text{EX}_2 \) and \( \text{EX}_2 \cdot \text{B} \) were found to be irreversible, suggesting that the corresponding radical ions are very unstable. Quasi-reversible oxidation waves were observed for \( \text{GeX}_2 \cdot \text{dioxane} \) and \( \text{GeCl}_2 \cdot \text{Py} \) complexes. Quasi-reversible reductions were found for the \( \text{GeCl}_2 \cdot \text{dioxane} \) and \( \text{GeI}_2 \) radical anions were estimated to be ca 4 and 2.5 s at 20°C, respectively.

The nature of ligand B affects the redox properties of \( \text{GeCl}_2 \cdot \text{B} \) complexes. The oxidation potentials increase in the order: \( \text{bpy} < \text{AsPh}_3 < \text{Py} \sim \text{PPh}_3 < \text{dioxane} \). The reduction potentials tend to become more negative in the opposite sequence: dioxane - PPh3 - Py - AsPh3 - bpy (Table 16). A linear correlation was found between the oxidation and reduction potentials of \( \text{GeCl}_2 \cdot \text{B} \), suggesting that the molecular orbitals involved in the electrochemical oxidation and reduction processes are located on the germanium moiety. Using a standard electrochemical method the equilibrium formation constants, \( K \), for \( \text{GeCl}_2 \cdot \text{PPh}_3 (K = 7 \times 10^3 \text{ mol}^{-1}, \text{MeCN}, 20°C) \) and \( \text{GeCl}_2 \cdot \text{AsPh}_3 (K = 2 \times 10^4 \text{ mol}^{-1}, \text{MeCN}, 20°C) \) were determined. The values obtained are close to that measured by using UV spectroscopy (for \( \text{GeCl}_2 \cdot \text{PPh}_3, K = 2 \times 10^3 \text{ mol}^{-1}, 23°C \), in \( \text{n-Bu}_2\text{O} \)).

### Table 16. Redox potentials and electrochemical gaps of dihalogermylenes, dihalostannylenes and their complexes with Lewis bases in MeCN at 20°C (platinum electrode, Bu4NBF4 as supporting electrolyte, vs. Ag/AgCl/KCl (sat.))

<table>
<thead>
<tr>
<th>EX2</th>
<th>B</th>
<th>( E_{1/2} ) (ox)(V)</th>
<th>( -E_{1/2} ) (red)(V)</th>
<th>( G(V)^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{GeCl}_2</td>
<td>\text{dioxane}</td>
<td>1.46(^b)</td>
<td>0.41(^b), 0.44(^c)</td>
<td>1.87</td>
</tr>
<tr>
<td>\text{GeCl}_2</td>
<td>\text{PPh}_3</td>
<td>1.14(2e)(^d)</td>
<td>0.58</td>
<td>1.72</td>
</tr>
<tr>
<td>\text{GeCl}_2</td>
<td>\text{AsPh}_3</td>
<td>1.05</td>
<td>0.59</td>
<td>1.64</td>
</tr>
<tr>
<td>\text{GeCl}_2</td>
<td>\text{Py}</td>
<td>1.12(^b)</td>
<td>0.56</td>
<td>1.68</td>
</tr>
<tr>
<td>2\text{GeCl}_2</td>
<td>\text{bpy}</td>
<td>0.91 (2e)(^e)</td>
<td>0.74</td>
<td>1.65</td>
</tr>
<tr>
<td>\text{GeBr}_2</td>
<td>\text{dioxane}</td>
<td>1.08(^b)</td>
<td>0.45</td>
<td>1.53</td>
</tr>
<tr>
<td>\text{GeBr}_2</td>
<td>\text{PPh}_3</td>
<td>0.72</td>
<td>0.38</td>
<td>1.10</td>
</tr>
<tr>
<td>\text{GeI}_2</td>
<td>—</td>
<td>—</td>
<td>0.99(^b)</td>
<td>&gt;3.59</td>
</tr>
<tr>
<td>\text{GeI}_2</td>
<td>\text{PPh}_3</td>
<td>1.44</td>
<td>—</td>
<td>&gt;3.15</td>
</tr>
<tr>
<td>\text{SnF}_2</td>
<td>—</td>
<td>—</td>
<td>0.94</td>
<td>&gt;3.54</td>
</tr>
<tr>
<td>\text{SnCl}_2</td>
<td>—</td>
<td>1.88</td>
<td>0.21, 1.20</td>
<td>2.09</td>
</tr>
<tr>
<td>\text{SnCl}_2</td>
<td>\text{dioxane}</td>
<td>1.67</td>
<td>0.78</td>
<td>2.45</td>
</tr>
<tr>
<td>\text{SnBr}_2</td>
<td>—</td>
<td>1.82</td>
<td>0.40, 1.31</td>
<td>2.22</td>
</tr>
<tr>
<td>\text{SnI}_2</td>
<td>—</td>
<td>1.16</td>
<td>0.02, 0.51</td>
<td>1.14</td>
</tr>
</tbody>
</table>

\(^a\)Electrochemical gap, \( G = E_{\text{ox}} - E_{\text{red}} \).

\(^b\)Quasi-reversible.

\(^c\)In DMF.

\(^d\)A two-electron wave is due to simultaneous oxidation of free PPh3 at this potential as well.

\(^e\)A two-electron wave is due to coordination of two GeCl2 moieties.

\(^f\)bpy = \(\alpha, \alpha\)-bipyridinyl.
Taking GeI$_2$ and SnCl$_2$ as examples, one can conclude that in general the complexation with n-donors results in a decrease of the oxidation potentials and in shifts of the reduction potentials of the CAs to the more cathodic region, as expected.

The values of the oxidation potentials of dihalogermylenes (stannylenes) and their complexes with the Lewis bases indicate that these compounds should react as typical reducing agents. However, the low reduction potentials of these compounds suggest that they should be quite strong oxidizing agents too. Indeed, the reduction potentials of GeX$_2$ · B (X = Cl, Br; B = dioxane, PPh$_3$, AsPh$_3$, Py) lie in the region from $-0.4$ to $-0.60$ V, which is typical of the convenient organic [e.g. p-benzoquinone, $E_{1/2}(\text{red}) = -0.52$ V] or inorganic [e.g. O$_2$, $E_{1/2}(\text{red}) = -0.82$ V] oxidizing agents. Of the compounds studied, SnI$_2$ was found to be the most powerful oxidizing agent. Its reduction potential ($-0.02$ V) is close to the reduction potential of such a strong oxidant as TCNQ (+0.12 V). Several reactions illustrating the oxidizing properties of dihalogermylenes, dihalostannylenes and their complexes were found.

An electrochemical gap ($G = E_{\text{ox}} - E_{\text{red}}$) characterizes the energy gap between the HOMO and LUMO. The GeBr$_2$ · PPh$_3$ complex and SnI$_2$ have the smallest $G$ value while GeI$_2$ and GeI$_2$ · PPh$_3$ have the largest (Table 16). Thus, one may expect that, of the compounds studied, SnI$_2$ and the GeBr$_2$ · PPh$_3$ complex, possessing both low oxidation and reduction potentials, have a tendency to give a radical or a single electron transfer radical ion reaction, while ionic processes would be more effective with GeI$_2$, GeI$_2$ · PPh$_3$ and SnF$_2$.

X. QUANTUM-CHEMICAL CALCULATIONS

A wide range of quantum-chemical methods have been used for studying properties of carbene analogs R$_2$E (E = Ge, Sn, Pb) and various aspects of their chemistry. They include semiempirical methods (MNDO, AM1 and PM3), ab initio calculations at various levels and approaches based on density functional theory (DFT) which, in the last decade, emerged as a reliable and economic tool for modeling ground state properties and reaction dynamics of intermediates.

Most of the R$_2$E are transient species. Even their formation typically occurs via sequences of complex chemical reactions. A priori several reaction channels involving these intermediates could be envisaged. Quantum-chemical calculations have been used to explore and compare possible pathways.

The chemistry of carbenes and silylenes was developed extensively in the last decades. Parallels in the chemistry of singlet carbenes and silylenes with that of their heavier analogs are widely recognized heuristic tools to characterize reactivity of these less studied species. Calculations allow one to study in detail the trends in the prototype series of model chemical systems involving the derivatives of two-coordinated C, Si, Ge, Sn, Pb and thus get a deeper insight into the chemistry of these species. Moreover, quantum-chemical calculations are an important tool used in the interpretation of photoelectron, IR and UV spectra of CAs.

It is often difficult to deduce from the restricted experimental data the main trends in reactivity. Theoretical calculations could give the needed information to fill these gaps. In other words, they could be used to sometimes ‘interpolate’ scarce experimental data, e.g. in studying substituent effects. To examine general trends in the series of Group 14 elements carbene analogs, data for silylenes and even for carbenes are presented in this section for some cases.

A. Methods

Relativistic effects are known to be important for molecules with heavy elements. The influence of these effects on the ground state properties of hydrides EH$_2$ (E = Si,
Ge, Sn, Pb) has been studied by Dyall at the SCF level using all-electron molecular DHF calculations\textsuperscript{340}. The known relativistic shortening of bond lengths involving a heavy atom in the series of EH\textsubscript{2} was estimated to be 0.00004 Å (E = Si), 0.003 Å (E = Ge), 0.011 Å (E = Sn) and 0.044 Å (E = Pb). The same effect on the H–E–H bond angle in EH\textsubscript{2} is very small (<0.4°). More significant changes were induced on the dipole moments of EH\textsubscript{2} (0.02, 0.10, 0.25, and 0.69 D for E = Si, Ge, Sn, and Pb, respectively). An analysis of the electron density in EH\textsubscript{2} shows that relativistic effects reduce the electronegativity of the heavy atom. Relativistic effects decrease the calculated stretching frequencies.

Relativistic effects in heavy atoms are most important for inner-shell electrons. In \textit{ab initio} and DFT calculations these electrons are often treated through relativistic effective core potentials (RECP), also known as pseudopotentials. This approach is sometimes called quasirelativistic, because it accounts for relativity effects in a rather simplified scalar way. The use of pseudopotentials not only takes into account a significant part of the relativistic corrections, but also diminishes the computational cost.

Geometry optimization followed by vibrational frequency calculations is now common practice in quantum-chemical studies. Thus structural information as well as harmonic IR band positions are produced in most computational studies of CAs. A recent survey\textsuperscript{289} on the structure of symmetric dihalides EHal\textsubscript{2} (E = Si, Ge, Sn, Pb, Hal = F, Cl, Br, I) shows that \textit{ab initio} calculations reproduce nicely both bond lengths and bond angles\textsuperscript{289}. The observed variations in the structural parameters both down Group 14 and from fluoride to iodide are also well reproduced. The only notable exception is the bond angle in SnF\textsubscript{2}, where experiment and theory are in obvious disagreement\textsuperscript{289}. Arguments based on the trend established for other EX\textsubscript{2} dihalides favor the \textit{ab initio} value\textsuperscript{289}.

DFT-based methods are also proved to be quite reliable for calculations of both geometry and vibrational frequencies of CAs (see, for example, references\textsuperscript{341–343}).

In recent years IR frequency calculations of CAs have been carried out routinely not only for IR spectra interpretations itself, but also for reaction studies in order to verify the nature of stationary points found and for predicting vibrational band shifts upon complexation. Several papers\textsuperscript{342,344} were devoted to comparative study of the accuracy of various DFT functionals for calculating various properties of germynes, stannynes and plumbylenes. A complete set of EX\textsubscript{2} and EX\textsubscript{4} (E = C, Si, Ge, Sn, Pb; X = F, Cl, Br, I) molecules was studied by DFT methods using RECP\textsuperscript{342}. Semilocal and hybrid functionals and B3LYP especially were found to be superior to the Hartree–Fock level for calculating reaction energies. It should be noted that functionals which do not rely on empirical adjustments (like the currently most popular B3LYP) but on universal physical constraints (so-called nonempirical functionals) are expected to give more accurate predictions for all systems, including elements from the whole Periodic Table. One of these nonempirical density functionals, PBE\textsuperscript{345}, was tested extensively\textsuperscript{346,347} and compared with \textit{ab initio} G2 calculations in a study of germylene cycloaddition reactions\textsuperscript{348}.

B. Calculations of Electronic Transition Energies. Singlet–Triplet Energy Separations $\Delta E_{ST}$

According to calculations all experimentally known silylenes\textsuperscript{3}, germynes, stannynes and plumbylenes have a singlet ground state. Theory predicts a triplet ground state for SiLiH, SiLi\textsubscript{2}\textsuperscript{3}, GeHLi and GeLi\textsubscript{2}\textsuperscript{349,123}. These lithiated species are of interest from a purely theoretical point of view because they have little chance of being experimentally observed. Recent DFT calculations by Apeloig and coworkers\textsuperscript{125} predicted a triplet ground state for several organic silylenes bearing bulky substituents with $\alpha$-electropositive atoms with ($t$-Bu\textsubscript{3}Si)\textsubscript{2}Si being the most promising candidate for experimental verification (calculated singlet–triplet splitting $\Delta E_{ST} = -0.31$ eV). No such predictions were reported
for germylenes as well as for stannylenes and plumbylenes. Spectroscopic studies on singlet–triplet transitions are very limited compared to the wealth of data on singlet–singlet transitions. Quantum-chemical calculations were used to fill this gap. Most of these were performed for tri- and tetraatomic germylenes, stannylenes and plumbylenes. Below we briefly consider the results obtained using the most advanced methods. In discussing trends within the ER$_2$ series we restrict ourselves to data obtained at the same computational level. Values of $\Delta E_{ST}$ calculated at \textit{ab initio} and DFT levels are presented and compared with available experimental data in Table 17.

### Table 17. Calculated singlet–triplet splitting $\Delta E_{ST}$ (eV) in germylenes, stannylenes and plumbylenes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta E_{ST}$</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeH$_2$</td>
<td>1.05</td>
<td>MCSCF/ECP-DZP + SO</td>
<td>350</td>
</tr>
<tr>
<td>Ge$_2$</td>
<td>1.00</td>
<td>CAS + MCSCF RCI</td>
<td>351</td>
</tr>
<tr>
<td>GeH$_2$</td>
<td>0.99</td>
<td>MRD CI</td>
<td>352</td>
</tr>
<tr>
<td>GeH$_2$</td>
<td>0.93</td>
<td>CASSCF/TZ(2df,2p)</td>
<td>26</td>
</tr>
<tr>
<td>GeH$_2$</td>
<td>1.18</td>
<td>B3LYP/6–311G*</td>
<td>123</td>
</tr>
<tr>
<td>GeF$_2$</td>
<td>3.59 (3.79)$^a$</td>
<td>CCSD(T)/DZP</td>
<td>32</td>
</tr>
<tr>
<td>GeF$_2$</td>
<td>3.54</td>
<td>MRSDCI + Q</td>
<td>353</td>
</tr>
<tr>
<td>GeF$_2$</td>
<td>3.64</td>
<td>B3LYP/6–311G*</td>
<td>123</td>
</tr>
<tr>
<td>GeCl$_2$</td>
<td>2.61 (2.77)$^a$</td>
<td>CAS-MCSCF + MRCl</td>
<td>80</td>
</tr>
<tr>
<td>GeCl$_2$</td>
<td>2.76</td>
<td>B3LYP/6–311G*</td>
<td>123</td>
</tr>
<tr>
<td>GeBr$_2$</td>
<td>2.41 (2.36)$^a$</td>
<td>CAS-MCSCF + MRCl</td>
<td>80</td>
</tr>
<tr>
<td>GeBr$_2$</td>
<td>2.46</td>
<td>B3LYP/6–311G*</td>
<td>123</td>
</tr>
<tr>
<td>GeI$_2$</td>
<td>1.84 (1.86)$^a$</td>
<td>CAS-MCSCF + MRCl</td>
<td>80</td>
</tr>
<tr>
<td>GeHF</td>
<td>2.01</td>
<td>B3LYP/6–311G*</td>
<td>123</td>
</tr>
<tr>
<td>GeHCl</td>
<td>1.73</td>
<td>CAS-MCSCF + MRCl</td>
<td>80</td>
</tr>
<tr>
<td>GeHCl</td>
<td>1.83</td>
<td>B3LYP/6–311G*</td>
<td>123</td>
</tr>
<tr>
<td>GeHBr</td>
<td>1.64</td>
<td>CAS-MCSCF + MRCl</td>
<td>80</td>
</tr>
<tr>
<td>GeHBr</td>
<td>1.75</td>
<td>B3LYP/6–311G*</td>
<td>123</td>
</tr>
<tr>
<td>GeHI</td>
<td>1.51</td>
<td>CAS-MCSCF + MRCl</td>
<td>80</td>
</tr>
<tr>
<td>GeH$_2$I</td>
<td>$-0.20$</td>
<td>B3LYP/6–311G*</td>
<td>123</td>
</tr>
<tr>
<td>Ge$_2$I</td>
<td>$-0.26$</td>
<td>B3LYP/6–311G*</td>
<td>123</td>
</tr>
<tr>
<td>GeHMe</td>
<td>1.24</td>
<td>B3LYP/6–311G*</td>
<td>123</td>
</tr>
<tr>
<td>GeMe$_2$</td>
<td>1.33</td>
<td>B3LYP/6–311G*</td>
<td>123</td>
</tr>
<tr>
<td>GeMe$_2$</td>
<td>0.61</td>
<td>SCF/DZP</td>
<td>129</td>
</tr>
<tr>
<td>Ge(NH$_2$)$_2$</td>
<td>2.42</td>
<td>B3LYP/6–311G*</td>
<td>349</td>
</tr>
<tr>
<td>Ge(OH)$_2$</td>
<td>2.92</td>
<td>B3LYP/6–311G*</td>
<td>349</td>
</tr>
<tr>
<td>Ge = CH$_2$</td>
<td>2.50</td>
<td>CISD + Q/TZ(2df,2pd)</td>
<td>100</td>
</tr>
<tr>
<td>Ge = CH$_2$</td>
<td>2.56</td>
<td>B3LYP/6–311G*</td>
<td>123</td>
</tr>
<tr>
<td>SnH$_2$</td>
<td>1.03</td>
<td>MCSCF/ECP-DZP + SO</td>
<td>350</td>
</tr>
<tr>
<td>SnH$_2$</td>
<td>1.03</td>
<td>CAS + MCSCF RCI</td>
<td>351</td>
</tr>
<tr>
<td>SnF$_2$</td>
<td>3.40 (ca 2.48)$^a$</td>
<td>MRSDCI + Q</td>
<td>353</td>
</tr>
<tr>
<td>SnCl$_2$</td>
<td>2.60 (2.76)$^a$</td>
<td>CASSCF + MRSDCI</td>
<td>354</td>
</tr>
<tr>
<td>SnBr$_2$</td>
<td>2.41 (2.23)$^a$</td>
<td>CASSCF + MRSDCI</td>
<td>354</td>
</tr>
<tr>
<td>SnI$_2$</td>
<td>2.04 (2.11)$^a$</td>
<td>CASSCF + MRSDCI</td>
<td>354</td>
</tr>
<tr>
<td>PbH$_2$</td>
<td>1.70</td>
<td>MCSCF/ECP-DZP + SO</td>
<td>350</td>
</tr>
<tr>
<td>PbH$_2$</td>
<td>1.76</td>
<td>CAS + MCSCF RCI</td>
<td>351</td>
</tr>
<tr>
<td>PbF$_2$</td>
<td>4.08 (5.03)$^a$</td>
<td>MRSDCI + Q</td>
<td>353</td>
</tr>
<tr>
<td>PbCl$_2$</td>
<td>3.02</td>
<td>CASSCF + MRSDCI</td>
<td>354</td>
</tr>
<tr>
<td>PbBr$_2$</td>
<td>2.82</td>
<td>CASSCF + MRSDCI</td>
<td>354</td>
</tr>
<tr>
<td>PbI$_2$</td>
<td>2.33 (2.50)$^a$</td>
<td>CASSCF + MRSDCI</td>
<td>354</td>
</tr>
</tbody>
</table>

$^a$Experimental $\Delta E_{ST}$ values in parentheses are taken from Table 1.
The differences between the calculated and experimental $\Delta E_{ST}$ values are usually less than 10%, the only exceptions being SnF$_2$ with its large experimental uncertainty in $\Delta E_{ST}$ (see above) and PbF$_2$. It is worth noting the good accuracy achieved in DFT calculations for $\Delta E_{ST}$ of germynes and dihalostannylenes.

Halogen substitution in germynes, stannylenes and plumbylenes increases the singlet–triplet gap in the same way as in carbenes and silylenes. It is often implicitly assumed that $\Delta E_{ST}$ as well as many other characteristics should change down the Periodic Table in a monotonous way. Thus the expected order of $\Delta E_{ST}$ in the CA series is SiR$_2$ < GeR$_2$ < SnR$_2$ < PbR$_2$. The data of Table 17 show an interesting irregularity in going from germynes to stannylenes. Calculations by Gordon and coworkers on the EH$_2$ series predict a small increase (0.02 eV) in $\Delta E_{ST}$ on going from GeH$_2$ to SnH$_2$. Previous CAS+MCSCF RCI calculations by Balasubramanian gave a ‘normal’ ordering: $\Delta E_{ST}$(GeH$_2$) < $\Delta E_{ST}$(SnH$_2$), but with a very small (0.03 eV) difference between both values. For most dihalides EHHal$_2$ (Hal = F, Cl, Br) calculations at the MRSDCI level and available experimental data (Table 17) show an ‘inverted’ order $\Delta E_{ST}$(GeR$_2$) > $\Delta E_{ST}$(SnR$_2$). On going from SnR$_2$ to PbR$_2$ the $\Delta E_{ST}$ values grow sharply due to strong relativistic effects in PbR$_2$ (see below). The ‘special’ position of stannylenes in the series GeF$_2$, SnF$_2$ and PbF$_2$ was also mentioned while comparing some calculated ground state characteristics like IP, F−E−F bond angle, E−F overlap and E−F bond strengths (E = Ge, Sn, Pb).

The role of relativistic effects in low-lying states of GeH$_2$, SnH$_2$ and PbH$_2$ has been analyzed by Balasubramanian using CAS MCSCF computations followed by large-scale relativistic CI, which include the spin–orbit integrals. The spin–orbit mixings of the $^1A_1$ and $^3B_1(A_1)$ states in the relativistic CI wave functions of PbH$_2$ and SnH$_2$ were found to be quite significant, especially for PbH$_2$. This mixing lowers the $^1A_1$ state of PbH$_2$ by 1308 cm$^{-1}$ while the $^3B_1(A_1)$ state is raised by 1371 cm$^{-1}$ with respect to the $^3B_1$ state without the spin–orbit splitting. Thus relativistic effects increase $\Delta E_{ST}$ in PbH$_2$ by 0.33 eV, which accounts for half the difference between the respective values for SnH$_2$ and PbH$_2$ (Table 17). A similar conclusion was reached by Gordon and coworkers, who explored the coupling of the $^1A_1$ and $^3B_1$ states in EH$_2$ (E = C, Si, Ge, Sn and Pb) with a different approach. Relativistic potential energy surfaces were constructed using a spin–orbit coupling term. The relativistic effect does not affect the singlet-triplet gap in CH$_2$, SiH$_2$ and GeH$_2$ since the spin-orbit coupling in these molecules is relatively small. The relativistic $\Delta E_{ST}$ values in SnH$_2$ and PbH$_2$ are about 0.04 eV and 0.25 eV larger than the corresponding adiabatic ones.

Use of ab initio calculations to assign the singlet–singlet transitions in spectroscopic studies of small germynes, stannylenes and plumbylenes has now become standard practice for unsymmetric trimotomics HGeR (R = Cl, Br, I), ab initio calculated geometric parameters were used to resolve some problems in determining molecular structures for both the ground and excited states.

C. Reactions of R$_2$E

Quantum-chemical calculations have been used to probe all the characteristic chemical reactions of CAs (at least in the case of silylenes and germynes). The theoretical studies cover intramolecular rearrangements, insertions into $\sigma$-bonds, additions to double and triple bonds and dimerizations. Note that experimental data on the mechanisms of these reactions are still scarce and the results of theoretical studies are needed to understand the main trends in the reactivity of germynes, stannylenes and plumbylenes.
1. Intrinsic stability of R₂E. Intramolecular isomerizations

The reactions that eventually determine the existence of any species are intramolecular isomerizations and fragmentations. CAs are usually considered to be stable toward fragmentations, though numerical data on bond energies are scarce.

Calculated\textsuperscript{353,354,356} and experimental energies of dissociation reactions EX\textsubscript{2} → EX + X (E = Ge, Sn, Pb; R = H, F, Cl, Br, I) are collected in Table 18. Dissociation could produce EX and X in various low-lying electronic states. The bond energies ΔE in Table 18 correspond to the lowest electronic state of the products. The trends in bond energies for dihalides EX\textsubscript{2} are similar to those in tetrahalides EX\textsubscript{4}: ΔE decreases in the series Ge > Sn > Pb and, with the same E, in the series F > Cl > Br > I. The high values of ΔE (Table 18) support the general assumption of stability of the two coordinated Ge, Sn and Pb species toward dissociation. However, ionization could dramatically reduce (to 37.9 kcal mol\textsuperscript{−1} for GeH\textsubscript{2}\textsuperscript{+}) the strength of the E–H bond\textsuperscript{356}.

Intramolecular rearrangement of germynes, stannylenes and plumbylenes into a doubly bonded isomer can be another cause of their intrinsic instability. For example, in the matrix IR study of 1-germacyclopent-3-en-1,1-ylidene, direct experimental evidence was obtained for a photochemical germylene–germene isomerization\textsuperscript{105,357}.

Isomerizations in the ground state were studied theoretically only in the case of germynes. Early \textit{ab initio} calculations show methylgermylene to be more stable compared to germaethene by 23\textsuperscript{358}, 15\textsuperscript{359}, and 17.6\textsuperscript{360} kcal mol\textsuperscript{−1}. The most recent theoretical estimates of isomerization energies and activation barriers\textsuperscript{361} for reactions HGeEH\textsubscript{3} → H\textsubscript{2}Ge = EH\textsubscript{2} (E = C, Si, Ge) are given in Table 19.

<table>
<thead>
<tr>
<th>EX\textsubscript{2}</th>
<th>Calculated\textsuperscript{a}</th>
<th>Exp.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeH\textsubscript{2}(^1\textit{A}\textsubscript{1})</td>
<td>69.2</td>
<td>66</td>
<td>356</td>
</tr>
<tr>
<td>GeF\textsubscript{2}(^1\textit{A}\textsubscript{1})</td>
<td>116.2</td>
<td>116</td>
<td>353</td>
</tr>
<tr>
<td>SnF\textsubscript{2}(^1\textit{A}\textsubscript{1})</td>
<td>113</td>
<td>112.8</td>
<td>353</td>
</tr>
<tr>
<td>SnCl\textsubscript{2}(^1\textit{A}\textsubscript{1})</td>
<td>78.6</td>
<td></td>
<td>354</td>
</tr>
<tr>
<td>SnBr\textsubscript{2}(^1\textit{A}\textsubscript{1})</td>
<td>70.3</td>
<td></td>
<td>354</td>
</tr>
<tr>
<td>SnI\textsubscript{2}(^1\textit{A}\textsubscript{1})</td>
<td>57.4</td>
<td></td>
<td>354</td>
</tr>
<tr>
<td>PbF\textsubscript{2}(^1\textit{A}\textsubscript{1})</td>
<td>86</td>
<td>88.7</td>
<td>353</td>
</tr>
<tr>
<td>PbCl\textsubscript{2}(^1\textit{A}\textsubscript{1})</td>
<td>73.6</td>
<td>76.1</td>
<td>354</td>
</tr>
<tr>
<td>PbBr\textsubscript{2}(^1\textit{A}\textsubscript{1})</td>
<td>70.6</td>
<td></td>
<td>354</td>
</tr>
<tr>
<td>PbI\textsubscript{2}(^1\textit{A}\textsubscript{1})</td>
<td>57.9</td>
<td></td>
<td>354</td>
</tr>
</tbody>
</table>

\textsuperscript{a}At the CASSCF/MRSDCI + RECP level.

<table>
<thead>
<tr>
<th>E</th>
<th>HGeEH\textsubscript{3}</th>
<th>TS</th>
<th>H\textsubscript{2}Ge=EH\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.0</td>
<td>21.7</td>
<td>11.4</td>
</tr>
<tr>
<td>Si</td>
<td>0.0</td>
<td>9.8</td>
<td>3.2</td>
</tr>
<tr>
<td>Ge</td>
<td>0.0</td>
<td>14</td>
<td>−2.0</td>
</tr>
</tbody>
</table>
Calculations show that the nature of the substituent $\text{EH}_3$ has a dramatic effect on the germylene stability. Thus, both methyl- and silylgermylene are more stable than germene and germasilene, while germylgermylene is slightly less stable than digermene. The isomerization barriers in systems with $E = \text{Si, Ge}$ are not high, implying a facile thermal interconversion.

The relative stabilities of divalent and tetravalent $\text{EH}_2\text{O}_2$ ($E = \text{C, Si, Ge, Sn, Pb}$) isomers were calculated using the BLYP and B3LYP density functionals with DZP and TZ2P basis sets, as well as CCSD and CCSD(T) single-point energies at the BLYP/TZ2P optimized geometries\textsuperscript{362}. Of four structures considered, $\text{E(OH)}_2$ was found to be a global minimum with $E = \text{Si, Ge, Sn, Pb}$. The difference in energies between the $\text{E(OH)}_2$ and $\text{HE}(\equiv \text{O})\text{OH}$ isomers increases in the series C, Si, Ge, Sn, Pb: $-42$, $8$, $30$, $50$ and $74$ kcal mol$^{-1}$, respectively.

2. Dimerization

Experimental aspects of the dimerization of germynes, stannylenes and plumbylenes were discussed in a review\textsuperscript{363}. Relations between the characteristics of $\text{ER}_2$ ($E = \text{C, Si, Ge, Sn, Pb}$; $R = \text{H, F}$) and the structure of their dimers $\text{E}_2\text{R}_4$ were studied theoretically by Trinquier and coworkers\textsuperscript{364–367}.

A total of six $\text{E}_2\text{R}_4$ ($E = \text{C, Si, Ge, Sn, Pb}$; $R = \text{H, F}$) structures 1–6 were considered on the singlet potential energy surface (PES) at the CI + MP2/DZP//SCF/DZP level\textsuperscript{364,365}. The most important trend observed in this series was a decrease in stability of the olefin-type structure 1 manifested in trans-bent structure 2 of Ge$_2$H$_4$, and a dramatic increase in the stability of the trans-bridged structures 4, which become a global minimum for Sn$_2$R$_2$ and Pb$_2$R$_2$ (Table 20). For every $E$ and $R$, the cis-structures 3 and 5 were found to be less stable compared to the corresponding trans-isomers 2 and 4.

\[
\begin{align*}
(1) & \quad \begin{array}{c}
\text{E} = \text{C, Si, Ge, Sn, Pb; } R = \text{H, F}
\end{array} \\
(2) & \quad \begin{array}{c}
\text{E} = \text{C, Si, Ge, Sn, Pb; } R = \text{H, F}
\end{array} \\
(3) & \quad \begin{array}{c}
\text{E} = \text{C, Si, Ge, Sn, Pb; } R = \text{H, F}
\end{array} \\
(4) & \quad \begin{array}{c}
\text{E} = \text{C, Si, Ge, Sn, Pb; } R = \text{H, F}
\end{array} \\
(5) & \quad \begin{array}{c}
\text{E} = \text{C, Si, Ge, Sn, Pb; } R = \text{H, F}
\end{array} \\
(6) & \quad \begin{array}{c}
\text{E} = \text{C, Si, Ge, Sn, Pb; } R = \text{H, F}
\end{array}
\end{align*}
\]

A simple rule for the occurrence of trans-bent distorted structures 2 at homopolar double bonds was derived from an elementary molecular orbital model treating $\sigma - \pi$ mixing\textsuperscript{364} and a valence bond treatment\textsuperscript{367}. The relation between the singlet–triplet separation ($\Delta E_{\text{ST}}$) of the constituent $\text{ER}_2$ and $\sigma + \pi$ bond energy $E_{\sigma + \pi}$ was used as a criterion for determining the expected structure of $\text{R}_2\text{E} = \text{ER}_2$. The trans-bent geometry 2 occurs when $1/4E_{\sigma + \pi} \leq \Delta E_{\text{ST}} < 1/2E_{\sigma + \pi}$. The first part of the inequality determines the trans-bending distortion of the double bond, while the second part determines the existence of a direct $\text{E} = \text{E}$ link.
Singlet potential surfaces for \( \text{E}_2\text{H}_4 \) (\( \text{E} = \text{C}, \text{Si}, \text{Ge}, \text{Sn} \)) systems were explored through ab initio SCF + CI calculations with DZP (\( \text{E} = \text{C}, \text{Si}, \text{Ge} \)) and DZP-ECP (\( \text{E} = \text{Sn}, \text{Pb} \)) bases. In all cases except \( \text{E} = \text{C} \), the bridged structures were found to be true minima. Planar or trans-bent \( 2\text{HE}_2 \) species were found to be true minima in all cases except \( \text{E} = \text{Pb} \), where it is only a saddle point. The most stable structures of \( \text{Si}_2\text{H}_4 \) and \( \text{Ge}_2\text{H}_4 \) are 2, while the most stable structures of \( \text{Sn}_2\text{H}_4 \) and \( \text{Pb}_2\text{H}_4 \) are the trans-bridged forms 4 (Table 20). The cis-bridged form 5 with \( \text{E} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb} \) is less stable relative to the trans-bridged 4 by ca 2 kcal mol\(^{-1}\). The \( \text{H}_3\text{EEH} \) isomers 6 lie between these two symmetrical forms and are never found to be at the absolute minimum on the PES. The trans-bridged structures have a rather constant binding energy (Table 20) with respect to \( 2\text{EH}_2 \) (\( 1\text{A}_1 \)) whatever the nature of the \( \text{E} \) atom (30 ± 3 kcal mol\(^{-1}\)). The stability of the bridged structures may be due to the significant ionicity of the bridges \( \text{E}^+——\text{H}——\text{E}^+ \) in the planar four-membered rings.

The effect of fluorine substituents in \( \text{ER}_2 \) on the structures and stability of 1–6 dimers was studied theoretically at the same level. The planar \( \pi \)-bonded structure 1 was found to be a true minimum on the \( \text{C}_2\text{F}_4 \) PES, but a saddle point on the \( \text{Si}_2\text{F}_4, \text{Ge}_2\text{F}_4 \) and \( \text{Sn}_2\text{F}_4 \) surfaces. The isomer 6 was found to be a true minimum in all cases except when \( \text{E} = \text{Pb} \). Two nearly degenerate doubly bridged structures (cis-5 and trans-4) were found to be true minima in all cases except when \( \text{E} = \text{C} \). The preferred isomers are tetrafluoroethylene for \( \text{C}_2\text{F}_4 \), \( \text{F}_3\text{SiSiF} \) for \( \text{Si}_2\text{F}_4 \), and the trans-bridged structures for \( \text{Ge}_2\text{F}_4, \text{Sn}_2\text{F}_4 \) and \( \text{Pb}_2\text{F}_4 \).

With respect to two singlet \( \text{EF}_2 \) fragments, the bridged structures have binding energies that increase regularly from 3 kcal mol\(^{-1}\) (in \( \text{Si}_2\text{F}_4 \)) to 62 kcal mol\(^{-1}\) (in \( \text{Pb}_2\text{F}_4 \)), whereas bridged \( \text{C}_2\text{F}_4 \) is largely unbound (Table 20). The potential wells corresponding to the bridged structures were found to be rather flat, possibly inducing small distortions associated with very slight energy changes. The in-plane \( \text{C}_{2h} \rightarrow \text{C}_1 \) deformation found for the planar four-membered ring of 4 (\( \text{E} = \text{Ge}, \text{R} = \text{F} \)) is in agreement with its solid state geometry. A structural and energetic comparison was made for fluorine bridges in

<table>
<thead>
<tr>
<th>( \text{E} )</th>
<th>( \text{R} = \text{H}^a )</th>
<th>( \text{R} = \text{F}^b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C} )</td>
<td>-192</td>
<td>-53.6</td>
</tr>
<tr>
<td>( \text{Si} )</td>
<td>-53.7</td>
<td>-51.7</td>
</tr>
<tr>
<td>( \text{Ge} )</td>
<td>-32.7</td>
<td>-31.2</td>
</tr>
<tr>
<td>( \text{Sn} )</td>
<td>-14.7</td>
<td>-26.9</td>
</tr>
<tr>
<td>( \text{Pb} )</td>
<td>15</td>
<td>-28.7</td>
</tr>
</tbody>
</table>

aReference 365; bReference 366.
E$_2$F$_4$ and the hydrogen bridges in E$_2$H$_4$. Some results were compared with available spectroscopic data for the monomers and dimers of SnF$_2$ and PbF$_2$.

Being very important, these results still raise some questions and provide an incentive for future studies. One is the influence of electronic correlation on the geometry of 1–6. Use of more advanced theoretical methods is clearly needed. The conspicuous differences between the hydrogen and fluorine bridges need to be rationalized. The reaction path for interconversion of E$_2$R$_4$ isomers should also be explored. The stability of olefin-type structures H$_2$E≡EH$_2$ (E = Ge, Sn) was studied computationally at the SOCI/3-21G(d)/MCSCF/3-21G(d) level using a four-electron four-orbital full optimized reaction space$^{368}$. The ability of germanium to form π bonds was found to be higher than that of tin.

3. Insertions of CAs into H–H bond and their reverse reactions

Reaction with molecular hydrogen (equation 8) is the simplest example of CA insertion:

$$\text{EH}_2 + \text{H}_2 \rightarrow \text{EH}_4 \quad (E = \text{Si, Ge, Sn, Pb}) \quad (8)$$

Reactions 8 of silylene, SiH$_2$$^3$ and germylene, GeH$_2$$^{369}$ are potentially of great significance in CVD systems where H$_2$ is present. The kinetics of SiH$_2$ reactions with H$_2$ were investigated in detail$^3$, $^{370}$. For the same reaction of GeH$_2$ experimental estimates of the reaction rate were also reported$^{369}$, whereas for SnH$_2$ and PbH$_2$ no kinetic studies are available. From the theoretical point of view reaction 8 is not only a prototype of all EH$_2$ insertions into single bonds but also provides a good test system for assessing the accuracy of various quantum-chemical schemes used for studying mechanisms of CA reactions.

The PES of the SiH$_2$ insertion reaction 8 was studied extensively at various theoretical levels$^3$. It was established that account for electron correlation has a dramatic effect on both the shape of the PES and the barrier height$^{371}$. The MP2 calculations$^{371}$ reveal the presence of a weak pre-reaction complex on the PES of the SiH$_2$ + H$_2$ system. In a recent paper$^{369}$ calculations at the QCSD(T) and DFT B3LYP levels have shown that GeH$_2$ also forms a pre-reaction complex with H$_2$. Complexes and transition states for SiH$_2$ and GeH$_2$ insertions have similar structures (Figure 1). Some geometrical parameters of these structures are shown in Table 21. Results from the B3LYP and QCISD calculations are in good agreement with each other, not only for the stable species (reagents and products) but also for the transition states and complexes. The differences between silylene and germyle complexes (Table 21) are of the degree to be expected from the characteristic differences in Ge–H and Si–H bond lengths. The calculated energies are shown in Table 22.

---

**FIGURE 1.** The stationary points of reactions EH$_2$ + H$_2$ → EH$_4$; E = Si$^{369,371}$, Ge$^{369}$, calculated with B3LYP, MP2, and QCISD methods. The symmetry group is given below each structure.
TABLE 21. Geometric parameters $R$ (Å), $A$ (deg) of stationary points of reactions $EH_2 + H_2 \rightarrow EH_4$ ($E = Si, Ge$) calculated by various methods. For atom numbering see Figure 1

<table>
<thead>
<tr>
<th>Structure</th>
<th>Method</th>
<th>$R(E-H^1)$</th>
<th>$R(E-H^3)$</th>
<th>$R(E-H^4)$</th>
<th>$R(H^3-H^4)$</th>
<th>$A(H^1-E-H^2)$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complex</td>
<td>MP2$^a$</td>
<td>1.505</td>
<td>1.858</td>
<td>1.787</td>
<td>0.792</td>
<td>94</td>
<td>371</td>
</tr>
<tr>
<td>Complex</td>
<td>QCISD$^b$</td>
<td>1.509</td>
<td>1.936</td>
<td>1.859</td>
<td>0.783</td>
<td>95</td>
<td>369</td>
</tr>
<tr>
<td>Complex</td>
<td>B3LYP$^c$</td>
<td>1.513</td>
<td>1.870</td>
<td>1.778</td>
<td>0.805</td>
<td>95</td>
<td>369</td>
</tr>
<tr>
<td>Transition State</td>
<td>MP2$^a$</td>
<td>1.477</td>
<td>1.636</td>
<td>1.515</td>
<td>1.135</td>
<td>110</td>
<td>371</td>
</tr>
<tr>
<td>Transition State</td>
<td>QCISD$^b$</td>
<td>1.479</td>
<td>1.661</td>
<td>1.522</td>
<td>1.117</td>
<td>110</td>
<td>369</td>
</tr>
<tr>
<td>Transition State</td>
<td>B3LYP$^c$</td>
<td>1.484</td>
<td>1.647</td>
<td>1.522</td>
<td>1.140</td>
<td>110</td>
<td>369</td>
</tr>
<tr>
<td>Complex</td>
<td>QCISD$^b$</td>
<td>1.589</td>
<td>2.276</td>
<td>2.225</td>
<td>0.758</td>
<td>92</td>
<td>369</td>
</tr>
<tr>
<td>Complex</td>
<td>B3LYP$^c$</td>
<td>1.590</td>
<td>2.108</td>
<td>2.033</td>
<td>0.773</td>
<td>92</td>
<td>369</td>
</tr>
<tr>
<td>Transition State</td>
<td>QCISD$^b$</td>
<td>1.539</td>
<td>1.742</td>
<td>1.573</td>
<td>1.215</td>
<td>111</td>
<td>369</td>
</tr>
<tr>
<td>Transition State</td>
<td>B3LYP$^c$</td>
<td>1.539</td>
<td>1.721</td>
<td>1.568</td>
<td>1.250</td>
<td>111</td>
<td>369</td>
</tr>
</tbody>
</table>

$^a$MP2/6-311G(2d,2p); $^b$QCISD/6-311G(d,p); $^c$B3LYP/6-311++G(3df,2pd).

TABLE 22. Energies ($\Delta E + ZPE$) (kcal mol$^{-1}$) of stationary points on the PES of reaction 8

<table>
<thead>
<tr>
<th>EH$_2$</th>
<th>EH$_2$ + H$_2$</th>
<th>Complex</th>
<th>TS$^a$</th>
<th>XH$_4$</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH$_2$ 0.0</td>
<td>—</td>
<td>5.0</td>
<td>—57.7</td>
<td>CCSD(T)$^b$</td>
<td>372</td>
<td></td>
</tr>
<tr>
<td>SiH$_2$ 0.0</td>
<td>—</td>
<td>3.1</td>
<td>—55.2</td>
<td>MP4$^c$</td>
<td>371</td>
<td></td>
</tr>
<tr>
<td>SiH$_2$ 0.0</td>
<td>3.3</td>
<td>1.4 (0.1)</td>
<td>—53.9</td>
<td>B3LYP$^d$</td>
<td>369</td>
<td></td>
</tr>
<tr>
<td>SiH$_2$ 0.0</td>
<td>—</td>
<td>2.1</td>
<td>—54.0</td>
<td>QCISD(T)$^e$</td>
<td>369</td>
<td></td>
</tr>
<tr>
<td>SiH$_2$ 0.0</td>
<td>—</td>
<td>—0.5</td>
<td>—57.1</td>
<td>Exp.</td>
<td>369</td>
<td></td>
</tr>
<tr>
<td>GeH$_2$ 0.0</td>
<td>—</td>
<td>16.7</td>
<td>—38.8</td>
<td>CCSD(T)$^b$</td>
<td>372</td>
<td></td>
</tr>
<tr>
<td>GeH$_2$ 0.0</td>
<td>—</td>
<td>13.4 (12.1)</td>
<td>—35.7</td>
<td>B3LYP$^d$</td>
<td>369</td>
<td></td>
</tr>
<tr>
<td>GeH$_2$ 0.0</td>
<td>0.9</td>
<td>10.0 (12.6)</td>
<td>—38.2</td>
<td>QCISD(T)$^d$</td>
<td>369</td>
<td></td>
</tr>
<tr>
<td>GeH$_2$ 0.0</td>
<td>—</td>
<td>5.0</td>
<td>—35.1 to —40.2</td>
<td>Exp.</td>
<td>369</td>
<td></td>
</tr>
<tr>
<td>SnH$_2$ 0.0</td>
<td>—</td>
<td>37.9</td>
<td>—15.5</td>
<td>CCSD(T)$^b$</td>
<td>372</td>
<td></td>
</tr>
<tr>
<td>PbH$_2$ 0.0</td>
<td>—</td>
<td>53.0</td>
<td>—7.7</td>
<td>CCSD(T)$^b$</td>
<td>372</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Transition state. $\Delta E$ values given in parentheses are calculated at 298 K.
$^b$CCSD(T)/ECP DZP.
$^c$MP4(SDTQ)/6-311++G(3df,3pd)//MP2/6-311G(2d,2p).
$^d$B3LYP/6-311++G(3df,2pd)//B3LYP/6-311++G(3df,2pd).
$^e$QCISD(T)/6-311++G(3df,2pd)//QCISD(T)/6-311G(d,p).

The pre-reaction complex in the reaction of germylene with $H_2$ is only about half as strong (−0.9 to −1.3 kcal mol$^{-1}$) as that found for silylene (−2.1 to −3.3 kcal mol$^{-1}$) (Table 22). Both calculations and experiment$^{369}$ show that the insertion of GeH$_2$ into the H−H bond require overcoming a high activation barrier (calculation ca 12.1 kcal mol$^{-1}$, experiment ca 15–20 kcal mol$^{-1}$) in contrast to the reaction of SiH$_2$ with $H_2$, which in fact has no barrier. The calculations revealed no mechanistic differences in silylene and germylene insertions.

For heavier carbene analogs $EH_2$ theoretical results on reaction 8 are more scarce and experimental data are absent. The thermochemistry of reaction 8 for $E = Si, Ge, Sn, Pb$
at the DHF level was investigated by Dyall. Activation barriers for the whole series of elements (Si, Ge, Sn, Pb) were computed by Hein, Thiel and Lee at the CCSD(T)/ECP DZP level (Table 22).

No complexes between EH₂ and H₂ were reported in Reference, probably because a search for them was not attempted. The question of complex intermediacy in reactions of SnH₂ and PbH₂ with H₂ remains open. One could expect their formation, but it is reasonable to assume that the complexes should be weaker compared to those formed by SiH₂ and GeH₂.

The reaction energies (Figure 2) increase significantly on going from E = Si to Pb and even become positive for E = Pb (Table 22). This reflects the increased stability of E(II) relative to E(IV) compounds for heavier Group 14 elements. Although PbH₄ is thermodynamically unstable with regard to PbH₂ elimination, it should be long-lived under normal conditions because the corresponding barrier is as high as 45.3 kcal mol⁻¹.

4. Insertions into other σ bonds

The first and so far only study on the whole set of EH₂ insertions into the H—E bond of the methane analogs EH₄ (E = C, Si, Ge, Sn, Pb) (equation 9) has been reported by Trinquier.

\[
EH₂ + EH₄ \rightarrow E₂H₆ (E = Si, Ge, Sn, Pb)
\]  

Calculations were conducted at the MP4/DZP//HF/DZP level (ECP DZP for X = Sn, Pb). Some conclusions of this work should be considered with caution due to restrictions of the SCF approach used in the geometry optimization. The most important conclusion, supported for E = Si and Ge by recent calculations using more sophisticated
12. Spectroscopic studies and quantum-chemical calculations

TABLE 23. Relative energies\(^a\) (kcal mol\(^{-1}\)) for reactions EH\(_4\) + EH\(_2\) → E\(_2\)H\(_6\)

<table>
<thead>
<tr>
<th>Structure</th>
<th>Si(^b)</th>
<th>Si(^c)</th>
<th>Ge(^b)</th>
<th>Ge(^d)</th>
<th>Sn(^b, e)</th>
<th>Pb(^b, e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EH(_4) + EH(_2)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Complex</td>
<td>-4.8</td>
<td>-12.3</td>
<td>-5.1</td>
<td>-6.0</td>
<td>-9.8</td>
<td>-9.1</td>
</tr>
<tr>
<td>TS</td>
<td>-5.0</td>
<td>-11.6 (0.8(^f))</td>
<td>1.0</td>
<td>-4.0 (-1.2(^f))</td>
<td>2.6</td>
<td>11.0</td>
</tr>
<tr>
<td>E(_2)H(_6)</td>
<td>-53.3</td>
<td>-56.4 (-54.4(^f))</td>
<td>-41.4</td>
<td>-42.2 (-39.7(^f))</td>
<td>-33.6</td>
<td>-17.9</td>
</tr>
</tbody>
</table>

\(^a\)MP4/DZP//HF/DZP level without ZPE corrections. \(^b\)Reference\(^373\). \(^c\)Reference\(^374\). \(^d\)Reference\(^375\). \(^e\)RECP + DZP used. \(^f\)Experimental value.

methods (see below), is that reactions 9 involve formation of H-bridged intermediate complexes with syn orientation of the EH\(_2\) group. A complex with anti orientation does not exist at the HF level, although later it was found in the course of MP2/6-311G(d,p) calculations on reactions with E = Si\(^374\) and Ge\(^375\). The reaction exothermicity falls steeply and \(E_a\) rises on going from carbenes to their heavier analogs (Table 23).

Detailed kinetic and theoretical studies have been performed on the prototype GeH\(_2\) insertions into Si–H\(^376\) and Ge–H\(^375\) bonds (equations 10 and 11).

\[
\text{GeH}_2 + \text{SiH}_4 \rightarrow \text{H}_3\text{SiGeH}_3 \quad (10)
\]

\[
\text{GeH}_2 + \text{GeH}_4 \rightarrow \text{Ge}_2\text{H}_6 \quad (11)
\]

Both reactions show the characteristic pressure dependence of a third-body assisted association reaction. The high pressure rate constants, obtained by extrapolation, gave the Arrhenius equations 12 and 13.

\[
\log(k^\infty / \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}) = (-11.73 \pm 0.06) + (1.10 \pm 0.10 \text{ kcal mol}^{-1}) / RT \ln 10 \text{ (reaction 10)} \quad (12)
\]

\[
\log(k^\infty / \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}) = (-11.17 \pm 0.10) + (1.24 \pm 0.17 \text{ kcal mol}^{-1}) / RT \ln 10 \text{ (reaction 11)} \quad (13)
\]

The Arrhenius parameters are consistent with a moderately fast reaction occurring at approximately one-thirtieth (one-fifth with GeH\(_4\)) of the collision rate. Both reactions are somewhat slower compared to SiH\(_2\) insertion in silane (equation 14) which is known to be a fast, nearly collisionally controlled process\(^340\) (equation 15).

\[
\text{SiH}_2 + \text{SiH}_4 \rightarrow \text{Si}_2\text{H}_6 \quad (14)
\]

\[
\log(k^\infty / \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}) = (-9.91 \pm 0.04) + (0.79 \pm 0.17 \text{ kcal mol}^{-1}) / RT \ln 10 \quad (15)
\]
Ab initio MP2/6-311G(d,p) and DFT B3LYP/6-311++G(3df,2pd) calculations have shown that these reactions proceed with intermediate formation of weak H-bridged complexes C1 and C2 which rearrange into the final products via TS1 and TS2, respectively. The topology of the PES of these systems and the linking of pathways revealed in the calculations374–376 are shown in Figure 3.

The potential energy surfaces of the reactions in equations 10 and 11 are more complex than that of equation 14 and involve reaction path bifurcation and low symmetry structures in each channel. The salient features of structures of these complexes and TSs are shown in Figure 4.

Variations in interatomic distances for the complexes and transition states on going from E = Si to Ge are rather small and of the same magnitude as those found in the products. Energies of stationary points for reactions 9 and 10 are presented in Table 24. An additional feature of the complex C1 is its C1 symmetry, and the existence as left (C1l) or right (C1r) handed forms, which are separated by the very low (Ea = 0.4 Kcal mol$^{-1}$) rotational transition state TS0. A similar situation was found for transition state TS2. It also has a C1 symmetry, and possesses left (TS2l) and right (TS2r) handed forms divided by a low rotational maximum.

For reactions 10 and 11, calculations show the C1 + TS1 pathway is favored energetically over the C2 + TS2 route. However, the energy differences between the two pathways are less than 1 kcal mol$^{-1}$ for reaction 10 and ca. 4.2 for reaction 11. It suggests that both channels are probably operative for reaction 10 and only one (C1 + TS1) for reaction 11. The energies and Ea for the reactions calculated by G2 (reactions 10 and 11) and B3LYP/6-311++G(3df,2pd) (reaction 10) methods are in good agreement with experimental estimates (Table 24). The main difference between these reactions is that the transition states for reactions 10 and 11 are tighter than that for reaction 14, and the high pressure limiting A factors of reactions 10 and 11 are smaller by a factor of approximately 10 than that of reaction 14.

Other insertion reactions of germylenes, stannylenes and plumblylenes studied theoretically so far are mostly limited to germylenes. Su and Chu123,349 have reported DFT B3LYP/6-311G* calculations on reactions of GeH2, Ge=CH2, GeHMe, GeMe2, GeHF, GeF2, GeHCl, GeCl2, GeHBr, GeBr2, GeHLi and GeLi2 with methane. All the germylenes react with initial formation of a loose donor–acceptor complex, followed by a high-energy three-membered-ring TS and an insertion product. Complexation energies $\Delta E_{cp}$ are less

![Figure 3. Topology of the potential energy surfaces for the reactions GeH2 + EH4 → H3GeEH3 (E = Si, Ge) and SiH2 + SiH4 → Si2H6, from MP2/6-311G(d,p) and B3LYP/6311++G(3df,2pd) (E = Si) calculations374–376. See text for definitions of left(l) and right(r) handed forms and Figure 4 for their structures](image-url)
12. Spectroscopic studies and quantum-chemical calculations

![Diagrams of GeH2 + EH4 → H3EGeH3 (E = Si, Ge) potential energy surfaces.](image-url)

FIGURE 4. Ab initio MP2/6-311G(d,p) calculated geometries of the local minima and TSs on the GeH2 + EH4 → H3EGeH3 (E = Si, Ge) potential energy surfaces. Point groups are given beside the structure label. Interatomic distances are in Å with values for E = Ge given in parentheses. The migrating H atom is marked by an asterisk. See text for definitions of left(l) and right(r) handed forms.

than 1 kcal mol⁻¹ (Table 25), the only exception being GeF2 (ΔEcp = 1.4 kcal mol⁻¹). Activation barriers $E_a$ are high. Even for the very reactive germynes GeH₂ and GeMe₂, the calculations gave $E_a$ values of 33.2 and 39.1 kcal mol⁻¹ (Table 25). These high $E_a$ values explain why germynes usually do not insert into C–H bonds⁵. A configuration mixing model based on the theory of Pross³⁷⁷ and Shaik³⁷⁸ has been used to interpret the barrier origin.³⁴⁹ It suggests that the singlet–triplet splitting $ΔE_{ST}$ in the GeXY species can be used as a guide to predict its activity in insertion reactions. For the series GeH₂, Ge≡CH₂, GeHMe, GeMe₂, GeH₂F, Ge₂F₂, GeHCl, GeCl₂, GeHBr and GeBr₂, a linear correlation between the calculated $E_a$ and $ΔE_{ST}$ (equation 16) was found³⁴⁹.

$$E_a = 0.818ΔE_{ST} + 13.5$$ (10 points, $R^2 = 0.94$)  

Likewise, a linear correlation between $E_a$ and the reaction enthalpy $ΔH$, also obtained at the same level of theory (Table 25), is given in equation 17.

$$E_a = 1.29ΔH + 69.6$$ (10 points, $R^2 = 0.95$)  

It was concluded³⁴⁹ that electronic rather than steric factors play a decisive role in determining the chemical reactivity of the germynes.
TABLE 24. *Ab initio* G2 and DFT\(^a\) calculated and experimental relative energies (kcal mol\(^{-1}\)) of stationary points of the PES for GeH\(_2\) + EH\(_4\) → H\(_3\)EGeH\(_3\) (E = Si, Ge) reactions

<table>
<thead>
<tr>
<th></th>
<th>GeH(_2) + EH(_4)</th>
<th>Complex C1</th>
<th>TS0(Rot)</th>
<th>TS1</th>
<th>Complex C2</th>
<th>TS2</th>
<th>H(_3)EGeH(_3)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>E = Si</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ΔE(0 K)</td>
<td>0.0</td>
<td>−6.0 (−4.6)</td>
<td>−5.7 (−4.5)</td>
<td>−1.2 (1.6)</td>
<td>−5.1 (−3.6)</td>
<td>−0.2 (2.1)</td>
<td>−35.7 (−34.8)</td>
<td>376</td>
</tr>
<tr>
<td>ΔE(298 K)</td>
<td>0.0</td>
<td>−6.2 (−4.8)</td>
<td>−6.3 (−5.1)</td>
<td>−1.6 (1.3)</td>
<td>−5.1 (−3.5)</td>
<td>−1.0 (1.4)</td>
<td>−36.2 (−35.2)</td>
<td>376</td>
</tr>
<tr>
<td>ΔH(298 K)</td>
<td>0.0</td>
<td>−6.8 (−5.4)</td>
<td>−6.9 (−5.7)</td>
<td>−2.2 (0.7)</td>
<td>−5.7 (−4.1)</td>
<td>−1.6 (0.8)</td>
<td>−36.8 (−35.8)</td>
<td>376</td>
</tr>
<tr>
<td>Experimental</td>
<td></td>
<td>−1.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E = Ge</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>−35.3</td>
<td>376</td>
</tr>
<tr>
<td>ΔE(0 K)</td>
<td>0.0</td>
<td>−6.0</td>
<td>−5.9</td>
<td>−4.0</td>
<td>−4.7</td>
<td>0.2</td>
<td>−42.2</td>
<td>375</td>
</tr>
<tr>
<td>Experimental</td>
<td>0.0</td>
<td>−1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(−39.7 ± 3)</td>
<td>375</td>
</tr>
</tbody>
</table>

\(^a\)B3LYP/6-311++G(3df,2pd) values are in parentheses.
A comparison of Arduengo-type carbene, silylene and germylene 7–9 insertion into the C–H bond of methane has been carried out using calculations at the B3LYP/6-31G* and CCSD(T)/6-31G**/B3LYP/6-31G* levels. These reactions also involve formation of pre-reaction complexes. The main energetic characteristics of the stationary points found are given in Table 26. The calculated singlet–triplet gap $\Delta E_{ST}$ in 7–9 is very high (3.6–2.2 eV) and shows an opposite trend compared to the $\Delta E_{ST}$ of the parent species (CH$_2$, SiH$_2$ and GeH$_2$), as well as to those of CAs with $\pi$-donor substituents [C(NH$_2$)$_2$, Si(NH$_2$)$_2$ and Ge(NH$_2$)$_2$]. This peculiarity is related to the unusual nature of the highest occupied MO of 7–9 detected by photoelectron spectroscopy (see Section IX). The activation barriers $E_a$ of insertions are also very high and obey the expected order C < Si < Ge. There is good agreement between the B3LYP and CCSD(T) values.

Insertion of GeMe$_2$ into the C–H, Si–H, N–H, P–H, O–H, S–H, F–H and Cl–H bonds was studied by DFT B3LYP/6-311G* and ab initio MP2/6-311G* methods. Results of CCSD(T) calculations for the same set of reactions were reported. All the reactions include an initial formation of a donor–acceptor complex, followed by the TS leading to the insertion product. The agreement between the geometries of the stationary points calculated at the MP2 and B3LYP levels is reasonably good for most structures. Energies of stationary points along the reaction paths, which are given in Table 27, show that the complexation energies range from 25 to ca 1 kcal mol$^{-1}$ and decrease in the order NH$_3$ > H$_2$O > PH$_3$ > H$_2$S ~ HF > HCl > SiH$_4$ ~ CH$_4$. It is noteworthy that the DFT B3LYP calculations systematically give lower (by ca 2.5 kcal mol$^{-1}$) complexation

---

**TABLE 25.** B3LYP/6-311G* calculated relative energies (kcal mol$^{-1}$) of stationary points in the reaction GeXY + CH$_4$ → HGeMeXY.

<table>
<thead>
<tr>
<th>GeXY</th>
<th>$\Delta E_{\text{comp}}^a$</th>
<th>$\Delta E_{\text{TS}}^b$</th>
<th>$\Delta H^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeH$_2$</td>
<td>-0.94</td>
<td>+33.2</td>
<td>-28.0</td>
</tr>
<tr>
<td>Ge=CH$_2$</td>
<td>-0.05</td>
<td>+58.0</td>
<td>-5.3</td>
</tr>
<tr>
<td>GeHLi</td>
<td>-0.45</td>
<td>+24.6</td>
<td>-28.6</td>
</tr>
<tr>
<td>GeL$_2$</td>
<td>+0.37</td>
<td>+29.3</td>
<td>-17.9</td>
</tr>
<tr>
<td>GeHMe</td>
<td>-0.19</td>
<td>+35.8</td>
<td>-26.8</td>
</tr>
<tr>
<td>GeMe$_2$</td>
<td>-0.02</td>
<td>+39.1</td>
<td>-25.1</td>
</tr>
<tr>
<td>GeHF</td>
<td>-0.98</td>
<td>+48.6</td>
<td>-17.1</td>
</tr>
<tr>
<td>GeF$_2$</td>
<td>-1.40</td>
<td>+77.7</td>
<td>+0.4</td>
</tr>
<tr>
<td>GeHCl</td>
<td>-0.23</td>
<td>+48.1</td>
<td>-15.6</td>
</tr>
<tr>
<td>GeCl$_2$</td>
<td>-0.09</td>
<td>+70.0</td>
<td>-0.1</td>
</tr>
<tr>
<td>GeHBr</td>
<td>-0.17</td>
<td>+48.2</td>
<td>-14.5</td>
</tr>
<tr>
<td>GeBr$_2$</td>
<td>+0.02</td>
<td>+68.3</td>
<td>+1.3</td>
</tr>
</tbody>
</table>

$^a$The stabilization energy of the precursor complex relative to GeXY + CH$_4$.

$^b$Energy of the TS relative to GeXY + CH$_4$.

$^c$The reaction enthalpy.

(7) E = C, (8) E = Si, (9) E = Ge
TABLE 26. Singlet–triplet splittings $\Delta E_{ST}$/eV in 7–9, and relative energies$^a$ (kcal mol$^{-1}$) for the process 7 (8 and 9) + CH$_4$ → Complex → TS → Product$^{379}$

<table>
<thead>
<tr>
<th>N</th>
<th>N</th>
<th>$\Delta E_{ST}$</th>
<th>$\Delta E_{\text{comp}}^b$</th>
<th>$\Delta E_{\text{ts}}^c$</th>
<th>$\Delta H^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>3.66 (3.58)</td>
<td>$-2.0$ (−2.0)</td>
<td>62.2 (56.4)</td>
<td>$-10.7$ (−8.7)</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2.83 (2.59)</td>
<td>$-0.5$ (−0.1)</td>
<td>75.8 (77.8)</td>
<td>$-1.2$ (−1.0)</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>2.34 (2.19)</td>
<td>$-2.9$ (−1.6)</td>
<td>82.9 (86.5)</td>
<td>13.0 (19.4)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$At the CCSD(T)/6-31G**//B3LYP/6-31G* and B3LYP/6-31G* (in parentheses) levels.
$^b$The stabilization energy of the precursor complex, relative to the corresponding reactants.
$^c$The energy of the TS, relative to the corresponding reactants.
$^d$The energy of the product, relative to the corresponding reactants.

TABLE 27. Relative energies (kcal mol$^{-1}$) for the process GeMe$_2$ + H-XH$_{n-1}$ → Complex → TS → Me$_2$Ge(H)XH$_{n-1}$ (X = C, N, O, F, Si, P, S, and Cl; n = 1–4) calculated by using the MP2/6-311G$^*$ and B3LYP/6-311G$^*$ (in parentheses) methods$^{343}$

<table>
<thead>
<tr>
<th>XH$_n$</th>
<th>GeMe$_2$ + XH$_n$</th>
<th>$\Delta E_{\text{comp}}^a$</th>
<th>$\Delta E_{\text{ts}}^b$</th>
<th>$\Delta H^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>0.0 (0.0)</td>
<td>$-1.1$ (−0.02)</td>
<td>35.6 (39.1)</td>
<td>$-32.6$ (−25.1)</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>0.0 (0.0)</td>
<td>$-25.0$ (−20.8)</td>
<td>22.7 (25.1)</td>
<td>$-40.4$ (−33.3)</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.0 (0.0)</td>
<td>$-16.2$ (−13.9)</td>
<td>15.1 (14.8)</td>
<td>$-50.2$ (−45.1)</td>
</tr>
<tr>
<td>HF</td>
<td>0.0 (0.0)</td>
<td>$-7.1$ (−7.2)</td>
<td>9.6 (7.4)</td>
<td>$-61.2$ (−59.1)</td>
</tr>
<tr>
<td>SiH$_4$</td>
<td>0.0 (0.0)</td>
<td>$-2.2$ (−0.6)</td>
<td>11.4 (15.7)</td>
<td>$-41.3$ (−33.8)</td>
</tr>
<tr>
<td>PH$_3$</td>
<td>0.0 (0.0)</td>
<td>$-14.1$ (−9.0)</td>
<td>8.1 (11.7)</td>
<td>$-46.1$ (−37.4)</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>0.0 (0.0)</td>
<td>$-9.7$ (−6.1)</td>
<td>3.9 (6.0)</td>
<td>$-54.9$ (−45.8)</td>
</tr>
<tr>
<td>HCl</td>
<td>0.0 (0.0)</td>
<td>$-3.7$ (−1.6)</td>
<td>2.5 (1.2)</td>
<td>$-64.2$ (−56.4)</td>
</tr>
</tbody>
</table>

$^a$The stabilization energy of the precursor complex, relative to reactants.
$^b$The energy of the TS, relative to the corresponding reactants.
$^c$The energy of the product, relative to the corresponding reactants.

energies compared to MP2. All germylene insertions into X–H bonds occur in a concerted manner via a three-membered-ring TS, and the stereochemistry at the heteroatom X center is preserved. Differences in $E_a$ calculated by both methods are of various signs with an average absolute deviation of 2.8 kcal mol$^{-1}$. The MP2 calculated $E_a$ increase in the order of substrates: HCl < H$_2$S < PH$_3$ < HF < SiH$_4$ < H$_2$O < NH$_3$ < CH$_4$. For all the substrates B3LYP calculations give lower exothermicity of insertion compared to the MP2 values (by ca 6.9 kcal mol$^{-1}$). In spite of some differences in the absolute values the general trend in $E_a$ and $\Delta H$ obtained by both methods is essentially the same. The larger the atomic number of the heteroatom X in a given row, the easier the insertion reaction of XH$_n$ hydrides occurs and the larger its exothermicity (Table 27). These results indicate that the B3LYP method could be recommended for investigations of molecular geometries, electronic structures and kinetic features of the germylene reactions.

MNDO calculations on insertion reactions of Me$_2$Sn into Cl–Sn and I–C bonds were reported by Dewar and coworkers$^{381}$. Two alternative pathways including concerted carbene-like insertion (a) and nonconcerted radical two-step insertion (b) were investigated.
In reactions of Me₂Sn with ClSnRMe₂ a concerted mechanism (equation 18a) is favored ($E_a = 10.1$ and 14.2 kcal mol$^{-1}$ for R = Cl and Me, respectively) over a radical route (equation 18b), $E_a = 20.0$ kcal mol$^{-1}$ (R = Cl) and 28.4 kcal mol$^{-1}$ (R = Me). In the case of MeI the situation is reversed: a radical mechanism (equation 19b) ($E_a = 33.0$ kcal mol$^{-1}$) is preferred over a carbene-like insertion (equation 19a, $E_a = 42.3$ kcal mol$^{-1}$).

5. Cycloadditions

The classical barrier heights and the thermodynamics of cycloaddition of EX₂ (E = C, Si, Ge, Sn; X = H, F) to acetylene were calculated by Boatz, Gordon and Sita using MP2/3-21G(d)//HF/3-21G(d) energies. The nature of the ring bonding in cyclo-(EX₂C₂H₂) was investigated via analysis of the total electron density and was found to have little or no $\pi$-complex character. The exothermicity of the cycloaddition falls dramatically in the order C > Si > Ge > Sn for both EH₂ and EF₂ species. For GeF₂ and SnF₂ the reactions even become endothermic ($\Delta E = 14.4$ and 16.5 kcal mol$^{-1}$). Cycloaddition of all hydrides EH₂ proceeds without a barrier. Fluorine substitution induces substantial barriers to the formation of all the corresponding heterocyclopropenes.

Horner, Grev and Schaefer compared the energies of the decomposition reactions cyclo-EH₂XH₂YH₂ → EH₂ + H₂X=YH₂ for E, X, Y = C, Si, Ge using results of CCSD/DZP calculations. Of the ten rings studied, germirane (cyclo-GeH₂CH₂CH₂) was by far the least stable with respect to dissociation, being only about 20 kcal mol$^{-1}$ more stable than the isolated GeH₂ + H₂C=CH₂. It was concluded that the known difficulties in germirane synthesis have a thermochemical origin. It agrees with the fact that the only known example of successful synthesis of germirane involved a special type of olefin and a Lappert-type germylene. The three-membered ring decomposition enthalpy can be predicted semiquantitatively from a simple model using the strain energies along with the single bond dissociation energies, $\pi$-bond energies and divalent state stabilization energies.

DFT B3LYP/6-31G* calculations have been performed on the potential energy surfaces for cycloaddition of germylenes GeH₂, GeMe₂, Ge(NH₂)₂, Ge(OH)₂, GeF₂, GeCl₂, GeBr₂ and Ge=CH₂ to the C=C double bond of ethylene. Unlike the case of silylene (SiH₂, SiF₂ and SiCl₂) additions, a $\pi$-complex intermediate is formed between...
germylenes and ethylene. Of the germynes studied, only reactions of GeH₂ and GeMe₂ are feasible from both a kinetic and a thermodynamic point of view (Table 28). Formation of three-membered rings by other germynes is an endothermic process. The origin of barrier heights was discussed using the aforementioned configuration mixing model of Pross and Shaik. A linear correlation was found between calculated $E_a$ and the singlet–triplet splitting $\Delta E_{ST}$ (equation 20 and Table 28).

$$E_a = 0.906 \Delta E_{ST} - 40.7 \quad (8 \text{ points}, R^2 = 0.923)$$ (20)

Calculations of the PES of GeH₂ cycloaddition to ethylene at the MP2/6-31G(d)//RHF/6–31G(d) level were followed by computation of kinetic properties at different temperatures using statistical thermodynamics and transition state theory. The reaction was shown to proceed without formation of an intermediate complex, which is in agreement with the results of Anwari and Gordon, but in clear disagreement with DFT B3LYP/6–31G(d) calculations. Calculations on this prototype reaction using more rigorous methods are needed.

Dihalogermylenes and dihalostannylenes are supposed to be rather inert species, yet MNDO calculations predict a low activation barrier ($E_a = 19.5 \text{ kcal mol}^{-1}$) for the cheletropic addition of Br₂Sn to butadiene with formation of cyclo-Br₂SnC₄H₆ (equation 21).

$$\text{Br}_2\text{Sn} + \text{SnBr}_2 \rightarrow \text{Br}_2\text{SnC}_4\text{H}_6$$ (21)

6. Miscellaneous

Ab initio MP2 calculations with DZ quality basis sets were performed on the reactions of C₂H₄ with GeHₙ (n = 0–3). Single-point calculations at the QCISD(T)/6-311G(3df,2p) level were performed. The results were used to speculate on the mechanisms of reactions occurring during radiolysis of germane/ethylene mixtures.

Formation of GeF₂ in reactions between GeF₄ and Si₂H₆ was studied by CCSD(T)//B3LYP calculations using the basis set of the DZP quality. These reactions are related...
12. Spectroscopic studies and quantum-chemical calculations

to the mechanism of silane activation in the low-temperature thermal CVD deposition of Ge films from a GeF$_4$ source. Several reactions between GeF$_4$ and SiH$_4$/Si$_2$H$_6$ were investigated. The most important are those leading to SiH$_3$GeF$_3$, which could easily decompose ($E_a = 31.9$ kcal mol$^{-1}$) into SiH$_3$F and GeF$_2$. Disilane was suggested to be an efficient activator because it more easily produces SiH$_3$GeF$_3$ compared to silane.

High level ab initio calculations have been reported on the PES of singlet SiH$_2$ and GeH$_2$ reactions with water, methanol, ethanol, dimethyl ether and trifluoromethanol$^{391}$. Besides the classical route for EH$_2$ (E = Si, Ge) insertion into X\(^{-}\)-O (X = H, C) bonds via 1,2 hydrogen atom shift reaction (equation 22), two new reaction channels (equations 23 and 24) were identified on each PES, except for reactions involving dimethyl ether. Equations 23 and 24 display routes for H$_2$ elimination, following the initial formation of an association complex.

The processes via transition states 12 and 13 have activation energies comparable with that of the classical route via TS 11 (Table 29). For reactions involving SiH$_2$ and water, a simple activated complex theory analysis predicts that these newly identified reaction channels (equations 23 and 24) are equally likely to be accessed as that in equation 22. For reactions involving GeH$_2$ and water, a similar analysis predicts that equations 23 and 24 will occur in preference to the 1,2 hydrogen shift in 10. Indeed, the room-temperature rate constant for H$_2$ elimination from the germanium complex 10 was predicted to be approximately 5 orders of magnitude larger than for the H atom migration channel.
TABLE 29. Relative energies (kcal mol$^{-1}$) of stationary points$^a$ on the PES of the reaction $\text{H}_2\text{E} + \text{ROH}$ calculated at the MP2/6-311++G(d,p)//MP2/6-311++G(d,p) level$^{391}$

<table>
<thead>
<tr>
<th>Reagents</th>
<th>$\text{SiH}_2 + \text{H}_2\text{O}$</th>
<th>$\text{SiH}_2 + \text{CH}_3\text{OH}$</th>
<th>$\text{SiH}_2 + \text{C}_2\text{H}_5\text{OH}$</th>
<th>$\text{SiH}_2 + \text{CF}_3\text{OH}$</th>
<th>$\text{GeH}_2 + \text{H}_2\text{O}$</th>
<th>$\text{GeH}_2 + \text{CH}_3\text{OH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>00</td>
<td>0.0</td>
<td>(0.0)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>10</td>
<td>−12.7</td>
<td>(−11.6)</td>
<td>−18.1</td>
<td>−18.8</td>
<td>−6.6</td>
<td>−11.0</td>
</tr>
<tr>
<td>11</td>
<td>9.2</td>
<td>(12.2)</td>
<td>3.0</td>
<td>2.1</td>
<td>9.3</td>
<td>20.2</td>
</tr>
<tr>
<td>12</td>
<td>9.2</td>
<td>(11.4)</td>
<td>3.8</td>
<td>3.1</td>
<td>7.0</td>
<td>13.5</td>
</tr>
<tr>
<td>13</td>
<td>8.8</td>
<td>(11.1)</td>
<td>3.6</td>
<td>2.7</td>
<td>6.8</td>
<td>13.5</td>
</tr>
<tr>
<td>14</td>
<td>−70.3</td>
<td>(−66.0)</td>
<td>−72.7</td>
<td>−73.1</td>
<td>−40.9</td>
<td>−42.8</td>
</tr>
<tr>
<td>15 + $\text{H}_2$</td>
<td>−26.6</td>
<td>(−25.2)</td>
<td>−30.6</td>
<td>−31.3</td>
<td>−16.7</td>
<td>−19.6</td>
</tr>
<tr>
<td>16 + $\text{H}_2$</td>
<td>−26.8</td>
<td>(−25.4)</td>
<td>−30.0</td>
<td>−30.8</td>
<td>−16.5</td>
<td>−19.0</td>
</tr>
</tbody>
</table>

$^a$ZPE correction included.

$^b$Values given in parentheses are calculated at the QCISD(T)/6-311++G(d,p)//QCISD(T)/6-311++G(d,p) level.

D. Complexes with Lewis Bases

In this section we consider the results of calculations devoted to studying properties of donor–acceptor complexes between CAs and Lewis bases.

Complexes of $\text{EH}_2$ ($\text{E} = \text{Si, Ge, Sn}$) with donor molecules, $\text{AH}_3$ ($\text{A} = \text{N, P, As, Sb, Bi}$) and $\text{AH}_2$ ($\text{A} = \text{O, S, Se, Te}$), were studied by Schöller and Schneider$^{189}$ with $ab\ initio$ MP2 calculations using RECP and basis sets of DZP quality. Association energies in the range of 15–30 kcal mol$^{-1}$ were found. They decrease in the order $\text{SiH}_2 > \text{GeH}_2 > \text{SnH}_2$. The population analysis indicates for $\text{NH}_3$ and $\text{BiH}_3$ only a weak bonding toward the $\text{EH}_2$ fragment while the higher homologs with $\text{A} = \text{P, As, Sb}$ form 1,2-dipolar ylide structures. A dual parameter relationship between (a) the HOMO energies of the donor (n-orbital of the $\text{AH}_3$ unit, n, p orbitals for $\text{AH}_2$) and (b) the known covalent bond energies versus the binding energies of the donor–acceptor complexes was examined and found to describe satisfactorily the essential features of the stabilities of the donor–acceptor structures.

Nowek and Leszczynski used $ab\ initio$ post-Hartree–Fock and DFT B3LYP calculations to resolve the problem of the structure of the $\text{H}_2\text{Ge} \cdots \text{OH}_2$ complex$^{274}$. The molecular geometries of the nonplanar 17 ($C_1$) and planar 18 ($C_s$) conformers were optimized at the DFT and MP2 levels of theory using TZP and TZ2P basis sets. The nonplanar complex 17 with a Ge\cdots O distance of 2.214 Å (MP2), 2.268 Å (B3LYP) corresponds to a global minimum while complex 18 was found to be very weakly bound (if bound at all).

```
H   H
\   /Ge
|   |-----O\H
\ H
```

(17)

```
H   H
\   /Ge
|   |-----H
\ H
```

(18)

Calculated interaction energies (corrected for the basis set superposition error and ZPE) are relatively large and amount to 9.8 kcal mol$^{-1}$ by B3LYP and 8.9 kcal mol$^{-1}$ by CCSD(T) methods. Harmonic vibration frequencies calculated for monomers and the complex are in reasonable agreement with experimental data$^{241}$. Agreement is good for IR band shifts due to complexation and isotopic substitution.

Formation of complexes with electron donors (Lewis bases) seems to be an ubiquitous feature of all CAs. Dihalostannylenes and dihaloplumbylenes which are inert in most
of the characteristic carbone analog reactions form complexes with such weak electron donors as heptyne, methyl chloride and even dinitrogen (see above). Quantum-chemical calculations in Nefedov’s group were used to assign the IR bands of these complexes recorded in low-temperature Ar matrices and to get information on their structure and stability.\(^{275,278,279,281}\)

Semiempirical AM1 and PM3 calculations on the reaction of SnF\(_2\) with hept-1-yne\(^{278,279}\) show the formation of \(\pi\)-complex 19 (Figure 5). Its stability was estimated as 7.4 (AM1) and 9.1 (PM3) kcal mol\(^{-1}\). In agreement with the study of the SnF\(_2\) reaction with acetylene\(^{382}\), the cycloaddition of SnF\(_2\) to the triple bond of hept-1-yne was calculated to be highly endothermic. PM3 calculations of the dimer Sn\(_2\)F\(_4\) give the bridged structure 4\(^{279}\), which agrees with spectral data.

The PES of the system SnF\(_2\) + CH\(_3\)Cl was studied by \textit{ab initio} MP2/3-21G(d)\(//\)HF/3-21G(d) and PM3 methods\(^{281}\). Calculations have shown that the reaction between SnF\(_2\) and CH\(_3\)Cl results in the formation of a donor–acceptor complex 20 (Figure 5). The orientation of SnF\(_2\) and CH\(_3\)Cl in 20 is determined by the dipole–dipole interaction. The complexation energy is 14.2 kcal mol\(^{-1}\) (MP2) and 15.7 kcal mol\(^{-1}\) (PM3). Rearrangement of 20 into the insertion product MeSnF\(_2\)Cl is favorable from an energetic point of view \([\Delta E = -47.4\) kcal mol\(^{-1}\) (MP2) and \(-15.8\) kcal mol\(^{-1}\) (PM3)] but the activation energy is very high: 47.0 (MP2) and 34.6 kcal mol\(^{-1}\) (PM3), so that this reaction does not occur under the experimental conditions\(^{281}\). Quantum-chemical calculations were used to interpret the IR spectrum of the complex recorded in Ar matrix.

\textit{Ab initio} MP2/3-21G(d2)\(//\)HF/3-21G(d2) calculations on the SnF\(_2\) + N\(_2\) and SnF\(_2\) + 2N\(_2\) systems\(^{275}\) have revealed the presence of the local minima corresponding to complexes 21 and 22 (Figure 6). Both are stabilized by interaction of the lowest unoccupied p-MO (LUMO) of SnF\(_2\) with the lone pair of N\(_2\) (p,p interaction). Alternative structures of complexes stabilized by interaction of the p-LUMO of stannylene with the occupied \(\pi\)-MO of dinitrogen (p,\(\pi\) interaction), an analog of 19 in reaction of SnF\(_2\) with hept-1-yne, or structures resulting from orbital \(\sigma,p\) and \(\sigma,n\) interactions employing \(\sigma\)-MO of the SnF\(_2\) stannylene center were not found.

Calculated MP2 interaction energies with one and two N\(_2\) molecules which include corrections for ZPE and basis set superposition error are 4.6 and 8.9 kcal mol\(^{-1}\), respectively. The calculations well reproduce the experimentally observed shifts of the valence vibrational bands of SnF\(_2\) upon complexation with N\(_2\). They also indicate a small polarization of the N\(_2\) ligands in the complexes, resulting in their nonzero intensities in the IR spectrum. However, these polarization effects are too small to be observed under the experimental conditions\(^{275}\).

![Figure 5. Main structural parameters of complexes 19 and 20 calculated by the PM3 and RHF/3-21G(d) (in parentheses) methods. Interatomic distances are in Å.](image-url)
The binding energies, changes in Sn–F bond lengths and SnF$_2$ frequency shifts in complex 22 with two N$_2$ moieties are approximately twice as big as in complex 21 with one N$_2$ ligand, i.e. complexation of SnF$_2$ with one N$_2$ molecule does not affect its interaction with the second N$_2$. This means that despite the relatively high stability of 21, its formation does not change the reactivity of SnF$_2$ in a dramatic way. Cycloaddition of SnF$_2$ to the triple N≡N bond is energetically extremely unfavorable, and the three-membered cycle SnF$_2$N$_2$ was found to be unstable$^{275}$.

XI. CONCLUSIONS

This review shows that despite the huge amount of information accumulated on fundamental structural, electronic and spectral characteristics of germylenes, stannylenes and plumbylenes, many gaps still exist in this area. Modern quantum-chemical calculations partially help to fill these gaps, but reliable experimental data are needed.

Very little is known about the nature of the weak interactions of CAs in solutions where a vast majority of their chemical reactions has been studied. Particularly, the study of donor–acceptor complexes of CAs by modern physical-chemical methods is still of great interest. Besides, complexation of CAs with donors or acceptors of electron density is a useful tool for modifying the stability, reactivity and spectral properties of CAs. Systematic investigations of the redox properties of CAs are needed in order to elucidate the role of electron transfer in the transformations of CAs.

The quest for CAs with a triplet ground state, as well as experimental determination of their structure in excited states, the values of singlet–triplet gaps and the reactivity of triplet CAs appear to be important venues in the chemistry of CAs in forthcoming years. The possibility of solving the aforementioned problems in the chemistry of CAs depends significantly on the availability of suitable precursors of CAs. In fact, only a few good precursors of germylenes, and especially of stannylenes and plumbylenes, are currently known. Therefore, the development of new precursors and new approaches to the generation of these species remain an urgent problem in the chemistry of germylenes, stannylenes and plumbylenes.

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836 Sergey E. Boganov, Mikhail P. Egorov, Valery I. Faustov and Oleg M. Nefedov

12. Spectroscopic studies and quantum-chemical calculations

CHAPTER 13

Multiply bonded germanium, tin and lead compounds

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I. INTRODUCTION

In the last two decades, remarkable progress has been made in the chemistry of low-coordinate compounds of heavier group 14 elements. Following the successful synthesis and isolation of the first stable silene and disilene in 1981, a variety of low-coordinated silicon compounds such as Si=Pn (Pn = N3, P4, As5) and Si=Ch (Ch = S6, Se7), 1-silaallenes, silabenzene, 2-silanaphthalene, and tetrasila-1,3-butadiene have been synthesized as stable compounds by taking advantage of kinetic stabilization with bulky substituents (so-called steric protection) and most of them are structurally well-characterized. These successful results in the chemistry of doubly bonded silicon compounds naturally provoked the challenge to extend this chemistry to that of their heavier congeners, i.e. the corresponding low-coordinated germanium, tin and lead compounds.

Although some review articles are now available on the syntheses and properties of low-coordinate species of heavier group 14 elements, most of them are restricted to those dealing with the most thoroughly investigated elements, silicon and germanium. In view of the present situation of low-coordinated compounds of heavier group 14 elements, it should be timely to survey the recent progress in this field and to make a systematic comparison of the multiply bonded systems with full periodic range covering germanium, tin and lead.

This review is divided into several sections according to the type of compounds, and in each section the similarity and/or difference among the germanium, tin and lead analogues will be delineated. Some comparisons with the related carbon and/or silicon analogues are added when necessary.

II. HEAVIER CONGENERS OF OLEFINs

Although a number of excellent review articles have appeared on disilenes and digermanes, the chemistry of dimetallenes of heavier group 14 elements, i.e. the heavier congeners of olefins, is summarized here again with the addition of updated examples. In this field it is very interesting to elucidate whether all the group 14 elements including the heaviest case of lead can generate a doubly bonded system and also how the character of such a heavy double bond differs from those of olefins and disilenes. In other words, a systematic investigation of these doubly bonded compounds is very important to determine whether or not the common concepts in the organic chemistry of elements in the second row, e.g. hybridization and conjugation, are acceptable to the whole group 14 elements.
A. Digermenes

Ge–Ge double-bond compounds, i.e. digermenes, do not exist in a monomer form under normal conditions, because they undergo ready oligomerization or polymerization as in the case of disilenes. The bulkiness of the substituents on the germanium atoms has a very large effect on the stability of digermenes. Thus, digermenes bearing small substituents are not isolable but transient, giving oligomers or polymers, while the substitution by too bulky ligands results in the formation of the corresponding germylenes. Only the digermenes bearing moderately bulky substituents such as 2,6-diethylphenyl, 2,6-diisopropylphenyl or bis(trimethylsilyl)methyl can exist as stable compounds. Some digermenes such as 1,2,3,4-tetrakis[bis(trimethylsilyl)methyl]digermene (1) retain their digermene structure but only in the solid state, while in solution they exist as equilibrium mixtures with the corresponding germylene (2) (Scheme 1).

\[
\begin{align*}
&[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Ge} \rightleftharpoons \text{Ge}[\text{CH}(-\text{SiMe}_3)_2]\text{Ge} \\
&\text{(1)} \quad \text{2} [(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Ge}: \\
&\text{(2)}
\end{align*}
\]

SCHEME 1

The molecular structures of some digermenes have been determined by X-ray structural analysis and it was found that most of the digermenes have trans-bent geometry except in a few cases. The pyramidal geometry of the germanium atoms in digermenes is in sharp contrast to the trigonal planar carbons of olefins. Even the sterically hindered digermenes are extremely sensitive to oxygen and moisture and exist as stable compounds only under an inert atmosphere.

1. Synthesis of digermenes

a. Synthesis of digermenes from germylenes. Tetraalkyldigermene 1 is synthesized by the reaction of a dichlorogermylene–dioxane complex with a Grignard reagent or by the reaction of a stable diaminogermylene with an organolithium reagent (Scheme 2). Tetraaryldigermenes are also prepared by the treatment of the corresponding dihalogermylenes with an appropriate organometallic reagent (Scheme 2).

\[
\begin{align*}
&\text{GeCl}_2\text{-dioxane} \quad 2\text{RMgCl} \\
&[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Ge:} \\
&\text{2RLi} \\
&\text{2 GeI}_2 \\
&\text{2 GeCl}_2\text{-dioxane}
\end{align*}
\]

SCHEME 2
b. Synthesis of digermenes by photolysis. Photolysis of cyclotrigermanes\textsuperscript{12} or bis(trialkylsilyl)germanes\textsuperscript{21,22} having bulky substituents gives the corresponding digermenes. For examples, digermenes 3 and 4 have been synthesized by these methods (Scheme 3). These methods can be utilized for the synthesis of both stable digermenes and transient ones, but they cannot be applied to the synthesis of extremely bulky digermenes. In such congested systems, the corresponding cyclotrigermanes or bis(trialkylsilyl)germanes are not available due to the steric repulsion between the substituents introduced.

\begin{equation}
\begin{array}{c}
\text{Ge} \\
\text{Ge} \\
\text{Ge}
\end{array}
\xrightarrow{\text{hv}}
\begin{array}{c}
\text{R}_2\text{Ge} \\
\text{GeR}_2
\end{array}
\xleftarrow{\text{hv}}
\begin{array}{c}
\text{R}_2\text{Ge(SiMe}_3)_2
\end{array}
\end{equation}

\text{(3) } R = \text{2,6-Et}_2\text{C}_6\text{H}_3 \text{ (Dep)}
\text{(4) } R = \text{2,4,6-i-Pr}_3\text{C}_6\text{H}_2 \text{ (Tip)}

\text{SCHEME 3}

c. Synthesis of digermenes by the reduction of dihalogermanes. Reactions of overcrowded diaryldihalogermanes with lithium naphthalenide give the corresponding digermenes 5, 6 and 10 (Scheme 4)\textsuperscript{13,19,23}. The tetrakis(trialkylsilyl)digermenes 7–9 can be prepared by a similar method\textsuperscript{17}. This route is particularly useful for the synthesis of sterically hindered digermenes, which cannot be produced from cyclotrigermanes due to their steric hindrance.

\begin{equation}
\begin{array}{c}
2 \text{R}_1\text{R}_2\text{GeX}_2
\end{array}
\xrightarrow{\text{LiNaph}}
\begin{array}{c}
\text{R}_1^1\text{R}_2^1\text{Ge} \\
\text{GeR}_1^1\text{R}_2^1
\end{array}
\end{equation}

\text{(5–10)}

\text{(5) } R_1^1 = R_2^1 = \text{2,6-i-Pr}_2\text{C}_6\text{H}_3 \text{ (Dip)}
\text{(6) } R_1^1 = \text{mesityl} \text{ (Mes)}; R_2^1 = \text{Dip}
\text{(7) } R_1^1 = R_2^1 = \text{i-Pr}_7\text{MeSi}
\text{(8) } R_1^1 = R_2^1 = \text{t-BuMe}_2\text{Si}
\text{(9) } R_1^1 = R_2^1 = \text{i-Pr}_3\text{Si}
\text{(10) } R_1^1 = \text{Mes} \text{; } R_2^2 = 2,4,6-[(\text{Me}_3\text{Si})_2\text{CH}]_3\text{C}_6\text{H}_2 \text{ (Tbt)}

\text{SCHEME 4}

There have already been several reports on the reduction of dichlorogermanes bearing bulky aryl groups with lithium naphthalenide (Scheme 5). Upon treatment with lithium naphthalenide, dichloro[bis(2,6-dimethylphenyl)]germane 11a and dichloro[bis(2,6-die-thylphenyl)]germane 11b afforded the corresponding cyclotrigermanes 12a,b\textsuperscript{12,24}. On the other hand, digermene 5 was obtained as a major product from dichloro[bis(2,6-diisopropylphenyl)]germane 11e under similar conditions (Scheme 5)\textsuperscript{13}.

In general, the reduction of a dichlorogermane (13) is considered to proceed as illustrated via 14–17 and 19, 20 to give 18 and 21 in Scheme 6\textsuperscript{1,13}. This mechanism involves a linear chain elongation mechanism. Dihalogermanes with small ligands gave oligomeric products by the chain elongation reaction.

As for dihalogermanes having relatively bulky ligands (2,6-dimethylphenyl or 2,6-diethylphenyl) on the germanium atom, the chain elongation may proceed to give a trimeric compound 19. The steric congestion due to the substituents used forces the
13. Multiply bonded germanium, tin and lead compounds

\[ \text{Ar}_2\text{GeCl}_2 \xrightarrow{\text{LiNaph}} \text{Ar}_2\text{Ge} \xrightarrow{\text{LiCl}} \alpha \text{ elimination} \xrightarrow{\text{LiCl}} \text{Ar}_2\text{Ge:} \]

\[ \xrightarrow{\text{Ar}_2\text{GeCl}_2} \]

\[ \xrightarrow{\text{LiNaph}} \text{Ar}_2\text{Ge} \xrightarrow{\text{LiCl}} \beta \text{ elimination} \xrightarrow{\text{LiCl}} \text{Ar}_2\text{GeGeAr}_2 \]

\[ \xrightarrow{\text{Ar}_2\text{GeCl}_2} \]

\[ \xrightarrow{\text{LiNaph}} \text{Ar}_2\text{GeGeAr}_2 \xrightarrow{\text{LiCl}} \text{ring closure} \xrightarrow{\text{LiCl}} \text{ArGeGeAr}_2 \]

\[ \xrightarrow{\text{Ar}_2\text{GeCl}_2} \]

R = Me (Dmp), R = Et (Dep), R = i-Pr (Dip)
ends of the chain to get close to one another so that the chain cyclotrimerizes. When the
substituents on the germanium atom become bulkier than those in 11a or 11b (i.e. 2,6-diisopropylphenyl in 11c), the intermediate 17 becomes too congested to permit the chain
elongation and it rather prefers to undergo β-elimination leading to the digermene 18. In
the case of an extremely hindered dichlorogermane such as Tbt(Mes)GeCl2, the attempted
reductive coupling of the initial intermediate 14 may be prevented by the steric repulsion
between the bulky ligands, and hence the intermediate undergoes an α-elimination to give
the germylene 15. This takes place in the case of digermene 10 in Scheme 423.

Actually, an equilibrium between digermene 10 and the corresponding germylene 22 was
observed in solution and the thermodynamic parameters were determined (Scheme 7)23.
Crystallographic analysis of digermene 10 revealed that it has a considerably elongated
Ge=Ge double bond25 which is in good agreement with the lability of this bond in solution (vide infra).

\[
\Delta H = 14.7 \pm 0.2 \text{ kcal mol}^{-1} \\
\Delta S = 42.4 \pm 0.8 \text{ cal mol}^{-1} \text{ K}^{-1}
\]

SCHEME 7

d. Equilibrium between the Digermene and Germylene. Tbt- and Mes-substituted ger-
mylene 22 was readily generated by the reduction of Tbt(Mes)GeX2 (X = Cl or Br) with
2 equivalents of lithium naphthalenide in THF23. The color of 22 in solution is blue
and 22 shows an absorption maximum at \(\lambda_{\text{max}} = 575\) nm, which is assignable to an n–p
transition. As for the electronic spectra of germynes, the steric effect of substituents
on n–p transitions is well investigated26. The electronic absorptions of some germynes
reported so far are listed in Table 126,27.

It can be seen in Table 1 that the bulkier the substituents on the germanium atom
become, the longer \(\lambda_{\text{max}}\) is observed for the germynes (Ph2Ge: (466 nm) < Dmp2Ge:

<table>
<thead>
<tr>
<th>Germynes(^a)</th>
<th>(\lambda_{\text{max}}) (nm)</th>
<th>Color</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me2Ge:</td>
<td>420</td>
<td>yellow</td>
<td>in 3-MP at 77 K</td>
</tr>
<tr>
<td>Et2Ge:</td>
<td>440</td>
<td>yellow</td>
<td>in 3-MP at 77 K</td>
</tr>
<tr>
<td>n-Bu2Ge:</td>
<td>440</td>
<td>yellow</td>
<td>in 3-MP at 77 K</td>
</tr>
<tr>
<td>MePhGe:</td>
<td>440</td>
<td>yellow</td>
<td>in 3-MP at 77 K</td>
</tr>
<tr>
<td>Ph2Ge:</td>
<td>466</td>
<td>yellow-orange</td>
<td>in 3-MP at 77 K</td>
</tr>
<tr>
<td>p-Tol2Ge:</td>
<td>471</td>
<td>yellow-orange</td>
<td>in 3-MP at 77 K</td>
</tr>
<tr>
<td>Mes(t-Bu)Ge:</td>
<td>508</td>
<td>red</td>
<td>in 3-MP at 77 K</td>
</tr>
<tr>
<td>Dmp2Ge:</td>
<td>543</td>
<td>purple</td>
<td>in 3-MP at 77 K</td>
</tr>
<tr>
<td>Dep2Ge:</td>
<td>544</td>
<td>purple</td>
<td>in 3-MP at 77 K</td>
</tr>
<tr>
<td>Mes2Ge:</td>
<td>550</td>
<td>purple</td>
<td>in 3-MP at 77 K</td>
</tr>
<tr>
<td>Tip2Ge:</td>
<td>558</td>
<td>purple</td>
<td>in 3-MP at 77 K</td>
</tr>
<tr>
<td>Mes(^*)2Ge:</td>
<td>430</td>
<td>orange</td>
<td>in hexane or THF</td>
</tr>
<tr>
<td>Dmtp2Ge:</td>
<td>578</td>
<td>purple</td>
<td>in ethyl ether</td>
</tr>
<tr>
<td>Tbt(Mes)Ge:</td>
<td>575</td>
<td>blue</td>
<td>in hexane at r.t.</td>
</tr>
</tbody>
</table>

\(^a\) p-Tol = 4-methylphenyl, Dmp = 2,6-dimethylphenyl, Dep = 2,6-diethylphenyl, Tip = 2,4,6-trisopropylphenyl, Mes\(^*\) = 2,4,6-tri-i-butylphenyl, Dmtp = 2,6-dimesitylphenyl
13. Multiply bonded germanium, tin and lead compounds

(543 nm) < Dep₂Ge: (544 nm); Mes₂Ge: (550 nm) < Tip₂Ge: (558 nm)]. In the theoretical CI calculation of H₂Ge: the equilibrium value of the H-Ge-H angle in the excited state is larger than that in the ground state (123.2 and 92.6°, respectively)²⁸.

When the R-Ge-R angle of a germylene becomes large, its ground state is destabilized, while the excited state is conversely stabilized. Thus, the energy difference between the ground state (¹A₁) and excited state (¹B₁) becomes small and hence a red shift of λ_max is observed (Scheme 8). The λ_max value (575 nm) of 2²² indicates that the bulkiness of the combination of Tbt and Mes group in 2 is similar to that of two Dmtp groups in the Power’s germylene 23 (Dmtp₂Ge:), which is isolated as stable crystals²⁷b.

Interestingly, a hexane solution of 2²² showed a unique thermochromic character. It is blue (λ_max = 575 nm) at room temperature, but it turns orange-yellow (λ_max = 439 nm) at a low temperature²³. The same change in color was observed in the process of concentration of the solution of 2. Although a dilute solution of 2²² is blue, its concentrated solution is orange-yellow²³.

X-ray crystallographic analysis of the orange single crystals, which were obtained after the removal of inorganic salts and naphthalene, has revealed that the structure of the orange crystal is that of the digermene (E)-Tbt(Mes)Ge=Ge(Mes)Tbt 10, the dimer of the germylene Tbt(Mes)Ge: 2²². The details of the structural analysis of 10 will be discussed later.

e. Synthesis of cyclic digermenes. In 1995, Sekiguchi and his coworkers reported the first cyclic digermenes, i.e. cyclotrigermenes 2⁴a,b, which were synthesized by the reaction of GeCl₂–dioxane complex with t-Bu₃SiNa or t-Bu₃GeLi (Scheme 9)¹⁶.

The successful isolation of these unique cyclic digermenes is of particular note not only for the extension to the synthesis of other cyclic digermenes ²⁵¹⁸ and germasilenes ²⁶–²⁸²⁹ but also for the application of this ring system to the chemistry of unprecedented germaaromatic systems, i.e. cyclotrigermenium ions ²⁹³⁰ (Scheme 9). The structures and properties of these novel cyclic digermenes ²⁴ and the related low-coordinated germanium compounds are not described here in detail, since they are fully accounted for in Chapter 14 of this volume.

2. Structure of digermenes

a. Acyclic digermenes. Digermenes have the following structural characteristics: (1) shortened Ge=Ge bond distances of 2.21–2.35 Å relative to the known Ge–Ge single bonds (2.457–2.463 Å)¹²¹⁷,¹⁰, and (2) trans-bent double bonds and bent angles. The angle δ formed by the R-Ge-R plane and Ge–Ge axis is 7–36°. Theoretical studies using various basis sets predict a trans-bent geometry for the parent system (H₂Ge=GeH₂) with relatively short Ge=Ge bond lengths of 2.27–2.33 Å and a significant bent angle of 34–40°¹⁵,³¹. The trans-bent conformation for digermenes is explained in terms of
the stabilization of the HOMO orbital by mixing with the Ge−Ge σ* orbital which predominates over destabilization of the Ge-Ge σ bonding. As a result, the trans-bent form becomes more stable than the planar form. As to the cis-bent form, the mixing of the HOMO orbital with the antibonding σ* orbital is forbidden by symmetry and the energy of the cis-bent form increases with increasing the bent angle δ.

As mentioned in the previous section, the unique equilibrium of the highly congested digermene (E)-10 with the corresponding germylene 22 implies a weakness of its Ge−Ge double bond23. Therefore, it should be important to make a systematic comparison of the structural features of (E)-10 with other digermenes, the results of which are summarized in Table 215,17,19,20,32. Although the twist angle (γ') along the Ge–Ge axis and the bent angles (the angle δ formed by the C–Ge–C plane and Ge–Ge axis) of (E)-10 are 12, 16 and 18°, respectively, being in the range of those for the previously reported digermenes, the Ge(1)-Ge(2) bond length [2.416(4) Å] of digermene (E)-10 is remarkably longer than those for the previously formed digermenes [2.21–2.35 Å] and close to the germanium–germanium single bond lengths [e.g. 2.465 Å in (Ph2Ge)33 or 2.463 and 2.457 Å in (Ph2Ge)34].

These results show that the large steric repulsion between the Tbt and Mes groups facing each other might be released by lengthening the germanium–germanium double
TABLE 2. Structural comparison of isolated digermenes

<table>
<thead>
<tr>
<th>Digermene</th>
<th>( r (\text{Å}) )</th>
<th>( \alpha (\text{deg}) )</th>
<th>( \beta (\text{deg}) )</th>
<th>( \gamma (\text{deg}) )</th>
<th>( \delta (\text{deg}) )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dep(_2)Ge=GeDep(_2) (3)(^d)</td>
<td>2.213(2)</td>
<td>115.4(2)</td>
<td>118.7(1)</td>
<td>20.4</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Ar(_2)Ge=GeAr(_2) (41)(^b)</td>
<td>2.2521(8)</td>
<td>128.0(2)</td>
<td>116.1(2)</td>
<td>115.0(2)</td>
<td>124.3(1)</td>
<td>20</td>
</tr>
<tr>
<td>(Z)-Dip(Mes)Ge=Ge(Mes)Dip (6)(^c)</td>
<td>2.301(1)</td>
<td>109.9(2)</td>
<td>116.6(2)</td>
<td>124.2(2)</td>
<td>7</td>
<td>19</td>
</tr>
<tr>
<td>Dis(_2)Ge=GeDis(_2) (1)(^d)</td>
<td>2.347(2)</td>
<td>112.5(2)</td>
<td>113.7(3)</td>
<td>123.5(0)</td>
<td>32</td>
<td>15, 32</td>
</tr>
<tr>
<td>([i-Pr](_2)MeSi)(_2)Ge=Ge[SiMe(Pr-(_i))-1(_2)] (7) (i)</td>
<td>2.266(1)</td>
<td>117.0(0)</td>
<td>120.9(0)</td>
<td>117.9(0)</td>
<td>0</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>2.268(1)</td>
<td>118.2(0)</td>
<td>121.4(0)</td>
<td>123.5(0)</td>
<td>0</td>
<td>5.9</td>
</tr>
<tr>
<td>([i-Pr](_3)Si)(_2)Ge=Ge[Si(Pr-(_i))-3] (9)</td>
<td>2.298(1)</td>
<td>115.3(0)</td>
<td>125.2(4)</td>
<td>116.5(5)</td>
<td>16.4</td>
<td>17</td>
</tr>
<tr>
<td>(E)-Tbt(Mes)Ge=Ge(Mes)Tbt (10)</td>
<td>2.416(4)</td>
<td>109.3(8)</td>
<td>130.3(6)</td>
<td>133.4(7)</td>
<td>12</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>108.5(9)</td>
<td>117.0(6)</td>
<td>113.9(6)</td>
<td>11.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Dep = 2,6-diethylphenyl.
\(^b\) Ar = 2-t-Bu-4,5,6-Me\(_3\)C\(_6\)H.
\(^c\) Dip = 2,6-diisopropylphenyl.
\(^d\) Dis = bis(trimethylsilyl)methyl.

bond. This may be the longest germanium–germanium double bond reported so far. The sums of the bond angles around Ge(1) and Ge(2) are 356.6 and 355.8°, respectively. A closely related doubly bonded system of silicon, an extremely hindered disilene bearing the same substituents as (E)-10, i.e., (E)-Tbt(Mes)Si=Si(Mes)Tbt (30), has already been synthesized and characterized by X-ray crystallographic analysis\(^{35}\). The twist angle and the bent angles of disilene 30 are 8.7, 14.6 and 9.4°, respectively. The Si=Si bond for disilene (E)-30 is 3.8% longer than the mean value of the Si=Si bond lengths (2.147 Å) in other carbon-substituted disilenes. In the case of digermene (E)-10, the Ge=Ge bond is lengthened by 6.0% as compared to the mean value of the Ge=Ge bond lengths (2.278 Å) in other carbon-substituted digermenes. The elongation of the Ge=Ge bond length of (E)-10 shows that the Ge–Ge double bond is softer than the Si–Si double bond, which is known to be again softer than the C–C double bond.

b. Cyclic digermenes. Some of the isolated cyclotrigermerenes have been characterized by X-ray crystallographic analysis. Although they are embedded in such a strained three-membered ring systems, the bond lengths of their Ge–Ge double bonds were found to lie in the range of previously reported acyclic digermenes. However, it should be noted that the planarity of the Ge–Ge double bond in cyclotrigermerenes is highly dependent on their substituents. Thus, cyclotrigermerene 24a has a completely planar geometry around its Ge–Ge double bond\(^{16}\), while unsymmetrically substituted cyclotrigermerene 25b showed an unusual \textit{cis}-bent geometry\(^{18}\). The detailed description is given in Chapter 14.
3. Reactions of digermenes

Tetraaryldigermenes react with various reagents as shown in Scheme 10. For example, addition of methanol gives methoxydigermenes. In a reaction with an appropriate chalcogen source, chalcogenadigermiranes, which are $[2 + 1]$ cycloadducts of the digermenes with chalcogen atoms, are obtained. Reactions with ketone or alkyne derivatives afford $[2 + 2]$ cycloadducts. Reactions with diazomethane and phenyl azide give three-membered ring compounds. Thus, digermenes are useful building blocks for the synthesis of small-ring compounds containing a germanium–germanium bond.

**Scheme 10**

*a. Estimation of $\pi$-bond energies.* Masamune and coworkers synthesized stable geometric isomers of digermenes and experimentally determined the $\pi$-bond strength from their isomerization (Scheme 11). The enthalpy of activation for 31 has been determined.

**Scheme 11**
from kinetic studies (for Z–E conversion $\Delta H^\ddagger = 22.2 \pm 0.3$ kcal mol$^{-1}$, and for E–Z conversion it is $20.0 \pm 0.3$ kcal mol$^{-1}$). These values are in good agreement with the calculated value.$^{41}$

b. Thermal behavior of digermenes. There have been some interesting reports on the thermolysis of digermenes. Thermolysis of hexamethylcyclotrigermane $^{32}$ in the presence of triethylsilane or 2,3-dimethyl-1,3-butadiene gave $^{33}$ and $^{34}$ or $^{35}$ and $^{36}$, respectively.$^{42}$ The most reasonable explanation for the generation of these products is as follows. Thermolysis of cyclotrigermane $^{32}$ affords digermene $^{37}$ and germylene $^{38}$ and the latter reacts with the silane or diene to afford $^{34}$ or $^{36}$, respectively. On the other hand, $^{37}$ may undergo 1,2-mesityl shift to give germylgermylene $^{39}$, which is then trapped with the silane or diene to afford $^{33}$ or $^{35}$, respectively (Scheme 12)$^{42}$.

![Scheme 12](image)

Tetrakis(2,6-diethylphenyl)digermene $^{3}$ is reportedly converted into hexakis(2,6-diethylphenyl)cyclotrigermane $^{12b}$ on heating in solution$^{1j}$. The proposed mechanism involves the dissociation of digermene $^{3}$ into two germynes Dep$_2$Ge: $^{40}$, followed by their
reaction with the second digermene 3 to form the cyclotrigermane \( 12b \) (Scheme 13). In this process the dissociation energy of tetrakis(2,6-diethylphenyl)digermene was estimated to be \(<30 \text{ kcal mol}^{-1} \).
of the germylene 43 with benzil (Scheme 15). The digermene 41 was found by cryoscopic molecular weight measurement to exist as the corresponding monomer, germylene 43, in solution.

Furthermore, as described in the previous section, the spectroscopic observation of an equilibrium between a digermene and germylenes was first achieved in the case of highly crowded digermene (E)-10 by UV-vis spectroscopy (see Scheme 7)23.

B. Germenes

Germenes43 are germanium analogues of alkenes, which play a very important role in organic chemistry. Their synthesis and isolation have been reported only in few papers, because of their tendency to undergo dimerization. The first stable germene was synthesized in 1987 by taking advantage of steric protection44. The structural analysis of some germenes has been reported and they are known to have the trigonal planar geometry on the Ge and C atoms in sharp contrast to digermenes, which have the pyramidal geometry on the Ge atoms.

Germenes are highly reactive and readily undergo 1,2-addition with various single-bond compounds or [2+n]cycloaddition with multiple-bond compounds to give germanium–carbon singly bonded compounds or germacycles, respectively.

1. Synthesis of germenes

The first stable germenes 46 were synthesized by Berndt and coworkers via the coupling reactions of stable nitrogen-substituted germylenes 45a,b with the electrophilic cryptocarbene 44 (44') (Scheme 16).

The boron atoms of 46a and 46b (δB = 66 and 65 ppm) are more strongly shielded than that of the 1,3-diboretane 47a (δB = 82 ppm)44b,45. Although the germanium–carbon double bond distance of 46a (1.827 Å) is shorter by 8% than that of a Ge–C single bond (1.98 Å)46, it is longer than that of the calculated value for the parent germene H2Ge=CH2 (1.71–1.81 Å)47. The sums of the bond angles of Ge and C atoms of a germene unit of 46a are 359.9 and 359.7°, respectively. These facts show that a large amount of negative
charge is located on the boron atoms and germenes 46 are stabilized by resonance with an ylide form 46'.

Escudié, Sagé and coworkers have reported the synthesis of the first germene 49 bearing only carbon substituents by dehydrofluorination of the corresponding fluorogermane 4844a,c. X-ray crystallographic analysis revealed that the length of the germanium–carbon double bond of 49 is 1.80 Å, which is shorter by 9% than that of the germanium–carbon single bond and consistent with the calculated value47. The sums of the bond angles of Ge and C atoms of the germene unit of 49 are 360.0 and 360.0°, respectively. This synthetic route has been used extensively for other germenes1p.
In connection with this method, the treatment of fluorovinylgermane 50 with \textit{t}-BuLi resulted in the formation of dimesityleneopentylgermene 51 via an addition–elimination reaction (Scheme 17)\(^{48}\).

Tokitoh, Okazaki and coworkers have reported the synthesis of another unique germene 53 by the reaction of overcrowded diarylgermylene 52 with carbon disulfide (Scheme 18)\(^{49}\). The structure of 53 was confirmed by X-ray crystallographic analysis\(^{49}\). The distance of the germanium-carbon double bond of 53 is 1.77 Å, which is shorter by 11\% than that of a typical Ge-C single bond length (1.98 Å). The sums of the bond angles of Ge and C atoms of the germene unit of 53 are 359.7 and 360.0°, respectively.

In addition to the stable germenes mentioned above, an ylide-type compound 56 was synthesized by the reaction of the nitrogen-substituted germylene 45a with bis(dialkylamino)cyclopropenylidene 55 prepared \textit{in situ} by the treatment of cyclopropenium cation
The structure of 56 was confirmed by X-ray crystallographic analysis, where the distance (2.08 Å) between the germanium and the carbene-C atoms is appreciably longer than that of other germenes (1.77–1.83 Å) and close to that of a single bond (1.98 Å). The sum of the bond angles around the Ge atom (ΣGe) of 56 is 303.0°, indicating a trigonal–pyramidal structure. This structural feature is different from that of other germenes, which have a trigonal–planar geometry for the germene unit (ΣGe = 359.7–360.0° and ΣC = 359.7–360.0°).

2. Reactions of germenes

Germenes react with various reagents as shown in Scheme 20. For example, addition of methanol affords a methoxygermane. In the reactions with ketones and aldehydes oxagermetane derivatives are obtained. The reactions of α,β-unsaturated aldehydes and ketones afford [4+2]cycloadducts. These reactions proceed regiospecifically, according to the Geδ+−Cδ− polarity.

In the case of germaketenedithioacetal 53, unique reaction with molecular oxygen has been reported (Scheme 21). On exposure of 53 to air, dihydroxygermane 57 and 1,3,2-dithiagermeta-4-one 58 were obtained as the reaction products. On the other hand, the reaction of 53 with oxygen in the presence of methanol afforded 57 and 58 together with hydroxymethoxygermane 59, i.e. the methanolysis product of germanone 61. The formation of 57, 58 and 59 can be reasonably explained as shown in Scheme 21. Germene 53 reacts with oxygen to form an intermediary [2+2]cycloadduct, 1,2,3-dioxagermetane 60, the cycloreversion of which may give 58 and germanone 61. Since germanones are known to be highly reactive and unstable species, the intermediate 61 might quickly react with H2O or methanol to give 57 or 59.

Brook and coworkers have already reported a similar reaction mode in the reaction of silene with oxygen. In that case the intermediary silanone which arises from the
SCHEME 20
breakdown of 1,2,3-dioxasiletane undergoes a ready trimerization to afford the cyclic siloxane\(^{53}\). The lack of such a polymerization product of germanone \(61\) suggests the effectiveness of the steric protection system. Indeed, Tokitoh and coworkers have reported the formation and reaction of the first stable germanone in solution derived from a kinetically stabilized germylene\(^{54}\). It is interesting and noteworthy that the same type of reactions are observed in the oxidation of a silene and a germene.

The germanium–carbon double bond in germene \(53\) was found to undergo an interesting thermal dissociation (Scheme 22). When the benzene-\(d_6\) solution of germene \(53\) was
13. Multiply bonded germanium, tin and lead compounds

heated at 95°C in the presence of 2,3-dimethyl-1,3-butadiene in a sealed tube, germa-
cyclopentene 62, a [1+4]cycloadduct of germylene 63 with butadiene, was obtained55.
The formation of 62 indicates the generation of germylene 63 in the thermolysis of
germene 53. This mechanism was supported by the fact that carbon disulfide, the coun-
terpart of the thermal dissociation of 53, was detected by 13C NMR spectroscopy52.

Raasch has reported that the thermolysis of a ketenedithioacetal resulted in the disso-
ciation into the corresponding thiketene and thiketone56. It should be noted that it is
not the retro[2+2]cycloaddition similar to the carbon analogue, but the cleavage of the
germanium–carbon double bond that has taken place in the thermolysis of germene 53.

C. Distannenes and Stannenes

In contrast to the extensively studied doubly bonded systems of silicon and germanium,
the chemistry of the corresponding tin compounds, i.e. distannenes and stannenes, has not
been fully disclosed yet probably due to the much higher reactivity and instability of such
low-coordinated organotin compounds. In the following sections we briefly describe the
synthesis and properties of stable distannenes and stannenes.

1. Distannenes

In 1976, the first stable distannene 64 bearing two bis(trimethylsilyl)methyl groups on
each tin atom was isolated as brick red crystals by Lappert and coworkers (Scheme 23)57.
Crystallographic analysis of 64 revealed that it is nonplanar and centrosymmetric with
each tin atom in a pyramidal environment (sum of the angles at tin is 342°, compared
with 360° expected for pure sp2 hybridization at Sn or 327° for sp3 hybridization) having
a fold angle of 41°. (The fold angle is defined as the angle between the Sn–Sn vector
and the SnC2 plane of each monomer.) The Sn–Sn bond distance is 2.768 Å, which is
comparable to an average Sn–Sn single bond length.

According to the molecular orbital calculations of a tin–tin double bond, a calculated
equilibrium structure is predicted to be trans-bent, which is consistent with the exper-
imental findings. This structural distortion from a planar form to a trans-bent form is
achieved through mixing an M–M p-orbital (bu) (HOMO) with an M–M σ∗ orbital. On
the other hand, the energy of an M–M σ orbital (ag) increases upon trans-folding, mainly
due to the loss of M–M σ bonding. For distannene, the energy drop of the bu orbital
predominates over destabilization of the ag orbital. When calculations are performed
on a *cis*-folded form, mixing of a \( b_u \) (HOMO) with an antibonding \( \sigma^\ast \) is forbidden by symmetry and the energy increases with the fold angle. In solution, distannene 64 was found to exist as a distannene–stannylene 65 equilibrium mixture. Attempts to observe its \(^{119}\text{Sn}\) NMR in solution at room temperature were not successful, but two signals at 165 K in either ether or toluene at 740 and 725 ppm assignable to distannene 64 were observed.\(^{58}\) At 375 K, only the signal of the stannylene 65 was observed at 2315 ppm. The NMR studies show quite a small dissociation energy of 12.8 kcal mol\(^{-1}\) and a low \( ^1J(119\text{Sn}–117\text{Sn}) \) value of 1340 ± 10 Hz. Both theoretical and experimental findings suggest that the Sn=Sn bond in 64 is exceptionally weak and not a covalent bond in the usual sense. The bonding mode in 64 is described as a double dative bond, in which the lone pair on each monomer interacts with the empty \( p_z \) orbital on the other as shown in Scheme 23.

The first aryl-substituted distannene 66 was synthesized by Masamune and Sita through photolysis of the corresponding cyclotristannane 67 in solution at \(-78\, ^\circ\text{C}\) (Scheme 24).\(^{59}\) Although \(^{119}\text{Sn}\) NMR of 66 at \(-68\, ^\circ\text{C}\) showed a singlet at 427 ppm with considerably larger tin–tin coupling satellites \([ ^1J(119\text{Sn}–117\text{Sn}) = 2930 \text{ Hz}]\) than that of 64, there is a thermal equilibrium between 66 and 67. Cyclotristannane 67 is stable in an inert solvent at 0 \(^\circ\text{C}\) or lower temperature to \(-78\, ^\circ\text{C}\), but a rapid equilibrium between 66 and 67 occurs at room temperature or above with 66 being favored at higher temperature.

![Scheme 24](image)

Weidenbruch and coworkers reported that the \(^{119}\text{Sn}\) NMR signal of the corresponding stannylene 68 appeared at 1420 ppm (40 \(^\circ\text{C}\)) in the equilibrated mixture of 66 and 67 (Scheme 25).\(^{60}\)

![Scheme 25](image)

Later, they also reported the first X-ray structural analysis of the aryl-substituted distannene by introduction of 2-t\(^\text{-butyl-4,5,6-trimethylphenyl groups}\).\(^{61}\) A conspicuous feature of its structure is the long tin–tin bond length of 2.91 Å, which is markedly longer than that the typical tin–tin single bond. In its \(^{119}\text{Sn}\) NMR at 373 K a sharp signal at 1401 ppm is observed in the same region as that of 68 assignable to a monomeric
stannylene. At room temperature no $^{119}\text{Sn}$ NMR signals can be observed as in the case of 64. This temperature dependence in $^{119}\text{Sn}$ NMR shows that it also exists as a monomer–dimer equilibrium mixture. A distannene which does not dissociate into stannynes in solution is still unknown.

### 2. Stannenes

The chemistry of stannenes, which are also analogous to ethylene, has been less developed than that of silenes and germenes. In 1987, two stannenes 69 and 70 stabilized by not only steric protection but also by electronic perturbation were synthesized and characterized by X-ray crystallographic analysis by Berndt and coworkers (Scheme 26)\(^{45,62}\).

$$\begin{align*}
\text{(Me}_2\text{Si)}_2\text{C} & \quad \text{Sn} = \text{C} & \quad \text{C(SiMe}_3)_2 \\
\text{(Me}_2\text{Si)}_2\text{C} & \quad \text{H} & \quad \text{Sn} = \text{C} & \quad \text{C(SiMe}_3)_2
\end{align*}$$

### SCHEME 26

A decisive proof for the presence of tricoordinated tin in 69 is provided by the very low-field chemical shift of the $^{119}\text{Sn}$ NMR signal at $\delta = 835$. The Sn=C bond length is 2.025 Å in 69 which is comparable to calculated values for H$_2$C=SnH$_2$ [2.063 Å at MCSCF/3-21 GG(d)$^{31e}$ and 1.98 Å at SCF/3-21 GG(d)$^{63}$]. The average twist angle around the Sn=C bond is 61° and the Sn atom is slightly pyramidalized. In 1992, Satgé and coworkers reported the synthesis of bis(2,4,6-triisopropylphenyl)(fluorenylidene)stannene 71 (Scheme 27) by dehydrofluorination of the corresponding fluorostannane\(^{64}\).

$$\begin{align*}
\text{Tip}_2\text{Sn} & \quad \text{C} & \quad \text{OEt}_2 & \quad \text{Tip}_2\text{Sn} & \quad \text{C} & \quad \text{SnTip}_2 \\
\text{Tip}_2\text{Sn} & \quad \text{C} & \quad \text{R}_2 & \quad \text{Tip}_2\text{Sn} & \quad \text{C} & \quad \text{SnTip}_2
\end{align*}$$

### SCHEME 27
Although the X-ray structural analysis of this stannene 71 was not carried out, its formation was inferred from its low $^{119}$Sn NMR resonance (288 ppm). In comparison with the doubly bonded tin derivatives mentioned above, however, it shows a higher field chemical shift. This high chemical shift can be rationalized in terms of complexation of tin with ether used in the synthesis, as evidenced by the broad signal for the OCH$_2$ hydrogens in the $^1$H NMR spectrum. At room temperature, 71 slowly converts to the head-to-tail dimer 72 (Scheme 27). When two bis(trimethylsilyl)methyl groups were used as substituents on the tin atom instead of two Tip groups in 71, attempts to stabilize a stannene were unsuccessful$^{65}$. In 1995, it was found that bis(2,4,6-triisopropylphenyl)stannylene 74 reacted with 4,5-dimethyl-1,3-diisopropylimidazol-2-ylidene 73 to furnish an adduct 75 (Scheme 28)$^{66}$. An X-ray structural analysis of 75 revealed the presence of a long tin–carbon double bond with a length of 2.379 Å. The geometry of the molecule observed here clearly indicates that the adduct 75 is better described as the limiting formula 75b rather than as the stannene form 75a.

\[ \text{Scheme 28} \]

**D. Diplumbenes**

In contrast to the remarkable progress in the chemistry of divalent organic compounds of silicon, germanium and tin, the heaviest congeners of this series, i.e. divalent organolead compounds (plumbylenes), are less investigated. They usually occur as reactive intermediates in the preparation of plumbanes R$_4$Pb and undergo polymerization and/or disproportionation in the absence of suitable stabilizing groups on the lead atom$^{67}$. However, there has been very little information on the dimers of plumbylenes,
i.e. diplumenes. Furthermore, so far no experimental information is available on the chemistry of lead–carbon doubly bonded systems, i.e. plumbenes.

1. Stable plumbylenes

In 1974 the first stable diaminoplumbylene (76) was synthesized by Lappert and coworkers\textsuperscript{68} and since then many other stable plumbylenes with heteroatom substituents have been reported. Recently, the synthesis and characterization of a stable aryl(arylthio)-plumbylene (77), which is one of the rare examples of heteroleptic plumbylenes, have also been reported (Scheme 29)\textsuperscript{69}.

In contrast to the heteroatom-substituted plumbylenes, a few plumbylenes bearing only carbon substituents have been reported. Some of them are stabilized by intramolecular coordination of the lone pair of a donor group in the organic substituent, thus giving the lead a coordination number greater than 2 as can be seen in the diarylplumbylene $R_2^1\text{Pb}$.
(78; $R^f = \text{bis}[2,4,6\text{-tris(trifluoromethyl)phenyl}]$) and the alkylarylplumbylene (79)$^{70}$. On the other hand, kinetically stabilized plumbylenes bearing only organic substituents that do not contain donor groups are scarce, and their structures and reactivities are almost unexplored. The first dialkylplumbylene, $\text{Dis}_2\text{Pb}$ [80; $\text{Dis} = \text{bis}(\text{trimethylsilyl})\text{methyl}]$, was obtained in only 3% yield,$^{57b,c,71}$ and its structure was crystallographically determined recently.$^{72}$ Another dialkylplumbylene 81 with a lead atom in a seven-membered ring system was synthesized and characterized by X-ray diffraction (Scheme 30)$^{73}$. Two stable diarylplumblenes, 82$^{70}$ and 83$^{70}$, were also structurally characterized (Scheme 30). Furthermore, an extremely hindered diarylplumbylene, $\text{Tbt}_2\text{Pb}$: (84), has recently been obtained by the nucleophilic substitution reaction of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Pb}$: (76) with two molar amounts of TbtLi as stable blue crystals (Scheme 30)$^{74}$.

\[
[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Pb}:
\]

(80)

\[
\begin{array}{c}
\text{Mes} \\
\text{SiMe}_3 \\
\text{C} \\
\text{Pb} \\
\text{Me}_3\text{Si} \\
\text{C} \\
\text{Me} \\
\text{SiMe}_3 \\
\text{Me} \\
\text{Si} \\
\text{Me} \\
\text{SiMe}_3 \\
\text{Me}
\end{array}

\text{Mes}

\begin{array}{c}
\text{Mes} \\
\text{SiMe}_3 \\
\text{C} \\
\text{Pb} \\
\text{Me}_3\text{Si} \\
\text{C} \\
\text{Me} \\
\text{SiMe}_3 \\
\text{Me} \\
\text{Si} \\
\text{Me} \\
\text{SiMe}_3 \\
\text{Me}
\end{array}

(81)

\[
\begin{array}{c}
\text{r-But} \\
\text{Pb} \\
\text{Me} \\
\text{Me} \\
\text{Me} \\
\text{Me}
\end{array}

(83)

\[
\begin{array}{c}
\text{R} \\
\text{R} \\
\text{Pb} \\
\text{R} \\
\text{R}
\end{array}

[\text{R} = \text{CH(SiMe}_3)_2]

(84)

SCHEME 30

In all cases mentioned above, the isolated plumbylenes exist as V-shaped monomers, and no evident bonding interaction between the lead centers was observed for the plumbylenes.
either in solution or in the solid state. In other words, until quite recently there has been no experimental information for the existence of a lead–lead double bond (diplumbene), the dimer of plumbylenes.

2. Lead–lead double bonds in the solid state

In 1998, Klinkhammer and coworkers found a quite interesting feature for their new heteroleptic plumbylene Rf[(Me3Si)3Si]Pb: (86)\textsuperscript{75}. Although plumbylene 86 was synthesized by a novel ligand disproportionation between the corresponding stannylene Rf\textsuperscript{2}Sn: (85) and plumbylene [(Me3Si)3Si]\textsubscript{2}Pb:, the crystallographic analysis of the isolated lead product revealed that 86 has a dimeric form 86\textsuperscript{'}, in the solid state with a considerably short Pb···Pb separation [3.537(1) Å] and a trans-bent angle of 40.8° (Scheme 31). Weidenbruch and coworkers also reported the synthesis of another heteroleptic plumbylene (87), the structural analysis of which showed a dimeric structure 87\textsuperscript{'}, in the solid state with a similar short Pb···Pb separation [3.370(1) Å] and a trans-bent angle of 46.5° (Scheme 32)\textsuperscript{70}.

\[
Rf\textsuperscript{2}Sn: + [(Me3Si)3Si]\textsubscript{2}Pb: \rightarrow \begin{array}{c}
\text{Sn} \\
\text{Sn}
\end{array} \\
\begin{array}{c}
(Me3Si)3Si \\
Si(SiMe3)3
\end{array} \\
\begin{array}{c}
Rf \\
\end{array}
\]

\[Rf = 2,4,6-(CF3)3C6H2\]

\textbf{SCHEME 31}

Although these two plumbylenes 86 and 87 were found to have a close intramolecular contact and exist as a dimer in the solid state, the lead–lead distances in their dimeric form are still much longer than the theoretically predicted values (2.95–3.00 Å) for the parent diplumbene, H\textsubscript{2}Pb=\textsubscript{2}H\textsubscript{2}\textsuperscript{31d,f,76}. In 1999, however, Weidenbruch and coworkers succeeded in the synthesis and isolation of the dimer of less hindered diarylplumbylene Tip\textsubscript{2}Pb: (88), i.e. Tip\textsubscript{2}Pb=\textsubscript{2}Tip\textsubscript{2} (89) (Scheme 33)\textsuperscript{77}. Compound 89 showed a rather shorter Pb–Pb length [3.0515(3) Å] and much larger trans-bent angles (43.9° and 51.2°) than those observed for 86\textsuperscript{'} and 87\textsuperscript{'} strongly indicating that 89 is the first molecule with a lead–lead double bond in the solid state, although 89 was found to dissociate into the monomeric plumbylene 88 in solution. Furthermore, they examined the synthesis of a heteroleptic plumbylene, Tip[(Me3Si)3Si]Pb: (90), by the treatment of diarylplumbylene 88 and disilylplumbylene [(Me3Si)3Si]\textsubscript{2}Pb:. The X-ray structure analysis revealed that the product has the centrosymmetrical diplumbene structure 91 in the solid state (Scheme 33) with a trans-bent angle of 42.7° and a Pb–Pb bond length of 2.9899(5) Å\textsuperscript{78}, which is even shorter than that of 89 and very close to the theoretically predicted value for the parent diplumbene.

In order to elucidate the relationship between the structure of plumbylene dimers and the bulkiness of substituents, Weidenbruch and coworkers synthesized and characterized
much less hindered diarylplumbylene Mes₂Pb: (92), which was isolated as a plumbylene dimer (93) stabilized with coexisting magnesium salt [MgBr₂(THF)₄] (Scheme 34). The large Pb···Pb separation [3.3549(6) Å] and trans-bent angle (71.2°) of 93 suggest that the character of the lead–lead bonding interaction in plumbylene dimers is delicate and changeable.
E. Conjugated Doubly Bonded Systems

In the last few years, further progress has been made in the chemistry of doubly bonded compounds of heavier group 14 elements. The successful isolation and characterization naturally prompted the chemists to examine the synthesis of the more sophisticated systems such as conjugated doubly bonded systems.

Thus, in 1997 Weidenbruch and coworkers have reported the synthesis and isolation of the first stable conjugated Si–Si double-bond compound, i.e. hexatipyltetrasilabuta-1,3-diene \(^{94}\). Tetrasilabutadiene \(^{94}\) was prepared through a rather unique synthetic route starting from the corresponding tetraaryl-substituted disilene \(^{95}\) via the mono-lithiated disilene \(^{96}\) as shown in Scheme 35.

\[
\text{Tip}_2\text{Si} \rightleftharpoons \text{SiTip}_2 \xrightarrow{2\text{Li}} \text{Tip}_2\text{Si} \rightleftharpoons \text{SiTip}(-\text{Li}) \xrightarrow{\text{MesBr}} \text{Tip}_2\text{Si} \rightleftharpoons \text{SiTip}(-\text{Br})
\]

SCHEME 35

In the same year, Tokitoh and coworkers have succeeded in the synthesis and isolation of the first stable 2-silanaphthalene \(^{97}\) by taking advantage of the steric protection afforded by the Tbt group (Scheme 36)\(^{10}\). These two compounds \(^{94}\) and \(^{97}\) should be noted as the first examples which showed that double bonds containing a silicon can make a conjugated system as well as the parent carbon analogues. In 2000, a stable silabenzene \(^{98}\), a much simpler silaaromatic system than \(^{97}\), was also synthesized and isolated using a similar kinetic stabilization method (Scheme 36)\(^9\).

1. Conjugated double-bond compounds containing germanium

Weidenbruch and coworkers have recently succeeded in extending their chemistry of tetrasilabutadiene (\textit{vide supra}) to its heavier congener, i.e. hexaaryltetragermanabuta-1,3-diene \(^{100}\). In this case, tetragermabutadiene \(^{100}\) was prepared from digermene 4 via \(^{99}\) by the synthetic method similar to that of its silicon analogue (Scheme 37)\(^{79}\).

Although the crystallographic analysis of the structure of \(^{100}\) revealed the existence of two Ge–Ge double bonds, no information has been given concerning the possible conjugation between the two digermene units. A more convincing insight was obtained from the electronic spectrum of \(^{100}\). The longest wavelength absorption at 560 nm for
100 in hexane is reasonably interpreted in terms of the bathochromic shifts of those observed for digermenes, which showed yellow or orange color in solution ($\lambda_{\text{max}} = 408–440$ nm)\(^1\text{p},20,23\).

In view of the successful isolation of tetragermabutadiene 100 and its conjugated electronic properties, it may be possible to construct other types of conjugated systems containing germanium atom(s). Actually, Tokitoh and coworkers have recently succeeded in isolating a stable 2-germanaphthalene 101 bearing a Tbt group on the Ge atom\(^81\). The synthesis of germanaphthalene 101 should be noted not only as giving a new example of a cyclic conjugated germene, but also as the first stable example of a neutral germaaromatic compound (Scheme 38).

**Scheme 36**

**Scheme 37**

**Scheme 38**
III. HEAVIER CONGENERS OF KETONES

Carbonyl compounds such as ketones and aldehydes are another important class of doubly bonded systems in organic chemistry. However, their heavier element congeners, "heavy ketones", are much less explored because of the extremely high reactivities.

In the past few decades, almost all of the heavier chalcogen analogues of ketones, i.e. thioketones\textsuperscript{82}, selenoketones\textsuperscript{83}, and telluroketones\textsuperscript{84}, have been synthesized and characterized. Both thermodynamic and kinetic stabilization methods have been applied to stabilize these unstable double-bond species. In contrast to the doubly bonded systems between carbon and heavier chalcogens, heavier group 14 element analogues of ketones are much more reactive and unstable and hence their structures and properties have not been fully disclosed until recently\textsuperscript{85}.

In the series of silicon-containing heavy ketones, however, some suggestive theoretical calculations by Kudo and Nagase\textsuperscript{86} and the first isolation of the thermodynamically stabilized silanethione 102\textsubscript{a,b} by Corriu and coworkers\textsuperscript{87} have strongly stimulated the chemistry of this field (Scheme 39). Then, in 1994 Okazaki, Tokitoh and coworkers reported the synthesis and isolation of the first example of a kinetically stabilized silanethione 103 by taking advantage of steric protection using the extremely bulky aryl group, Tbt (Scheme 39)\textsuperscript{6,88}.

\begin{align*}
(102a) \quad & \text{Ar = Ph} \\
(102b) \quad & \text{Ar = } \alpha\text{-Naph}
\end{align*}

SCHEME 39

The detailed background of the chemistry of heavy ketones and the recent progress in the field of silicon-containing heavy ketones has already appeared as a chapter in the previous volume of this series\textsuperscript{85a} and also in other reviews\textsuperscript{88}. Therefore, in the following sections we will discuss the chemistry of the heavier congeners containing germanium, tin and lead. Systematic comparisons for silicon through lead compounds reveal interesting differences in their properties depending on the elements. At first, it may be useful to compile the calculated $\sigma$ and $\pi$ bond energies of all the combinations of doubly bonded systems between group 14 and 16 elements (Table 3)\textsuperscript{6,88}. As can be seen in Table 3 all doubly bonded systems have an energy minimum, suggesting the possibility of their isolation if an appropriate synthetic method is available.

A. Germanium-containing Heavy Ketones

Until recently, there were only two examples of stable Ge–S double-bond compounds and one each for Ge–Se and Ge–Te double-bond compounds, but both of them are stabilized by the intramolecular coordination of a nitrogen ligand to the germanium center.
TABLE 3. Bond energies (kcal mol$^{-1}$) and lengths (Å) for H$_2$M=X systems calculated at the B3LYP/TZ(d,p) level

<table>
<thead>
<tr>
<th>H$_2$M=X</th>
<th>O</th>
<th>S</th>
<th>Se</th>
<th>Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$C=X</td>
<td>$\sigma^a$</td>
<td>93.6</td>
<td>73.0</td>
<td>65.1</td>
</tr>
<tr>
<td></td>
<td>$\pi^b$</td>
<td>95.3</td>
<td>54.6</td>
<td>43.2</td>
</tr>
<tr>
<td></td>
<td>$d^c$</td>
<td>1.200</td>
<td>1.617</td>
<td>1.758</td>
</tr>
<tr>
<td></td>
<td>$\Delta^d$</td>
<td>15.5</td>
<td>11.9</td>
<td>11.1</td>
</tr>
<tr>
<td>H$_2$Si=X</td>
<td>$\sigma^a$</td>
<td>119.7</td>
<td>81.6</td>
<td>73.7</td>
</tr>
<tr>
<td></td>
<td>$\pi^b$</td>
<td>58.5</td>
<td>47.0</td>
<td>40.7</td>
</tr>
<tr>
<td></td>
<td>$d^c$</td>
<td>1.514</td>
<td>1.945</td>
<td>2.082</td>
</tr>
<tr>
<td></td>
<td>$\Delta^d$</td>
<td>8.1</td>
<td>9.4</td>
<td>9.3</td>
</tr>
<tr>
<td>H$_2$Ge=X</td>
<td>$\sigma^a$</td>
<td>101.5</td>
<td>74.1</td>
<td>67.8</td>
</tr>
<tr>
<td></td>
<td>$\pi^b$</td>
<td>45.9</td>
<td>41.1</td>
<td>36.3</td>
</tr>
<tr>
<td></td>
<td>$d^c$</td>
<td>1.634</td>
<td>2.042</td>
<td>2.174</td>
</tr>
<tr>
<td></td>
<td>$\Delta^d$</td>
<td>8.6</td>
<td>9.5</td>
<td>9.2</td>
</tr>
<tr>
<td>H$_2$Sn=X</td>
<td>$\sigma^a$</td>
<td>94.8</td>
<td>69.3</td>
<td>64.3</td>
</tr>
<tr>
<td></td>
<td>$\pi^b$</td>
<td>32.8</td>
<td>33.5</td>
<td>30.6</td>
</tr>
<tr>
<td></td>
<td>$d^c$</td>
<td>1.802</td>
<td>2.222</td>
<td>2.346</td>
</tr>
<tr>
<td></td>
<td>$\Delta^d$</td>
<td>7.6</td>
<td>8.9</td>
<td>8.5</td>
</tr>
<tr>
<td>H$_2$Pb=X</td>
<td>$\sigma^a$</td>
<td>80.9</td>
<td>60.9</td>
<td>57.0</td>
</tr>
<tr>
<td></td>
<td>$\pi^b$</td>
<td>29.0</td>
<td>30.0</td>
<td>27.8</td>
</tr>
<tr>
<td></td>
<td>$d^c$</td>
<td>1.853</td>
<td>2.273</td>
<td>2.394</td>
</tr>
<tr>
<td></td>
<td>$\Delta^d$</td>
<td>8.5</td>
<td>9.2</td>
<td>8.9</td>
</tr>
</tbody>
</table>

$^a$ $\sigma$ bond energy.

$^b$ $\pi$ bond energy.

$^c$ Length of the M=X double bond.

$^d$ Value of % reduction in a bond length defined as [(single bond length − double bond length)/single bond length] × 100.

In 1989, Veith and coworkers reported the synthesis of a base-stabilized Ge=S double-bond species 104 (Scheme 40)$^{89}$. The X-ray structural analysis$^{40}$ shows that the sum of the bond angles around Ge atom was 355°, which indicates that the geometry for the Ge atom can be described as distorted tetrahedral, or better still as trigonal planar with an additional bond (N $\rightarrow$ Ge). The Ge=S bond distance of 2.063(3) Å was about 0.2 Å shorter than the value for a Ge=S single bond. The $^1$H NMR spectrum showed three signals assigned to nonequivalent $t$-butyl groups which also indicate this coordination of the nitrogen atom. The synthesis of a germanone bearing the same substituent from the corresponding germylene 105 was also studied (Scheme 40)$^{89a}$, but the trial was unsuccessful, since it resulted in the formation of 106, a dimer of the corresponding germanium–oxygen double-bond species. This is most likely due to the high polarity of the Ge=O bond$^{90}$ in spite of the thermodynamic stabilization.

As another synthetic approach to the doubly bonded systems containing a germanium, Kuchta and Parkin reported the synthesis of a series of terminal chalcogenido complexes of germanium 107, 108 and 109 (Scheme 41)$^{91}$. X-ray structural analyses of 107, 108 and 109 revealed that they have unique germachalcogenourea structures stabilized by the intramolecular coordination of nitrogen atoms but the central Ge−X (X = S, Se, Te) bond of 107, 108 and 109 should be represented by a resonance structure, Ge$^+−X^−$ $\leftrightarrow$ Ge=X.
13. Multiply bonded germanium, tin and lead compounds

\[ \text{(105)} \]

\[ \text{(106)} \]

SCHEME 40

SCHEME 41

(107) \( X = S \)
(108) \( X = \text{Se} \)
(109) \( X = \text{Te} \)
Their bond lengths are somewhat longer compared to the sums of theoretically predicted double-bond covalent radii: 2.110(2) Å for Ge=S (107), 2.247(1) Å for Ge=Se (108) and 2.446(1) Å for Ge=Te (109).

1. Synthetic strategies for stable germanium-containing heavy ketones

A variety of preparation methods are known for transient germanium–chalcogen double-bond species; some of them seem to be also useful for the synthesis of kinetically stabilized systems. Indeed, Tokitoh, Okazaki, and coworkers found that the reaction of a germylene with an appropriate chalcogen source is one of the most versatile and general methods for the synthesis of stable germanium-containing heavy ketones (Scheme 42)85b.

\[
\begin{array}{c}
\text{Ge} \quad \text{R} \quad \text{R'}
\end{array}
\quad \quad
\text{[Ch]}
\quad \quad
\begin{array}{c}
\text{Ge} \equiv \text{Ch}
\end{array}
\quad \quad
\begin{array}{c}
\text{n} \text{R}_3 \text{P} \quad \text{Ch}
\end{array}
\quad \quad
\begin{array}{c}
\text{R} \quad \text{Ge} \quad \text{R'}
\end{array}
\quad \quad
\begin{array}{c}
\text{Ch}_{n+1}
\end{array}
\]

\[
\text{Ch} = \text{O, S, Se, Te}
\]

SCHEME 42

As in the case of silanethione 103, there has been developed an efficient synthetic method for stable germanethiones and germaneselones, i.e. germanium–sulfur and germanium–selenium double-bond compounds, via dechalcogenation reactions of the corresponding overcrowded germanium-containing cyclic polychalcogenides with a phosphine reagent (Scheme 42)85b. This method is superior to the direct chalcogenation of germylenes in view of the easy separation and isolation of the heavy ketones by simple filtration of the phosphine chalcogenides formed. However, it cannot be applied to the synthesis of germanones and germanetellones due to the lack of stable precursors, i.e. cyclic polyoxides and polytellurides.

\[a. \text{Synthesis of a stable diarylgermanethione.} \]

A series of overcrowded cyclic polysulfides bearing two bulky aryl groups, i.e. 1,2,3,4,5-tetrathiagermolanes 110a–c, have been synthesized as the precursors for kinetically stabilized germanethiones92. The desulfurization of tetrathiolane 110a resulted in the formation of 1,3,2,4-dithiadigermetane 111a, a dimer of germanethione 112a, suggesting that the combination of Tbt and Mes groups is not sufficient to stabilize the reactive Ge=S system (Scheme 43)93.

In contrast, desulfurization of 110b bearing a bulkier Tip group gave germanethione Tbt(Tip)Ge=S 112b without forming any dimer (Scheme 43)94. Although 112b is highly reactive toward water and oxygen, it can be isolated quantitatively under argon atmosphere as orange-yellow crystals. It should be noted that 112b is the first kinetically stabilized isolable germanethione94. It melted at 163–165 °C without decomposition, and no change was observed even after heating its hexane solution at 160 °C for 3 days in a sealed tube. The absorption maximum at 450 nm observed for the orange-yellow hexane solution of 112b was attributable to the n–π* transition of the Ge=S double bond.

Desulfurization of tetrathiagermolane 110c bearing a Dep group, having a bulk between those of Mes and Tip, also gave a dimer of the corresponding germanethione 111c as in the case of 110a (Scheme 43)95. At the beginning of the reaction, however, the electronic spectrum of the hexane solution is reported to show the appearance of a transient absorption at 450 nm attributable to the intermediary germanethione 112e.
These results can be reasonably interpreted in terms of the bulkiness of the protecting groups on the germanium atom, indicating that a combination of Tbt and Tip groups is necessary in order to isolate a germanethione.$^{95}$

**b. Synthesis of a stable diarylgermaneselone.** As in the case of germanethiones, it is known that the treatment of less hindered tetraselenagermolane Tbt(Mes)GeSe$_4$ $^{113a,95,96}$ with triphenylphosphine gives only 1,3,2,4-diselenadigermetane $^{115}$, a dimer of the corresponding germaneselone Tbt(Mes)Ge=Se ($^{114}$), even in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene. This result clearly shows the high reactivity of a germaneselone and the insufficient steric protection by the combination of Tbt and Mes groups (Scheme 44)$^{95}$.

By contrast, Tokitoh, Okazaki and coworkers have reported that deselenation of the bulkier precursor Tbt(Tip)GeSe$_4$ $^{113b}$ with 3 molar equivalents of triphenylphosphine in refluxing hexane under argon resulted in the quantitative isolation of the first stable germaneselone Tbt(Tip)Ge=Se $^{116}$ as red crystals (Scheme 44).$^{95,97}$ Dimerization of $^{116}$ was not observed even in refluxing hexane, in spite of the longer Ge=Se bond distance than that of Ge=S. Germaneselone $^{116}$ was extremely sensitive to moisture but thermally quite stable under inert atmosphere. One can see that the combination of Tbt and Tip groups is sufficiently effective to stabilize the reactive germaselenocarbonyl unit of $^{116}$, as is the case of the germanethione $^{112b}$.

**c. Stable diaryl-substituted germanetellone.** In contrast to the extensive studies on thio-carbonyl and selenocarbonyl compounds,$^{7,8}$ the chemistry of tellurocarbonyl compounds has been much less studied owing to their instabilities.$^{83c,98}$ The chemistry of a germanetellone, the germanium analogue of a tellone, has also been very little explored. Theoretical calculations for H$_2$Ge=Te at B3LYP/TZ(d,p) level have predicted that it has even smaller $\sigma$ (59.1 kcal mol$^{-1}$) and $\pi$ (30.3 kcal mol$^{-1}$) bond energies than those of the
corresponding germanethione and germaneselone, but it still exists at an energy minimum, suggesting the possibility of its isolation. Kuchta and Parkin have already reported the synthesis and crystallographic structure of germatellurourea (Scheme 41), which is stabilized by intramolecular coordination of nitrogen atoms onto the Ge atom, as the only report on the chemistry of germanium−tellurium double-bond species. In view of these facts, the synthesis and isolation of a kinetically stabilized germanetellone are significant not only in order to clarify the character of the Ge−Te double bond by itself, but also to elucidate systematically the properties of germanium-containing heavy ketones.

The successful isolation of stable germanethione and germaneselone suggests that an overcrowded cyclic polytelluride might be a useful precursor for a germanetellone, if it is available. However, no isolable cyclic polytelluride has been obtained, probably owing to the instability of polytellurides. Hence, another synthetic approach was necessary to generate and isolate the germanetellones.

Tokitoh, Okazaki and coworkers have reported that when the stable diarylgermylene, obtained by reduction of the corresponding dibromide with lithium naphthalenide, was allowed to react with an equimolar amount of elemental tellurium in THF, a germanetellone was obtained directly (Scheme 45).

The color change of the solution from blue (λ_max = 581 nm) due to 117 to green (λ_max = 623 nm) was indicative of the generation of a germanetellone. The trapping experiment with mesitonitrile oxide leading to the formation of 37% oxatellurazagermole, the [3+2]cycloadduct of 118, also suggested the generation of 118 as a stable species.
in solution (Scheme 45)\textsuperscript{99,100}. Although this is the first generation and direct observation of a kinetically stabilized germanetellone, an alternative synthetic method for 118 was considered to be necessary for its isolation in view of the low efficiency of its generation and the practical purification procedures.

d. Isolation of a stable germanetellone. Tokitoh, Okazaki and coworkers have reported that when germylene 117, generated from dibromogermane Tbt(Tip)GeBr\textsubscript{2} and lithium naphthalenide, was allowed to react with diphenylacetylene it afforded germirene 120 in good yield as white crystals (Scheme 46)\textsuperscript{101}. This germirene is kinetically stable owing to the bulky groups, in contrast to previously reported germirenes\textsuperscript{102} which are known to be hydrolyzed rapidly in air. They found that germirene 120 was thermally labile and, on heating at 70 °C in the presence of 2,3-dimethyl-1,3-butadiene, it gave germacyclopentene 121 (95%) and diphenylacetylene (100%) with complete consumption of the starting material (Scheme 46). This cheletropic reaction is reversible; in the absence of the trapping reagent, the colorless solution at room temperature turns pale blue at 50 °C showing the regeneration of germylene 117, and becomes colorless again on cooling. These results indicate that germirene 120 is a useful precursor for diarylgermylene 117 under neutral conditions without forming any reactive byproducts (Scheme 46)\textsuperscript{101}.

For the synthesis of germanetellone 118, germirene 120 and an equimolar amount of elemental tellurium were allowed to react in benzene-\textit{d}\textsubscript{6} at 80 °C. On heating the mixture for 9 days and monitoring by \textit{1}H NMR, the appearance of new signals along with those of diphenylacetylene at the expense of those assigned to 120 was observed and the solution turned green. The almost quantitative generation of germanetellone 118 was confirmed by the trapping experiment with mesitonitrile oxide giving the corresponding [3+2]cycloadduct 119 in 94% yield (Scheme 47)\textsuperscript{99,100}. Removal of the solvent from the green solution without the addition of mesitonitrile oxide gave quantitatively germanetellone 118 as green crystals (Scheme 47)\textsuperscript{99,100}. This is the first isolation of a kinetically stabilized germanetellone. Germanetellone 118 was sensitive toward moisture, especially in solution, but thermally quite stable; it melted at 205–210 °C without decomposition.

e. Synthesis of alkyl,aryl-substituted germanium-containing heavy ketones\textsuperscript{85a}. Furthermore, Tokitoh, Okazaki, and coworkers have examined the chalcogenation of an alkyl,aryl-disubstituted germylene, 122\textsuperscript{101}, for a systematic synthesis and isolation of alkyl, aryl-disubstituted germanium-containing heavy ketones (Scheme 48). Germylene 122 was generated by the loss of diphenylacetylene from the corresponding germirene 123 under the conditions similar to those for diarylgermylene 117.
Thermal reaction of germirene 123 was performed in the presence of 1/8 molar amount of S\textsubscript{8} to give germanethione Tbt(Dis)Ge=S (124) quantitatively; it was isolated as yellow crystals in a glove box under pure argon (Scheme 48). Similarly, germaneselone Tbt(Dis)Ge=Se (125) and germanetellone Tbt(Dis)Ge=Te (126) were also synthesized quantitatively and isolated as orange-red and blue-green crystals, respectively (Scheme 48)\textsuperscript{99,103}. In case of germanethione 124, an alternative synthetic route starting from the corresponding tetra(thi)agermolane Tbt(Dis)GeS\textsubscript{4} (127) was examined. The desulfurization of 127 with three molar equivalent amounts of triphenylphosphine in hexane resulted in the formation of the expected germanethione 124 as a major product together with a tetra(thi)adigermacyclohexane derivative 128 as a minor product (Scheme 48).

f. Synthesis of stable dialkyl-substituted germanium-containing heavy ketones. Although there have so far been no reports on the synthesis of kinetically stabilized germanium-containing heavy ketones bearing only alkyl substituents, pentacoordinate germanechalcogenones 130–132 bearing two alkyl ligands were recently synthesized by the chalcogenation of the corresponding base-stabilized germynes 129 (Scheme 49)\textsuperscript{104}. 
Their crystallographic analysis revealed that these pentacoordinate Ge complexes have pseudo-trigonal bipyramidal geometry with a trigonal planar arrangement of the chalcogen and the two carbon atoms around the germanium center. The Ge–chalcogen bond lengths of 130–132 were found to be intermediate between typical single and double bond lengths (vide infra).

### g. Heteroatom-substituted germanium–chalcogen double-bond compounds

In addition to the extensive studies on Ge-containing heavy ketones, there have been recently reported several examples of stable germanium–chalcogen doubly bonded systems having two heteroatom substituents. These include 134\(^{105}\), 136\(^{106}\), 137\(^{106a}\) 139a,b\(^{107}\) and 140a–d (Scheme 50)\(^{107}\) which were mostly prepared by the direct chalcogenation of the corresponding germynes 133, 135 and 138 which are thermodynamically stabilized by the heteroatom substituents.

### B. Tin-containing Heavy Ketones

#### a. Synthesis of stable stannanethiones and stannaneselones

The successful isolation of Si- and Ge-containing heavy ketones naturally provoked the challenge for the synthesis and isolation of the much heavier congeners, i.e. tin–chalcogen doubly bonded systems. However, the combination of Tbt and Tip groups is not bulky enough to stabilize the stannanethione Tbt(Tip)Sn=S 141\(^{108}\), in contrast to the lighter analogues such as silanethione 103 and germanethione 112b.

Although the stability of stannanethione 141, which was generated in the sulfurization of the corresponding stannylene Tbt(Tip)Sn: (142) with elemental sulfur, was evidenced by the characteristic absorption maxima (\(\lambda_{\text{max}} = 465\) nm) in its electronic spectra, concentration of the reaction mixture resulted in the dimerization of 141 giving 1,3,2,4-dithiadistannetane derivative 143 (Scheme 51)\(^{108a,c}\). Stannanethione 141 can also be formed in the desulfurization of the corresponding tetraethylstannolane 144 with triphenylphosphine, but the formation of 141 has been confirmed only by trapping experiments (vide infra)\(^{108b}\) and the \(^{119}\)Sn NMR chemical shift for the central tin atom of 141.
(a) R = Me, R' = c-Hex, R'' = C(Me)=N(Hex-c)
(b) R = t-Bu, R' = c-Hex, R'' = C(Me)=N(Hex-c)
(c) R = Me, R' = R'' = SiMe₃
(d) R = t-Bu, R' = R'' = SiMe₃

SCHEME 50
was not measured. The formation of similarly substituted stannaneselone 146 was also demonstrated by the intramolecular trapping experiments \textit{(vide infra)}, but no spectroscopic evidence was obtained (Scheme 51).108b,109

\begin{equation}
\text{Tbt} \quad \text{Tip} \quad \text{Sn} \quad \text{Y}
\end{equation}

\begin{equation}
\text{Tbt} \quad \text{Tip} \quad \text{Sn} \quad \text{Y} \quad \text{Y} \quad \text{Tip}
\end{equation}

\begin{equation}
\text{Tbt} \quad \text{Sn} \quad \text{Y} \quad \text{Tbt}
\end{equation}

\begin{equation}
\text{Tbt} \quad \text{Tip} \quad \text{Sn} \quad \text{Y} \quad \text{Y} \quad \text{Tip}
\end{equation}

\begin{equation}
\text{Tbt} \quad \text{Sn} \quad \text{Y} \quad \text{Sn} \quad \text{Tbt}
\end{equation}

\begin{equation}
\text{Tbt} \quad \text{Sn} \quad \text{Y} \quad \text{Tbt}
\end{equation}

\begin{equation}
\text{Y} = \text{S}
\end{equation}

\begin{equation}
\text{Y} = \text{Se}
\end{equation}

\begin{equation}
\text{Y} = \text{S}
\end{equation}

\begin{equation}
\text{Y} = \text{Se}
\end{equation}

\begin{equation}
\text{Y} = \text{S}
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\begin{equation}
\text{Y} = \text{Se}
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\begin{equation}
\text{Y} = \text{S}
\end{equation}

\begin{equation}
\text{Y} = \text{Se}
\end{equation}

\begin{equation}
\text{Y} = \text{S}
\end{equation}

\begin{equation}
\text{Y} = \text{Se}
\end{equation}

SCHEME 51

The high reactivity of tin–chalcogen double bonds was somewhat suppressed by the modification of the steric protection group combined with the Tbt group from the Tip group to more hindered ones such as 2,4,6-tricyclohexylphenyl (Tcp), 2,4,6-tris(1-ethylpropyl)-phenyl (Tpp) and 2,2''-dimethyl-m-terphenyl (Dmtp) groups110,111. Thus, in these bulkier systems, the corresponding stannanethiones (148, 151 and 154) and stannaneselones (157, 160 and 163), formed respectively from 147, 150 and 153 and from 156, 159 and 162, showed characteristic orange and red colors, respectively, and all of them showed considerably deshielded $^{119}$Sn NMR chemical shifts ($\delta_{\text{Sn}} = 467$ to 643 ppm) at ambient temperature, suggesting the $sp^2$ character of their tin centers and also their stability in solution (Scheme 52). On concentration of the samples used for the NMR measurements, however, these tin-containing heavy ketones underwent dimerization to give the corresponding dimers (149, 152, 155, 158, 161 and 164) although it was unsuccessful in isolating them as a stable solid or crystallines.

As the final goal of the synthesis and isolation of tin–chalcogen double-bond species, further modification of Dmtp group was examined111. Thus, the fine tuning of the side chains of the terphenyl unit of Dmtp, i.e. the use of 2,2''-diisopropyl-m-terphenyl (Ditp) group which bears two isopropyl groups instead of methyl groups in 2 and 2'' positions, allowed isolation of the corresponding stannanethione 166 and stannaneselone 168 as stable orange and red crystals, respectively. Both 166 and 168 were synthesized by the dechalcogenation of the corresponding Tbt- and Ditp-substituted tetrachalcogenastannolanes 165 and 167 with three equivalents of phosphine reagents (Scheme 53)111. No dimerization of 166 and 168 was observed even after concentration to the solid state, and the molecular geometry of stannaneselone 169 was definitively determined by X-ray crystallographic analysis.

In addition to the successful isolation of the stable stannaneselone 168, it should be noted that deselenation of 167 with two molar equivalents of triphenylphosphine resulted in the isolation of a novel tin-containing cyclic diselenide, i.e. diselenastannirane 169, as a stable crystalline compound111.
(147) Ar = Tcp, Y = S  
(150) Ar = Tpp, Y = S  
(153) Ar = Dmtp, Y = S  
(156) Ar = Tcp, Y = Se  
(159) Ar = Tpp, Y = Se  
(162) Ar = Dmtp, Y = Se  

(148) Ar = Tcp, Y = S  
(151) Ar = Tpp, Y = S  
(154) Ar = Dmtp, Y = S  
(157) Ar = Tcp, Y = Se  
(160) Ar = Tpp, Y = Se  
(163) Ar = Dmtp, Y = Se  

(149) Ar = Tcp, Y = S  
(152) Ar = Tpp, Y = S  
(155) Ar = Dmtp, Y = S  
(158) Ar = Tcp, Y = Se  
(161) Ar = Tpp, Y = Se  
(164) Ar = Dmtp, Y = Se  

SCHEME 52

(165) Y = S  
(167) Y = Se  
(166) Y = S  
(168) Y = Se

(169) Y = S

Ditp group = 2,6-(2′-i-PrC₆H₄)₂C₆H₃

SCHEME 53
C. Lead-containing Heavy Ketones\textsuperscript{74b}

a. Synthesis of plumbanethiones by desulfurization of tetrathiaplumbolanes. In anticipation of kinetic stabilization of a plumbanethione, the heaviest congener of metallanethiones of group 14 elements, a series of hindered tetrathiaplumbolanes 170–172, were desulfurized with 3 equivalents of hexamethylphosphorous triamide at low temperature (−78 °C) in THF. The color of the reaction solution turned red for 170 and 171 or orange for 172, indicating the generation of plumbanethiones 173, 174 or 175, respectively\textsuperscript{74b}. Subsequent addition of mesitonitrile oxide to these solutions at −78 °C gave the corresponding oxathiazaplumboles 176–178, the [3+2]cycloadducts of plumbanethione 173–175, in moderate yields in each case (Scheme 54)\textsuperscript{74b,112}. Plumbanethiones 173 and 175 were also trapped with phenyl isothiocyanate to give the [2+2]cycloaddition products 179 and 181, respectively, though 174 did not afford such an adduct 180. The formation of new Pb-containing heterocycles 176–178, 179 and 181 is noteworthy as the first examples of the trapping of plumbanethiones. Observation of the color changes of the reaction solution suggests that plumbanethiones 173–175 thus formed are stable in solution, at least below −20 °C.

![Scheme 54](image)

Ttm group = 2,4,6-(CH\textsubscript{2}SMe\textsubscript{3})\textsubscript{3}C\textsubscript{6}H\textsubscript{2}

In order to elucidate the thermal stability of the plumbanethione 174, tetrathiaplumbolane 171 was desulfurized at higher temperature. Reaction of 171 with 3 equivalents of triphenylphosphine in toluene at 50 °C gave a deep red solution, from which plumbylene 182 was precipitated as pure deep red crystals (Scheme 55)\textsuperscript{113}. Besides 182, 1,3,2,4-dithiadiplumbetane 183 was obtained as another lead-containing major product. It should

![Scheme 55](image)
be noted that the final product 182 bears only Tbt groups, while 183 has only Tip groups, though the starting material 171 bears both Tbt and Tip groups on the lead atom.

The fact that the final products, 182 and 183, bear only Tbt and Tip groups, respectively, indicates the presence of some comproportionation process in their formation from 174. A plausible mechanism is shown in Scheme 56 for the formation of 182 and 183, though a detailed reaction mechanism is not clear at present\textsuperscript{113}. The tetrathiaplumbolane 171 is first desulfurized to provide plumbanethione 174, as has been seen in the desulfurization of 171 at low temperature. Plumbanethione 174 might undergo 1,2-aryl migration to give plumbylenes 184 and 185, which subsequently react to afford an arylsulfido bridged organolead heterocycle 186, since a less hindered arylthioplumbylene is known to have a tendency to oligomerize, forming a cyclic compound\textsuperscript{114a}. The retro [2+2]cycloaddition reaction of 186 affords 182 and 187. Dithiaadiplumbetane 183 may be obtained from the less crowded plumbylene 187.

X-ray crystallographic analysis reveals that plumbylene 182 exists as a monomer and there is no intermolecular interaction between the lead and sulfur atoms\textsuperscript{113a}, while other heteroatom-substituted plumbylenes so far known exist as the heteroatom-bridged cyclic oligomers\textsuperscript{114}.

\textit{b. Synthesis of plumbanethione by sulfurization of plumbylene.} In order to prove the 1,2-aryl migration process proposed for plumbanethione 174, the synthesis of plumbanethione 189 by sulfurization of a diarylplumbylene 188 with one atom equivalent of elemental sulfur at low temperature and the successive trapping reaction of 189 with mesitonitrile oxide were carried out (Scheme 57)\textsuperscript{74b}. The formation of cycloadduct 190 indicates the generation of intermediary plumbanethione 189. Furthermore, the fact that heating of a toluene solution of isolated plumbylene 188 with one atom equivalent of elemental sulfur at 50°C gave 182 clearly demonstrates the occurrence of 1,2-aryl migration in 189 (Scheme 57)\textsuperscript{74b}. The formation of 182 in this experiment is the first experimental demonstration that R(RS)Pb is more stable than R\textsubscript{2}Pb=S.

This interpretation of the experimental results was corroborated by \textit{ab initio} calculations on the relative stabilities of a series of double-bond compounds, [H\textsubscript{2}Pb=X], and
their plumbylene-type isomers, [trans-H-Pb-X-H] and [cis-H-Pb-X-H] (X = O, S, Se, and Te)\(^{74b}\). The results of the theoretical calculations and experiments for lead–chalcogen double-bond species are in sharp contrast to those of the other group 14 element analogues which do not isomerize to the divalent compounds\(^{88}\).

### D. Structures and Properties of Heavy Ketones

It is very important to reveal the structural features of heavy ketones and to make a systematic comparison with features of the carbonyl analogue such as the bond shortening and the trigonal planar geometry which result from the \(sp^2\) hybridization between the carbon and oxygen atoms. In the following sections, the experimentally and theoretically obtained features of heavy ketones, including the silicon-containing heavy ketones, are systematically compared.

#### 1. X-ray crystallographic analysis

First, a crystallographic analysis of the thermodynamically stabilized silanethione was established for the bulky silanethione 102b (Scheme 39). Although the Si–S bond [2.013(3) Å] in 102b is shorter than a typical Si–S single bond (2.13–2.16 Å)\(^{115}\), suggesting that it has a double-bond character to some extent, it is still 0.07 Å longer than the calculated value for the parent silanethione H\(_2\)Si=S. The Si–N distance (1.964 Å) in 102b, which is slightly longer than a Si–N \(\sigma\) bond (1.79 Å), supports a very strong coordination of the nitrogen atom of the dimethylaminomethyl group in 102b to the central silicon atom. Such intramolecular coordination in turn makes the silathiocarbonyl unit of 102b considerably deviant from the ideal trigonal planar geometry; the sum of the angles around the central silicon atom is 344.9°. The authors concluded that a resonance betaine structure contributes strongly to the electronic distribution of the internally coordinated silanethiones 102a,b.

Therefore, the elucidation of the intrinsic structural parameters of heavy ketones has to be done with kinetically stabilized systems. Most of the heavy ketones synthesized by taking advantage of the steric protection with the Tbt group have provided single crystals suitable for X-ray structural analysis. The results for silanethione 103, germanethione
TABLE 4. Structural parameters of heavy ketones Tbt(R)M=X

<table>
<thead>
<tr>
<th>Compound</th>
<th>M–X (Å)</th>
<th>Δ₁/obs</th>
<th>Σ₁M (deg)</th>
<th>Tip</th>
<th>Tip</th>
<th>Tip</th>
<th>Dis</th>
<th>Dis</th>
<th>Tip</th>
<th>Dis</th>
<th>Ditp</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>103</td>
<td>112b</td>
<td>116</td>
<td>125</td>
<td>118</td>
<td>126</td>
<td>168</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M–X (Å)</td>
<td>1.948(4)</td>
<td>2.049(3)</td>
<td>2.180(2)</td>
<td>2.173(3)</td>
<td>2.398(1)</td>
<td>2.384(2)</td>
<td>2.375(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Δ₁/obs (%)*</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>8</td>
<td>9</td>
<td>8</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Σ₁M (deg)</td>
<td>359.9</td>
<td>359.4</td>
<td>359.3</td>
<td>360.0</td>
<td>359.5</td>
<td>360.0</td>
<td>359.9</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

*R The bond shortening (%) compared to the corresponding single bonds.

*Summation of the bond angles around the M atom.

112b, germaneselones 116, 125, germanetellones 118, 126 and stannaneselone 168 are summarized in Table 4.

The structural parameters of all heavy ketones examined show that they have an almost completely trigonal planar geometry and a distinct double-bond nature. The observed double-bond lengths and Δ₁/obs [bond shortening (%) compared to the corresponding single bonds] values are in good agreement with calculated values for H₂M=X₆b,88. These findings clearly indicate that heavy ketones have structural features similar to those of a ketone, although their double-bond character is lower than that of the corresponding carbon analogues as judged by their Δ₁/obs values.

It should be noted that all the M=X bond lengths observed are significantly shorter than those reported for the corresponding double-bond compounds stabilized by intramolecular coordination of heteroatoms. In other words, thermodynamically stabilized systems suffer from considerable electronic perturbation by heteroatom substituents.

Although some examples of thermodynamically stabilized double-bond systems between group 14 and 16 elements showed trigonal planar geometry due to their structural restriction, almost all of their bond lengths are longer than those of kinetically stabilized systems and of the values theoretically predicted116. These results clearly show that considerable electronic perturbation is inevitably involved in the thermodynamically stabilized systems.

2. NMR spectra

As in the case of ¹³C NMR, low-field chemical shifts are characteristic of sp²-hybridized nuclei also in the heavy ketones. For example, the ²⁹Si chemical shifts of silanethione 103 and silaneselone [Tbt(Dip)Si=Se (191)]⁸⁸,¹¹⁷ are 167 and 174 ppm, respectively. Silanetellone [Tbt(Dip)Si=Te (192)]⁸⁸,¹¹⁷ also shows its ²⁹Si NMR signal at 171 ppm. In contrast, the ²⁹Si NMR signal of Corriu’s compound 102a (X=S) appears at 22.3 ppm⁸⁷, indicating the high sp³ nature of the silicon centers in 102a. In the cases of the above-mentioned silaneselone and silanetellone, the characteristic low-field ⁷⁷Se and ¹²⁵Te chemical shifts of 191 (δSe = 635) and 192 (δTe = 731) are also indicative of their sp²-hybridized chalcogen atoms.

Similarly, stannanethione 166 and stannaneselone 168 kinetically stabilized by Tbt and Ditp groups have ¹¹⁹Sn chemical shifts of 531 and 440 ppm, respectively. Kuchta and Parkin have reported the synthesis of stable terminal chalcogenido complexes of tin 193 (Scheme 58), and the chemical shifts for the central tin atom appears at a much higher field, i.e. −303 ppm (193a, X=S) and −444 ppm (193b, X=Se)⁹¹. This clearly shows that the thermodynamically stabilized tin–chalcogen double bonds in 193 (X=S, Se) are electronically perturbed to a great extent.
On the other hand, such information is not available for germanium-containing heavy ketones because of the difficulty in observing Ge NMR spectra, but the low-field shifted $^{77}$Se and $^{125}$Te NMR signals of germaneselenones [δSe = 941 (for 116) and 872 (for 125)]$^{95,97}$ and germanetellones [δTe = 1143 (for 118) and 1009 (for 126)]$^{99,103}$ are in agreement with the $sp^2$-hybridization of these elements as in the cases of silaneselonel 191 and silanetellone 192.

3. UV-vis spectra

Table 5 lists characteristic visible absorptions observed for the heavy ketones kinetically stabilized by the Tbt group.

It is known that the $n$–$\pi^*$ absorptions of a series of $R_2C=X$ ($X = O, S, Se, Te$) compounds undergo a systematic red shift on going down the Periodic Table.$^{84}$ A similar tendency is observed also for the Si, Ge and Sn series of Tbt(R)Si=$X$ ($X = S, Se$), Tbt(R)Ge=$X$ ($X = S, Se, Te$) and Tbt(R)Sn=$X$ ($X = S, Se$). In contrast, one can see a very interesting trend in the absorption maxima of two series Tbt(R)M=S and

| TABLE 5. Electronic spectra ($n$–$\pi^*$) of doubly bonded compounds between group 14 elements and chalcogens |
|---|---|---|---|
| Observed $\lambda_{\text{max}}$ (nm)$^a$ | Calcd$^j$ | |
| | | $\lambda_{\text{max}}$ (nm) | $\Delta\varepsilon_{\text{LUMO}}^* (\text{eV})^k$ |
| TbtCH=$X$ | 587$^b$ | 792$^c$ | H$_2$C=S | 460 | 10.81 |
| Tbt(R)Si=$X$ | 396$^d$ | 456$^e$ | H$_2$Si=S | 352 | 10.27 |
| Tbt(R)Ge=$X$ | 450$^g$ | 519$^g$ | H$_2$Ge=S | 367 | 9.87 |
| Tbt(R)Sn=$X$ | 473$^h$ | 531$^i$ | H$_2$Sn=S | 381 | 9.22 |

$^a$In hexane.
$^b$Reference 127.
$^c$Reference 128.
$^e$In THF. R = Dip.
$^f$X = Te: R = Tip, $\lambda_{\text{max}}$ 640 nm. Reference 99.
$^g$R = Tip. Reference 85.
$^h$R = Tip. Reference 108c.
$^i$R = Ditp. Reference 111.
$^j$CIS/TZ(d,p)//B3LYP/TZ(d,p).
$^k$LUMO($\pi^*$) − HOMO($n$).
Tbt(R)M=Se (M = C, Si, Ge, Sn). In both series the $\lambda_{\text{max}}$ values are greatly blue-shifted on going from carbon to silicon congeners, whereas the $\lambda_{\text{max}}$ values of silicon, germanium and tin congeners are red-shifted with increasing atomic number of the group 14 elements. This trend is also found in the calculated values for H2M=S (M = C, Si, Ge, Sn)\(^6,88\). Since the calculated $\Delta\epsilon_{n\pi^*}$ values increase continuously from H2Sn=S to H2C=S, a long wavelength absorption for H2C=S (and hence for TbtCH=S\(^69\)) most likely results from a large repulsion integral ($J_{n\pi^*}$) for the carbon–sulfur double bond, as in the case of H2C=O vs H2Si=O\(^118\).

4. Raman spectra

The stretching vibrations of the M=X bond were measured by Raman spectra for silanethione \(^103\) (724 cm\(^{-1}\)), germanethiones \(^112\) (521 cm\(^{-1}\)) and \(^124\) (512 cm\(^{-1}\)), and germanetellones \(^118\) (381 cm\(^{-1}\)) and \(^126\) (386 cm\(^{-1}\)). These values are in good agreement with those calculated for H2M=X compounds \([723 (\text{Si}=\text{S}), 553 (\text{Ge}=\text{S}) \text{ and } 387 (\text{Ge}=\text{Te}) \text{ cm}^{-1}\], respectively\(^6,88\). It is noteworthy that the observed value for Tbt(Tip)Ge=S \(^112\) is very close to that observed by IR spectroscopy for Me2Ge=S \(^119\) in a argon matrix at 17–18 K\(^119\), indicating similarity in the nature of the bond of both germanethiones in spite of the great difference in the size and nature of the substituents.

E. Reactivities of Heavy Ketones

As mentioned in the previous sections, heavy ketones undergo ready head-to-tail dimerization (or oligomerization) when the steric protecting groups on the group 14 element are not bulky enough to suppress their high reactivity. Indeed, Tbt(Mes)M=X (M = Si, Ge; X = S, Se) cannot be isolated at an ambient temperature and instead the dimerization products are obtained. In the cases of tin-containing heavy ketones, the dimerization reactions are much easier than in the lighter group 14 element congeners, and only the combination of Tbt and Ditp groups can stabilize the long and reactive tin–chalcogen double bonds (\textit{vide supra}).

Although the high reactivity of metal–chalcogen double bonds of isolated heavy ketones is somewhat suppressed by the steric protecting groups, Tbt-substituted heavy ketones allow the examination of their intermolecular reactions with relatively small substrates. The most important feature in the reactivity of a carbonyl functionality is the reversibility in the reactions across its carbon–oxygen double bond (via the addition–elimination mechanism via a tetracoordinate intermediate) as is observed, for example, in reactions with water and alcohols. The energetic basis of this reversibility is that there is very little difference in the $\sigma$ and $\pi$ bond energies of the C=O bond (Table 3). In contrast, an addition reaction involving a heavy ketone is highly exothermic and hence essentially irreversible because of the much smaller $\pi$ bond energy than the corresponding $\sigma$ bond energy of these species.

All heavy ketones kinetically stabilized by a Tbt group react with water and methanol almost instantaneously to give tetracoordinate adducts (Scheme 59). They also undergo cycloadditions with unsaturated systems such as phenyl isothiocyanate, mesitonitrile oxide and 2,3-dimethyl-1,3-butadiene to give the corresponding [2+2]-, [2+3]- and [2+4]cycloadducts, respectively (Scheme 59). The former two reactions proceed at room temperature, while the reaction with the diene takes place at higher temperature, with the lighter homologues requiring more severe conditions.

Reaction of \(^112\) with methyllithium followed by alkylation with methyl iodide gives a germophilic product \(^194\). The [2+4]cycloaddition of \(^112\) with 2-methyl-1,3-pentadiene affords \(^195\) regioselectively. When a hexane solution of \(^195\) is heated at 140 °C in a sealed tube in the presence of excess 2,3-dimethyl-1,3-butadiene, a dimethylbutadiene adduct \(^196\)
is obtained in a high yield, indicating that the Diels–Alder reaction of germanethione 112b with a diene is reversible, and hence that a diene adduct such as 195 or 196 can be a good precursor of germanethione 112b (Scheme 60). Similar reactivity was observed for germaneselone 116, and the retrocycloaddition of 197 (shown by the formation of 198) takes place at a much lower temperature (50°C) than that for 195, suggesting a weaker C–Se bond than a C–S bond (Scheme 60).
In contrast to the considerable thermal stability of the isolated heavy ketones of silicon, germanium and tin, a plumbanethione behaves differently. When stable plumbylene $\text{Tbt}_2\text{Pb}$ was sulfurized by 1 molar equivalent of elemental sulfur at $50^°\text{C}$, the heteroleptic plumbylene $\text{TbtPbSTbt} (182)$ was obtained (Scheme 57) instead of plumbanethione $\text{Tbt}_2\text{Pb}=\text{S} (189)$, which is an expected product in view of the reactivity observed for divalent species of silicon, germanium and tin (vide supra). The formation of 182 is most reasonably explained in terms of 1,2-migration of the Tbt group in the intermediate plumbanethione 189, and this observation is supporting evidence for the 1,2-aryl migration in plumbanethione 174 proposed in the reaction shown in Scheme 56. This unique 1,2-aryl migration in a plumbanethione is in keeping with a theoretical calculation which reveals that plumbylene HPb(SH) is about 39 kcal mol$^{-1}$ more stable than plumbanethione $\text{H}_2\text{Pb}=\text{S}$.74b.

IV. HEAVIER CONGENERS OF ALLENES

a. Silaallene. As can be seen in the previous sections, a variety of heavier element analogues of alkenes and ketones have been isolated by taking advantage of kinetic stabilization using bulky substituents and their structures have been characterized by X-ray crystallographic analysis. Also, there have been reported some stable examples of heavier congeners of imines such as silaneimines, $\text{R}_2\text{Si}=\text{NR}_1$.3 and germaneimines, $\text{R}_2\text{Ge}=\text{NR}_1$.121. On the other hand, the chemistry of cumulative double-bond compounds of heavier group 14 elements is less explored. In 1993, the first stable silacumulene, 1-silaallene 200, was synthesized by the reaction of well-designed alkynyl fluorosilane 199 with $\text{t}$-butyllithium by West and coworkers (Scheme 61)8a. Silaallene 200 was isolated as stable crystals and characterized by X-ray structural analysis, but very little is known about its reactivity8.

b. Germaallenes. Regarding the cumulene-type compounds containing a germanium atom, germaphosphaallene 202 was synthesized by Escudié and coworkers in 1996 using the reduction of (fluorogermyl)bromophosphaalkene 201 (Scheme 62)122. Although the generation of 202 was confirmed by $^{13}\text{C}$ and $^{31}\text{P}$ NMR at $-40^°\text{C}$, 202 dimerized at room temperature to afford two types of dimers, i.e. 203 and 204 (Scheme 62)122. This result shows that the combinations of the substituents on the germanium and phosphorous atoms were not bulky enough to prevent dimerization of 202.

In 1997, Tokitoh, Okazaki and coworkers reported evidence for the generation of a kinetically stabilized 1-germaallene 207. It was synthesized by two different synthetic approaches as shown in Scheme 63. One is the dechalcogenation reaction of the corresponding alkylidenetelluragermirane 205 with a phosphine reagent, and the other is the reduction of (1-chlorovinyl)chlorogermane 206 with $\text{t}$-butyllithium.

Both reactions afforded an identical product as judged by its NMR spectrum, and 1-germaallene 207 was found to be marginally stable in solution, showing the characteristic low-field $^{13}\text{C}$ NMR chemical shift for its central $sp$ carbon atom ($\delta_c = 243.6$ in C$_6$D$_6$). The down-field shift for the central $sp$ carbon has been also observed for 1-silaallene 200 ($\delta_c = 226$)8 and germaphosphaallene 202 ($\delta_c = 281$)122. Although 207 can be trapped with methanol, mesitonitrile oxide and elemental sulfur to give the corresponding adducts 208–210, it slowly undergoes an intramolecular cyclization in solution at room temperature to give compound 211 (Scheme 64)25,123. Concentration and isolation of 207 as crystals at low temperature has failed, and no crystallographic information has been obtained for 207 so far.

In 1998, West and coworkers succeeded in the synthesis and isolation of 1-germaallene 212, the first example of a stable 1-germaallene either in solution or in the solid state.
13. Multiply bonded germanium, tin and lead compounds

(Scheme 65)\textsuperscript{124}. \textbf{212} was stable in ether solution up to 0 °C but is completely decomposed after 15 h at 25 °C, whereas it remained unchanged in toluene up to 135 °C. Gemallene \textbf{212} was isolated by crystallization from ether at −20 °C as colorless crystals, which showed a low-field \textsuperscript{13}C NMR signal at 235.1 ppm in toluene-$d_8$ as in the case of \textbf{207}\textsuperscript{124}.

A crystallographic analysis of \textbf{212} had revealed the structural parameters for this unique cumulative bonding\textsuperscript{124}. The G=C bond length is 1.783(2) Å and the Ge=C=C unit is not linear, having a bending angle of 159.2°. The sum of the bond angles at Ge (348.4°) indicates a strong pyramidalization around the Ge center.

c. Tristannaallene. Quite recently, Wiberg and coworkers reported the first example of 1,2,3-tristannaallene \textbf{214} by taking advantage of the tri-$t$-butylsilyl (supersilyl) group\textsuperscript{125}. It was synthesized by the reaction of diaminostannylene \textbf{213} with supersilyl sodium (Scheme 66).
At the first stage below $-25 \, ^\circ\mathrm{C}$ (in pentane/C$_6$D$_6$) this reaction yields the tristannaallene 214, but it rearranges at $25 \, ^\circ\mathrm{C}$ to the isomeric cyclotristannene 215. The formation of 214 can be interpreted in terms of an initial formation of disupersilylstannylene 216 (Scheme 67)$^{125}$. 

\[ \text{Mes}^* = 2,4,6-(t-Bu)_3C_6H_2 \]

SCHEME 62

SCHEME 63
Although several examples of heavy allenes have been synthesized as stable compounds, most of them are isolated as marginally stable species at room temperature. Further systematic progress is necessary in order to elucidate the intrinsic properties of these interesting doubly bonded systems of heavier group 14 elements.
This chapter outlines the recent progress in the chemistry of multiply bonded species of Ge, Sn, and Pb. As can be concluded from this chapter and related recent reviews which deal with the chemistry of this family of compounds which are stable at room temperature, the field of low-coordinated species of heavier group 14 elements has matured considerably in recent years.

For example, we can now make a systematic comparison for heavy ketones through silicon to lead. However, heavy ketones containing an oxygen atom are still elusive species and neither their isolation nor spectroscopic detection has been achieved so far probably due to their extremely high reactivity caused by their highly polarized structure. The most fascinating and challenging target molecules in this area should be the stable oxygen-containing heavy ketones (Scheme 68).

As for the multiply bonded systems of heavier group 14 elements, all the homonuclear double bonds were successfully isolated and characterized by the end of the last century. However, the chemistry of heteronuclear double bonds and those of conjugated systems are still in growth. The synthesis and isolation of unprecedented cumulative systems such as (Scheme 68) and aromatic systems containing Ge, Sn and Pb atoms, e.g. (219–222) (Scheme 68), will also be within the range of this future chemistry. Likewise, the synthesis and isolation of the triply bonded systems (Scheme 68) should be one of the most challenging projects in this field.

SCHEME 66

SCHEME 67

V. OUTLOOK AND FUTURE
As can be seen from this chapter, kinetic stabilization has been used as a much superior method to thermodynamic stabilization in order to elucidate the intrinsic nature of the chemical bonding containing low-coordinated heavier group 14 elements. However, it might be useful to combine the two types of different stabilization methods for the synthesis and isolation of much more reactive systems as mentioned above.

Elucidation of the intrinsic properties of unprecedented chemical bondings of heavier group 14 elements and their systematic comparison will be of great importance in efforts to extend the conventional organic chemistry to that of the whole main group elements.

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CHAPTER 14

Unsaturated three-membered rings of heavier Group 14 elements

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I. INTRODUCTION

The chemistry of stable, small cyclic compounds consisting of heavy Group 14 elements (i.e. Si, Ge and Sn) has a relatively short but very impressive history. In contrast to their transient congeners, which were proposed a long time ago, the stable three-membered
ring compounds were reported for the first time only in 1982 by Masamune’s group. After the synthesis of the first representatives of cyclotrismetallanes, cyclotrigermenes and cyclotristarstananes, the chemistry of such molecules has been greatly developed during the past two decades. These compounds, similar to their carbon analogue — cyclopropane, were found to be very reactive because of their significant ring strain and the weakness of the endocyclic metal–metal bonds. The most fundamental discovery of their reactivity was the cycloelimination reaction to produce two kinds of key reactive species — heavy carbene analogues and dimetallaalkenes (dimetallenes). This is now a well-established way to generate such reactive intermediates. Heterocyclotrismetallanes consisting of different heavier Group 14 elements can be easily imagined as a convenient source for the preparation of heterodimetallenes, which can possess unusual structural and chemical properties. Nevertheless, until now there have been only a few examples of such ‘mixed’ cyclotrismetallanes, which can be explained by the difficulties in their preparation relative to their ‘homo’ analogues.

Cyclotrimetallenes, compounds that combine the cyclotrismetallane skeleton and an endocyclic metal–metal double bond in one molecule, have not been synthesized until quite recently because of the great ring strain and high reactivity of the metal–metal double bond. Nevertheless, employment of bulky silyl substituents, which sterically protect the molecule and decrease the ring strain, makes possible the successful preparation of the cyclotrimetallenes. After the first report of the synthesis of cyclotrimetallenes, there was an explosive growth in the development of their chemistry. However, even now there is a very limited number of methods for their synthesis, which are not general and usually more complicated than in the case of cyclotrismetallanes. The reactivity of cyclotrimetallenes, which combine the chemical properties of both cyclotrismetallanes and dimetallenes, was found to be very rich. Various addition and cycloaddition reactions across the metal–metal double bond give access to new cyclic and bicyclic compounds, whereas insertion reactions into the three-membered ring produce ring enlargement products. In the present review, we will concentrate only on the very recent developments in the chemistry of cyclotrimetallenes (unsaturated three-membered ring systems) of heavier Group 14 elements. Special attention will be paid to the chemistry of the cyclotrigermenium cation — the free germyl cation with a $2\pi$-electron system. The chemistry of cyclotrismetallanes, that is, their saturated analogues, will not be considered in this article, since it has already been described in previous reviews.

II. CYCLOTRIMETALLENES — UNSATURATED THREE-MEMBERED RINGS OF HEAVIER GROUP 14 ELEMENTS

A. Cyclotrisilenes

The synthesis of the first cyclotrisilenes has required a longer time than for the cyclotrigermenes due to the lack of suitable stable silylenes, in contrast, for example, to the well-known dichlorogermylene–dioxane complex. The preliminary preparation of the silylene precursors, which can generate silylenes $\textit{in situ}$, was necessary for the successful synthesis of cyclotrisilenes. Until now, only two examples of cyclotrisilenes have been reported in the literature, of which only one was structurally characterized.

These first reports on the preparation of the stable cyclotrisilenes appeared in 1999, when two groups independently published consecutive papers on the cyclotrisilenes bearing different substituents. Cyclotrisilene, which was prepared in Kira’s group, has three tert-butyldimethylsilyl substituents and a bulky tris(tert-butyldimethylsilyl)silyl group attached to one unsaturated silicon atom. This compound was obtained by the reaction...
of \( R_3\text{Si}\text{SiBr}_2\text{Cl} \) (\( R = \text{SiMe}_2\text{Bu-}t \)) with potassium graphite in THF at \(-78^\circ\text{C} \) in 11\% yield as dark red crystals (Scheme 1). The existence of the doubly-bonded silicon atoms was determined from the \(^{29}\text{Si} \) NMR spectrum, which showed two down-field signals at 81.9 and 99.8 ppm. These are significantly shifted up-field relative to those for the acyclic tetrasyldisilenes (142–154 ppm)\(^{26} \). The structure of 1 was proved by reaction with \( \text{CCl}_4 \), for which the structure of the product 2 was established by X-ray crystallography. It is interesting that the final product of the reduction of \( R_3\text{Si}\text{SiBr}_2\text{Cl} \) depends strongly on the reducing reagent. Thus, treatment of \( R_3\text{Si}\text{SiBr}_2\text{Cl} \) with sodium in toluene at room temperature gave the cyclotetrasilene 3\(^{27} \) in 64\% yield without any formation of 1.

The second example of a cyclotrisilene was reported by Sekiguchi’s group\(^{15} \). This compound was prepared by the reductive coupling of \( \text{R}_2\text{SiBr}_2 \) and \( \text{RSiBr}_3 \) [\( R = \text{SiMe}_2\text{Bu-}t \)] \(_2 \) with sodium in toluene at room temperature (Scheme 2). Cyclotrisilene 4 was isolated as red-orange crystals in 9\% yield. The \(^{29}\text{Si} \) NMR spectrum of 4 showed a down-field signal at 97.7 ppm, which is attributable to the unsaturated silicon atoms, and an up-field signal at \(-127.3 \) ppm, which is typical for a saturated silicon atom in a three-membered ring system.

Cyclotrisilene 4 has a symmetrical structure (\( C_{2v} \) symmetry), which allowed the growth of a single crystal and the determination of its crystal structure (Figure 1). X-ray analysis has revealed an almost isosceles triangle with bond angles of 62.8(1), 63.3(1) and 53.9(1)\(^{\circ} \). The geometry around the \( \text{Si} = \text{Si} \) double bond is not planar, but \( \text{trans} \)-bent with a torsion angle \( \text{Si}_4 - \text{Si}_1 - \text{Si}_2 - \text{Si}_5 \) of 31.9(2)\(^{\circ} \). The \( \text{Si} = \text{Si} \) double bond length in 4 is 2.138(2) \( \text{Å} \), which was recognized as one of the shortest distances among the \( \text{Si} = \text{Si} \) double bond
lengths reported thus far. The UV-Vis spectrum of 4 showed four bands with maxima at 223 (ε = 7490), 259 (3610), 297 (1490) and 466 nm (440).

B. Cyclotrimerenenes

Historically, cyclotrimerenenes were the first cyclotrimetallenes of Group 14 elements to be prepared. At present, six cyclotrimerenenes have been described in the scientific literature, and four of them have been structurally characterized. In 1995, Sekiguchi and coworkers reported the unexpected formation of an unsaturated three-membered ring system consisting of Ge atoms by the reaction of dichlorogermyle–dioxane complex with tris(tert-butyl)silyl sodium or tris(tert-butyl)gernyl lithium at −70 °C in THF (Scheme 3). Cyclotrimerenenes 5 and 6 were isolated as dark-red crystals by gel-permeation chromatography. The NMR spectra of cyclotrimerenenes are very simple, because of their symmetrical structures, showing only two sets of signals in 1H, 13C and 29Si NMR spectra. The structures of both 5 and 6 were confirmed by X-ray crystallography, which showed the completely planar geometry around the Ge=Ge double bond.
bond with a Ge=Ge double bond length of 2.239(4) Å (for 5 see Figure 2). Such planarity is somewhat unusual, since all digermenes reported before have a trans-bent configuration of the Ge=Ge double bond with folding angles of 12–36°.29–32.

The mechanism of the formation of a three-membered unsaturated ring was clarified later, when this reaction was reexamined by the same authors in detail.18 They found that the reaction of dichlorogermylene–dioxane complex with one equivalent of t-Bu₃SiNa in THF at −78 °C led to the formation of cis,trans-1,2,3-trichloro-1,2,3-tris(tri-tert-butylsilyl)cyclotrigermene 7 in 98% yield (Scheme 4). The cis,trans conformation of 7 was established by NMR spectroscopy and X-ray analysis (Figure 3). Treatment of 7 with two equivalents of t-Bu₃SiNa in THF at −78 °C cleanly produced cyclotrigermene 5 (Scheme 4), which gives evidence that 7 is a precursor for 5.

Monitoring of the reaction by 29Si NMR allowed the detection of the reaction intermediates, which cannot be isolated, but were evidenced by trapping reactions (Scheme 5 and Figure 4). The first intermediate — digermenoid 8 (two signals at 21.9 and 23.7 ppm in the 29Si NMR spectrum) — was quenched with hydrochloric acid at −78 °C with the formation of a protonated product 9. With iodomethane, a methylated product 10 was quantitatively obtained. Above −8 °C the digermenoid 8 undergoes selective β-elimination to give another intermediate — digermene t-Bu₃Si(Cl)Ge=Ge(Cl)Si(Bu-t)3 11, which cannot be seen in the 29Si NMR spectrum, but can be trapped with dienes (Scheme 5). With both isoprene and 2,3-dimethyl-1,3-butadiene the corresponding cyclohexene derivatives 12 and 13 were obtained, whereas germacyclopentene derivatives were not found, which
$t$-Bu$_3$SiNa + GeCl$_2$·dioxane $\xrightarrow{\text{THF} \ -78^\circ \text{C} \to \text{RT}}$ $t$-Bu$_3$Si $\cdot$ Ge$\equiv$Ge $\cdot$ Si(Bu-t)$_3$

$\xrightarrow{-78^\circ \text{C} \to \text{RT}}$ $t$-Bu$_3$SiNa

$t$-Bu$_3$SiCl + $t$-Bu$_3$Si $\cdot$ Ge$\equiv$Ge $\cdot$ Si(Bu-t)$_3$

SCHEME 4

FIGURE 3. ORTEP drawing of cyclotrimerene 7. Reprinted with permission from Reference 18. Copyright 2000 American Chemical Society
indicates that α-elimination to generate a germylene species is not involved in the reaction pathway. Thus, the reaction of GeCl₂•dioxane with t-Bu₃SiNa can be explained by the following mechanism. First, insertion of dichlorogermylene into the Si−Na bond occurred to form the germlenoid t-Bu₃SiGeCl₂Na, which undergoes self-condensation to afford digermnenoid 8, stable at low temperature. Second, above −8 °C thermal decomposition of 8 gives digermene 11 as an intermediate. And finally, this digermene reacts with digermnenoid 8, followed by cyclization with formation of trichlorocyclotrigermene 7 and germlyenoid 14. The resulting 7 then transforms into the final cyclotrigermene 5.

Other examples of cyclotrigermenes were synthesized in a different way by Sekiguchi and coworkers, taking advantage of the previously prepared cyclotrigrermenium cation, whose synthesis will be described later (see Section II.E.3). Thus, unsymmetrically substituted cyclotrigrermenenes were prepared by the reactions of tris(tri-tert-butylsilyl)cyclotrigermenium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB⁻) 15 with the appropriate nucleophiles (Scheme 6)¹⁷. This method seems to be a convenient route for the preparation of new cyclotrigrermenenes. Thus, reaction of 15 with t-Bu₃SiNa, t-Bu₃GeNa, (Me₃Si)₃SiLi•3THF, (Me₃Si)₃GeLi•3THF or MesLi at −78 °C quickly produced the corresponding unsymmetrically substituted cyclotrigrermenenes 5, 16–19 in high yields. It was quite interesting to know that the geometry around the Ge=Ge
FIGURE 4. Reaction intermediate in the reaction of GeCl₂-dioxane with t-Bu₃SiNa in THF-d₈ monitored by ²⁹Si NMR spectroscopy: formation of digermenoid 8 and its thermal transformation to a cyclotrigermene 7. Reprinted with permission from Reference 18. Copyright 2000 American Chemical Society.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>NMR Spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>265 K</td>
<td>(a)</td>
</tr>
<tr>
<td>270 K</td>
<td>(b)</td>
</tr>
<tr>
<td>275 K</td>
<td>(c)</td>
</tr>
<tr>
<td>280 K</td>
<td>(d)</td>
</tr>
</tbody>
</table>

R-M / THF or Et₂O −100 °C to RT

**Scheme 6**

Double bond in 17 is not trans-bent, which is the general case for the dimetallenes of Group 14²⁹−³², but cis-bent with folding angles of 12.5° for the Ge3 atom and 4.4° for the Ge2 atom (Figure 5). The Ge=Ge double bond length is 2.264 Å, which lies in the normal region. Such an unusual cis-bent configuration was well reproduced by *ab initio* calculations: the cis folding angles are 8.8° and 5.8° for Ge3 and Ge2 atoms, respectively. No energy minimum was found for the trans-bent form. Therefore, the cis-bent geometry is caused by both steric and electronic effects of the substituents at the endocyclic saturated...
germanium atom, but not by a crystal packing force. As was mentioned above, usually the digermenes exhibit a trans-bent configuration, which becomes less pronounced upon the introduction of electropositive substituents, such as $R_3Si$ groups. In the case of cyclotrigermene 17, using such electropositive and bulky silyl substituents caused the formation of a Ge=Ge double bond with an unprecedented cis-bent geometry.

**C. Cyclotristannene**

Until now, there was only one example of a cyclotristannene—tetrakis(tert-butyldimethylsilyl)cyclotristannene 20 reported by Wiberg and coworkers in 1999. The title compound 20 was prepared by the reaction of $t$-Bu$_3$SiNa with stable stannylenes $Sn[SiMe_3]_2$ or $Sn(OBu-t)_2$ in pentane at room temperature (Scheme 7). It was isolated as dark, red-brown crystals in 27% yield. In agreement with the symmetrical structure of the molecule, 20 exhibits only two sets of signals in the $^1H$, $^{13}C$ and $^{29}Si$ NMR spectra. The most important and informative was the $^{119}Sn$ NMR spectrum, which showed both up-field (−694 ppm) and down-field (412 ppm) resonances. The last one is typical for the three-coordinated doubly-bonded tin atoms, whereas the first one can be assigned to an endocyclic Sn atom in a three-membered ring system.

The structure of 20 was determined by X-ray analysis, which showed an almost planar environment around the Sn=Sn double bond. All the previously reported distannenes have a trans-bent configuration around the Sn=Sn double bond. The Sn=Sn double bond

\[ \text{Sn}[\text{SiMe}_3]_2 + t\text{-Bu}_3\text{SiNa}/\text{pentane} \rightarrow \text{R}_2\text{Sn} \equiv \equiv \text{SnR}_2 \]  
(21) $R = \text{Si(Bu-t)}_3$

\[ \text{Sn(OBu-t)}_2 + t\text{-Bu}_3\text{SiNa}/\text{pentane} \rightarrow \text{R} \equiv \equiv \text{R} \]  
(20) $R = \text{Si(Bu-t)}_3$

**SCHEME 7**
length was only 2.59 Å — the shortest among all distannenes structurally characterized so far.\textsuperscript{34–38}

One of the most important findings of the reaction was a discovery of the intermediately formed tristannaallene 21, which is not very thermally stable and at room temperature rearranges to the isomeric cyclotristannene 20 (Scheme 7). Such rearrangement apparently implies the migration of one silyl substituent followed by cyclization. Nevertheless, it was possible to isolate compound 21 in 20% yield as dark-blue crystals, which were highly air and moisture sensitive and isomerized slowly at room temperature to form cyclotristannene 20. Such isomerization takes place by a first-order reaction with a half-life of 9.8 h at 25°C. The structure of the tristannaallene 21 was supported by \textsuperscript{119}Sn and \textsuperscript{29}Si NMR spectra. In the \textsuperscript{119}Sn NMR spectrum of 21, two down-field signals at 503 and 2233 ppm were observed with an intensity ratio 2 : 1. The first one was attributed to the terminal Sn atoms in an allene unit, which is in agreement with the only reported distannene compound that is stable at room temperature in solution, \((2,4,6-(i-Pr)\textsubscript{3}C\textsubscript{6}H\textsubscript{2})\textsubscript{2}Sn=Sn(2,4,6-(Pr-\textsubscript{i}\textsubscript{3}C\textsubscript{6}H\textsubscript{2})\textsubscript{2})\) (\(\delta = 427.3\)).\textsuperscript{34} The central allenic Sn atom, which formally has sp type hybridization, resonates at a much lower field (2233 ppm), which is the usual shift for the stannylenes\textsuperscript{39–41}. Such similarity suggests that the central tin atom in 21 has a considerable stannylenene character, therefore the bonding situation in 21 is best described by the resonance formula shown in Scheme 8. The \textsuperscript{29}Si NMR spectrum of 21 showed only one signal at 77.3 ppm.

The crystal structure of 21 was finally confirmed by X-ray analysis, which showed an unexpectedly short Sn=Sn double bond length of 2.68 Å (Figure 6). This bond length is the shortest among all distannenes reported thus far (2.77–2.91 Å)\textsuperscript{34–38}, although it is longer than that in 20 (2.59 Å). Another important feature of the allene 21 is a bent, rather
than linear, Sn₃ chain. Such a phenomenon was explained by the large contribution of the resonance formulae \[ R₂Sn ↔ SnR₂ \] in the structure of 21 rather than the real allenic structure. The geometry around the terminal tin atoms in the Sn₃ chain in 21 is not planar, as in the case of the corresponding carbon atoms in allenes. The (t-Bu₂Si)₂Sn groups in 21 adopt, similar to the R₂C groups in allenes, a gauche configuration; thus the four t-Bu₂Si groups mask the Sn₃ chain almost completely to prevent intermolecular reactions between the Sn₃ units.

D. ‘Mixed’ Cyclotrimetallenes

It was expected that ‘mixed’ cyclotrimetallenes—that is, the three-membered ring compounds consisting of different Group 14 elements—would possess some interesting and unusual properties that may distinguish them from their homonuclear analogues (cyclotrisilenes, cyclotrigermenes and cyclotristannenes). First, such interest concerned the structural characteristics and the specific reactivity of the ‘mixed’ cyclotrimetallenes. The synthesis of the title compounds was not obvious, and until now only two examples of such molecules have been reported. In 2000, Sekiguchi and coworkers reported the first representatives of such unsaturated molecules: 1- and 2-disilagermiresnes 22 and 23. 1-Disilagermirene 22 was prepared by the Wurtz-type reductive coupling reaction of R₂GeCl₂ and RSiBr₃ \[ R = SiMe(t-Bu)_2 \] with sodium in toluene (Scheme 9). Compound 22 was isolated as hexagonal ruby crystals in 40% yield and appeared to be highly air and moisture sensitive. The \(^1\text{H}\) and \(^13\text{C}\) NMR spectra corresponded well with a symmetrical structure for 22, showing only two sets of signals for methyl- and tert-butyl groups, whereas the \(^29\text{Si}\) NMR spectrum displayed three resonances at 18.7, 25.6 and 107.8 ppm, of which the first two belong to the silyl substituents, and the last one is characteristic of the Si=Si double bond.

![Scheme 9](image)

The molecular structure of 1-disilagermirene 22 was determined by X-ray crystallography (Figure 7). The three-membered ring represents an almost isosceles triangle with bond angles of 52.71(3), 63.76(3) and 63.53(3)°. The silicon–silicon double bond length of 22 is 2.146(1) Å, which is rather short compared with other Si=Si double bond lengths reported so far (2.138–2.289 Å). The average bond length between Ge and the two Si atoms in the ring is 2.417 Å, which is intermediate between the endocyclic Ge–Ge bond length of 2.522 (4) in cyclotrigermene and the Si–Si bond length of 2.358 (3) Å in cyclotrisilene. The geometry around the Si=Si bond is not planar, but trans-bent with a torsional angle Si3–Si1–Si2–Si4 of 37.0(2)°. One of the possible reasons for such twisting of the Si=Si double bond may be the eclipsed conformation of the two t-Bu₂MeSi substituents connected to the unsaturated silicon atoms.

Under photolysis of the benzene solution of 22 with a high pressure Hg lamp (λ > 300 nm) for 4 h, a migration of the silyl substituent with the formation of an endocyclic Si=Ge double bond system takes place (Scheme 10). The reaction proceeds quite cleanly.
and the 2-disilagermirene 23 was formed almost quantitatively. Compound 23 represents the first example of a stable germasilene reported to date, since the only previously reported example by Baines and Cooke, tetramesitylgermasilene, is unstable and can survive only at a low temperature.\(^{43}\)

\[ \text{Si}(6) \quad \text{Si}(5) \quad \text{Ge}(1) \quad \text{Si}(1) \quad \text{Si}(2) \quad \text{Si}(3) \]

**FIGURE 7.** ORTEP drawing of 1-disilagermirene 22. Reprinted with permission from Reference 19. Copyright 2000 American Chemical Society.

**SCHEME 10**
The 2-disilagermirene $^{23}$ was isolated from hexane solution as scarlet plate crystals and appeared to be extremely thermally stable with a melting point of 194–196 °C. The $^1$H and $^{13}$C NMR spectra of $^{23}$ are more complicated than those of $^{22}$, because the 2-disilagermirene $^{23}$ has lost the C$_{2v}$ symmetry of the 1-disilagermirene $^{22}$. Thus, the $^1$H NMR spectrum of $^{23}$ showed three resonances for three types of methyl groups and four resonances for non-equivalent tert-butyl groups, whereas the $^{13}$C NMR spectrum showed three sets of signals both for methyl and tert-butyl groups. The $^{29}$Si NMR spectrum showed five signals, of which three belong to the silyl substituents, 39.5, 27.8 and 6.9; the endocyclic doubly-bonded Si atom exhibits a down-field resonance at 106.7 and the endocyclic saturated Si atom has an up-field resonance at −120.1 ppm.

The molecular structure of 2-disilagermirene $^{23}$ was established by X-ray crystallography, which revealed a triangular structure composed of one saturated silicon atom, one unsaturated silicon atom and one unsaturated germanium atom. Although the accurate determination of bond lengths and angles in the three-membered ring was impossible because of significant disorder in the positions of doubly bonded Si and Ge atoms, it was possible to determine the geometry around the Si=Ge double bond, which also has a trans-bent configuration with a torsional angle of 40.3(5)°.

The isomerization of $^{22}$ to $^{23}$ can also be performed under thermal conditions. Thus, thermolysis of a solution of $^{22}$ in mesitylene at 120 °C cleanly produced 2-disilagermirene $^{23}$ in one day. Thermolysis can also be performed in benzene solution in a temperature interval from 80 to 100 °C, but it requires a longer reaction time, about 4 days. Thermal reaction of $^{22}$ produced an equilibrium mixture of $^{22}$ (2%) and $^{23}$ (98%), from which it was estimated that $^{23}$ is more stable than $^{22}$ by ca 3 kcal mol$^{-1}$. Thermolysis of $^{22}$ without solvent at 215 °C cleanly produces 2-disilagermirene $^{23}$ quantitatively in 20 minutes without any side products.

Ab initio calculations on the model H$_3$Si-substituted 1-disilagermirene $^{24}$ and 2-disilagermirene $^{25}$ at the MP2/DZd and B3LYP/DZd levels show the Si=Si double bond length in $^{24}$ to be 2.105 Å (MP2) and 2.107 Å (B3LYP), which agree well with the experimental value of 2.146 Å. The Si=Ge double bond length in $^{25}$ was predicted to be 2.180 Å (MP2) and 2.178 Å (B3LYP). It was also found that $^{25}$ is more stable than $^{24}$ by 3.9 (MP2) and 2.3 (B3LYP) kcal mol$^{-1}$. These values are in good agreement with the experimentally estimated value of ca 3 kcal mol$^{-1}$.

![Chemical structures](image-url)

E. Reactivity of Cyclotrimetallenes

The reactivity of the three-membered unsaturated rings of heavier Group 14 elements is still largely unknown, although one can easily expect them to have very interesting properties arising from their unusual structures, which combine both a highly reactive metal-metal double bond and highly strained three-membered skeleton in one molecule. From all the cyclotrimetallenes described above, the reactivity has been studied for...
cyclotrisilenes, cyclotrigermenes and “mixed” compounds. The chemistry of the only reported cyclotristannene is still open for investigation.

1. Addition reactions

a. Reactions with CCl₄. The reactivity of cyclotrimetallenes with CCl₄ was studied in the case of cyclotrisilenes and ‘mixed’ cyclotrimetallenes. Thus, cyclotrisilene 4, 1-disilagermirene 22 and 2-disilagermirene 23 were reacted with an excess of CCl₄ to form the corresponding trans-dichloro derivatives 26–28 even at low temperature in nearly quantitative yield (Scheme 11)²³. As was mentioned before, the cyclotrisilene 1 also reacts with CCl₄ to produce the trans-1,2-dichloro derivative 2¹⁴. The reaction proceeds selectively to produce only one isomer — trans, which can be explained by the steric requirements. The crystal structure of compound 27 is shown in Figure 8. It is interesting that the dichloro derivatives 26–28 can be quantitatively converted back to the corresponding starting cyclotrimetallenes 4, 22 and 23 by treatment with t-Bu₃SiNa (Scheme 11)²³.

![Scheme 11](image)

FIGURE 8. ORTEP drawing of 1,2-dichloro-1,2,3,3-tetrakis[di-tert-butyl(methyl)silyl]-1,2-disilagermirane 27
2. Cycloaddition reactions
   

   i. Reactions with phenylacetylene. The behavior of cyclotrimetallenes toward phenylacetylene was surprisingly different, showing the different nature of the three-membered ring compounds composed of the Si, the Ge, or both Si and Ge atoms. Thus, reaction of phenylacetylene with mesityl-substituted cyclotrigermene 19 proceeds as a [2 + 2] cycloaddition reaction with the formation of the resulting bicyclic three- and four-membered ring compound 29 as orange crystals in the form of two stereoisomers 29a and 29b (Scheme 12). The crystal structure analysis of 29a showed a highly folded bicyclic skeleton with a dihedral angle between the planes of the three- and four-membered rings of 97.4° (Figure 9).

   ![Scheme 12](image-url)

   The reaction of the ‘mixed’ cyclotrimetallenes 22 and 23 with phenylacetylene also proceeds through the initial [2 + 2] cycloaddition of the first molecule of phenylacetylene across the E=Si (E = Si, Ge) double bond with the formation of the three- and four-membered bicyclic compounds 30 and 31. But the reaction does not stop at this stage: valence isomerization of the bicyclic compound takes place to form the silole type structures 32 and 33 with one Si=C and one Ge=C double bond, which in turn
quickly isomerizes to give the thermodynamically more stable siloles 34 and 35 with one Si=Ge and one C=C double bond (Scheme 13). The silole-type compounds 34 and 35 react with a second molecule of phenylacetylene in a [2 + 2] cycloaddition manner to give the final four- and five-membered bicyclic compounds 36 and 37. In the case of 2-disilagermirene 23, it was possible to isolate the intermediate silole 35, representing the first metalladiene of the type E=E'-C=C (E,E' — heavier Group 14 elements). Two examples of the isolable metalladienes of Group 14 elements have been recently reported by Weidenbruch’s group: hexakis(2,4,6-tri-isopropylphenyl)tetrasila-1,3-butadiene 44 and hexakis(2,4,6-tri-isopropylphenyl)tetragerma-1,3-butadiene 45.

The structure of compound 35 was determined by means of all spectral data. Thus, the $^{29}$Si NMR spectrum showed five resonances, of which three belong to the silyl substituents: 19.4, 26.6 and 30.1 ppm, the down-field signal at 124.2 ppm was attributable to the doubly bonded silicon atom and the up-field signal at $-45.6$ ppm corresponds to the endocyclic sp$^3$ Si atom. X-ray analysis of 35 revealed an almost planar five-membered ring, although the Si=Ge double bond has a twisted (trans-bent) configuration with a torsional angle Si(6)−Ge(1)−Si(2)−Si(5) of 38.6(1)$^\circ$ (Figure 10). The Si=Ge double bond length, which was determined experimentally for the first time, is 2.250(1) Å, which is intermediate between the typical values for Si=Si and Ge=Ge double bond lengths. From the experimental data, i.e. X-ray crystallography, the UV-Vis spectrum and reactivity of the silole 35, it was found that there is almost no conjugation between the two double bonds in the cyclopentadiene ring of 35. This seems to be curious since all the known cyclopentadiene compounds were described as fully conjugated systems, for which

Diels–Alder cycloaddition reactions are typical. Apparently, such unusual behavior is caused by both the great energy difference and the difference in the size of the atoms of the Si=Ge and C=C double bonds, which prevent an effective overlapping of the molecular orbitals of the two π-bonds necessary for real conjugation. In contrast, for the symmetrical heavier Group 14 elements containing 1,3-diene systems with two equal double bonds, such as 2,3-digerma-1,3-butadiene H₂C=GeH−GeH=CH₂, theoretical calculations have predicted about half the degree of conjugation compared with that of the parent 1,3-butadiene. The cyclotrisilene also readily reacts with phenylacetylene to form finally a bicyclic compound similar to that of 36 and 37. In this case the isolation of the cyclopentadiene-type compound was impossible due to its very short life time.
ii. Reactions with aldehydes and ketones. Reaction with carbonyl compounds is also very sensitive to the steric requirements. Thus, highly sterically protected tetrakis(tri-tert-butylsilyl)cyclotrigermene 5 does not react with benzaldehyde\(^{39}\), whereas the reaction of 1-disilagermirene 22 with benzaldehyde proceeds almost immediately to give a set of products depending on the reaction conditions and the ratio of the reagents (Scheme 14)\(^{50}\).

Thus, at room temperature 1-disilagermirene 22 reacts with one molecule of benzaldehyde to give the bicyclic three- and four-membered ring compound 38, similar to the above case of phenylacetylene\(^{22}\). Compound 38 can be considered as a kinetically controlled product, which presumably is stabilized by an interaction of the electron-rich phenyl group and the empty \(\sigma^*\)-orbital of the exocyclic Ge–Si bond. Nevertheless, such an arrangement of the phenyl group is not favorable due to the steric repulsion with silyl substituents on the Ge atom; therefore, upon heating at mild conditions compound 38 was isomerized quantitatively to a thermodynamically more stable compound 39, whose structure was established by X-ray analysis (Figure 11). Compound 39 has a highly folded skeleton with a dihedral angle between the two planes of 107.8°.

The initially formed bicyclic compound 38 has a highly strained and very reactive bridgehead endocyclic Si–Si bond. It can easily react with a second molecule of benzaldehyde by the insertion pathway to form a new bicyclic compound 40 with a norbornane type skeleton (Scheme 14 and Figure 12). Although this last reaction closely resembles the previous case of phenylacetylene\(^{22}\), the mechanism is evidently different: in the case of phenylacetylene the final product 36 is a result of \([2 + 2]\) cycloaddition of the second molecule of phenylacetylene across the new Si=Ge double bond, whereas in the case of benzaldehyde the final norbornane 40 is a result of the insertion of the second molecule of benzaldehyde into the strained Si–Si single bond. Apparently, the reactions of disilagermirenes with phenylacetylene and benzaldehyde have the same initial steps to form bicyclic compounds, but then the reaction pathways become different due to the different nature of these intermediate bicyclic compounds.
14. Unsaturated three-membered rings of heavier Group 14 elements

\[ t\text{-Bu}_2\text{MeSi} \quad \text{SiMe(Bu-t)}_2 \]

\[ t\text{-Bu}_2\text{MeSi} \quad \text{Si} \quad \text{Si} \quad \text{SiMe(Bu-t)}_2 \]

\[ \text{C}_6\text{D}_6/\text{RT} \quad \text{PhCHO} \]

\[ \text{R} = \text{SiMe(Bu-t)}_2 \]

\[ \text{C}_6\text{D}_6/70^\circ\text{C}/0.5 \text{h} \]

**SCHEME 14**

**FIGURE 11. ORTEP drawing of bicyclic compound 39**
FIGURE 12. ORTEP drawing of bicyclic compound 40 with a norbornane type skeleton

\[
\begin{align*}
\text{CH}_3\text{COCOCH}_3
\end{align*}
\]

Intramolecular C=O insertion into Si-Ge bond

SCHEME 15
The reaction of 1-disilagermirene 22 with ketones is similar to the benzaldehyde case. Thus, reaction with butane-2,3-dione gives a final bicyclic product 41, which also has a norbornane type skeleton (Scheme 15, Figure 13). Formation of this compound can be reasonably explained by the initial [2 + 2] cycloaddition of one carbonyl group across the Si=Si bond to form the three- and four-membered ring bicyclic compound 42, followed by the isomerization of disilaoxetane 42 to an enol ether derivative 43. The intramolecular insertion of the second carbonyl group into the endocyclic Si−Ge single bond in 43 completes this reaction sequence to produce the final norbornane 41. In this case, C=O insertion occurred into the Si−Ge bond rather than the Si−Si bond, which is reasonable due to the weakness of Si−Ge bond.

b. [4 + 2] Cycloaddition reactions.

i. Reactions with 1,3-dienes. Conjugated dienes, such as 2,3-dimethyl-1,3-butadiene and isoprene, are traditionally widely used as trapping reagents, for both transient and stable dimetallenes of Group 14 elements to form the corresponding Diels−Alder adducts. While reacting with the cyclotrimetallenes of Group 14 elements, conjugated dienes have produced the corresponding [4 + 2] adducts in the form of fused three- and six-membered ring compounds. For example, the reaction of mesityl-substituted cyclotrigermene 19 with both 2,3-dimethyl-1,3-butadiene and isoprene yields bicyclic adducts 44 and 45 (Scheme 16).

X-ray analysis confirmed the structure of compound 44 (Figure 14). Only one of the two possible stereoisomers was formed, which corresponds to the attack of the isoprene on the Ge=Ge double bond from the mesityl side. This probably can be explained by the lower steric bulkiness of the mesityl group compared with the t-Bu₃Si group. Due to
SCHEME 16

FIGURE 14. ORTEP drawing of a [4 + 2] cycloadduct 44. Reproduced by permission of Wiley-VCH from Reference 21
steric reasons, the three $t$-Bu$_3$Si groups occupy the less hindered pseudoequatorial positions, whereas the mesityl group and CH$_2$C(Me)=CHCH$_2$ moiety occupy the pseudoaxial positions (Figure 14).

It is noteworthy that the bicyclic three- and six-membered compounds 44 and 45 can serve as precursors for both germylene and digermene at 70 °C$^{21}$. Such species can be effectively trapped by 2,3-dimethyl-1,3-butadiene to form germacyclopentene 48 and bicyclic compounds 49 and 50 (Scheme 17).

\[
\begin{align*}
(44) \quad & R = H \\
(45) \quad & R = Me
\end{align*}
\]

Mes = 2,4,6-Me$_3$C$_6$H$_2$

SCHEME 17

The most interesting point in these reactions is the ring contraction, which takes place in the intermediate digermacyclohexadienes 46 and 47 during reaction with diphenylacetylene (Scheme 18)$^{51}$. Thus, during thermolysis of the bicyclic
compounds 44 and 45, a formal migration of the CH₂ group from one Ge atom to another one in the intermediate digermenes 46 and 47 takes place, resulting in ring contraction to form germylgermylene species 51 and 52. These last germylenes can be trapped by diphenylacetylene to produce the corresponding germacyclopropenyl-substituted germacyclopentenes 53 and 54 (Scheme 18 and Figure 15). Similar digermene–germylgermylene rearrangement of tetramesityldigermene,⁵²,⁵³ and germasilene–silylgermylene rearrangement of tetramesitylgermasilene⁵³ were previously reported by Baines and Cooke.
3. Oxidation of cyclotrigermenes — formation of the ‘free’ germyl cation

It is well known that the cyclopropenium cation with a Hückel-type aromatic 2 $\pi$-electron system is the simplest and smallest aromatic compound, which is relatively stable due to its resonance stabilization despite the very large ring strain. Although the chemistry of the cyclopropenium cation is well established now, the analogues of this compound consisting of heavier Group 14 elements were unknown until recently. Theoretical calculations on the stability of $A_3H_3^+$ cations ($A = C, Si, Ge, Sn, Pb$) predicted a preference for the classical cyclopropenium cation structures with $D_{3h}$ symmetry for the carbon and silicon cases, whereas $C_{3v}$ hydrogen-bridged forms were expected to be favored for germanium, tin and lead. In contrast to these calculations, the first free germyl cation with a 2 $\pi$-electron system was reported by Sekiguchi and coworkers in 1997 as a classical cyclopropenium-type cation. Thus, tris(tri-1-tert-butylsilyl)cyclotrigermencium tetraphenylborate [(t-Bu$_3$SiGe)$_3$+$^+$TPB$^-$] (TPB$^-$ = tetraphenylborate) was prepared by the treatment of tetrakis(tri-1-tert-butylsilyl)cyclotrigermene with trityl tetraphenylborate in dry benzene and was isolated as air and moisture sensitive yellow crystals (Scheme 19).

![SCHEME 19](image)

The structure of 55 was determined on the basis of NMR spectral data and finally confirmed by X-ray crystallographic analysis (Figure 16). The three germanium atoms
form an equilateral triangle [Ge–Ge bond lengths 2.321(4)–2.333(4) Å and Ge–Ge–Ge bond angles 59.8(1)–60.3(1)]°. The Ge–Ge bond lengths observed in 55 are intermediate between the Ge=Ge double bond [2.239(4) Å] and the Ge–Ge single bond [2.522(4) Å] of the precursor 513. The closest distance between germanium and the aromatic carbon atoms of TPB− is greater than 4 Å, well beyond the range of any significant interaction. These structural features indicate that 55 has a cyclotrigermanium skeleton and it is a free germyl cation with a 2π-electron system. The aromatic stabilization of the cyclotrigermanium ion and the charge delocalization explain the observed lack of any close interaction with the counter anion.

However, the problem of TPB− was its chemical instability60, because 55 can survive in a solution of dichloromethane only at temperatures below −78 °C. [3,5-(CF3)2C6H3]4B− (TFPB−, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate)61, (C6F5)4B− (TPFPB−, tetrakis(pentafluorophenyl)borate)62 and [4-(t-BuMe2Si)C6F4]4B− (TSFPB−, tetrakis[4-[tert-butyl(dimethyl)silyl]-2,3,5,6-tetrafluorophenyl]borate)63,64 are known to be stable borate anions, which can increase the stability of the resulting cyclotrigermanium ion. Therefore, the reactions of cyclotrigermenes 5 and 6 with Ph3C+•TFPB−, Ph3C+•TPFPB− and Ph3C+•TSFPB− were studied with the hope of obtaining the stable cyclotrigermanium salts65–67. In fact, the reaction of (t-Bu3Si)4Ge3 with Ph3C+•TFPB− in benzene at room temperature produced the salt (t-Bu3SiGe)3+•TFPB− 15, which was isolated as a yellow powder in 81% yield (Scheme 20). The reaction of 6 with Ph3C+•TFPB− in benzene also proceeded smoothly to give (t-Bu3GeGe)3+•TFPB− 56 in 76% yield. In a similar way, the reaction of 5 and 6 with Ph3C+•TPFPB− in benzene produced (t-Bu3SiGe)3+•TPFPB− 57 (80%) and (t-Bu3GeGe)3+•TPFPB− 58 (80%), respectively. The reaction of 5 with Ph3C+•TSFPB− produced (t-Bu3SiGe)3+•TSFPB− 59 as orange crystals in 88% yield. The resulting germyl cations can survive for extensive periods without decomposition both in solution and in the solid state (Scheme 20).

The molecular structure of 15 is shown in Figure 17. The three-membered ring consisting of germanium atoms is almost an equilateral triangle with the Ge–Ge

![FIGURE 16. ORTEP drawing of [(t-Bu3SiGe)3+•TPB−] 55. Reprinted with permission from Reference 58. Copyright 1997, American Association for the Advancement of Science](image-url)
differences of the three-membered ring almost equal, ranging from 2.3284(8) to 2.3398(8) Å [av. 2.3333(8) Å]. The Ge–Si bond lengths [Ge1–Si1, 2.425(1); Ge2–Si2, 2.442(1); Ge3–Si3, 2.444(1) Å] of 15 are shortened compared with those of 5 [2.629(7) Å for the Ge–Si bond length of sp³ Ge atom and 2.448(7) Å for the Ge–Si bond length of sp² Ge atoms]. The perspective view appears to show a weak electrostatic interaction
between the germanium and fluorine atoms. The three closest distances range from 3.823 to 5.097 Å; however, these distances are longer than the sum (3.57 Å) of the van der Waals radii for germanium and fluorine atoms.

X-ray diffraction data were also obtained for 59. Due to the steric bulkiness of the \(t\)-BuMe\(_2\)Si group attached to the \textit{para} positions of the phenyl rings of the borate anion, no interaction between the cation moiety and the counter anion can be found (Figure 18). As a consequence, the skeleton of the three-membered framework forms an equilateral triangle; the Ge−Ge bond lengths are 2.3310(8) for Ge1−Ge2, 2.3315(7) for Ge1−Ge3 and 2.3349(8) Å for Ge2−Ge3, and the Ge−Ge−Ge bond angles are 60.10(2)° for Ge2−Ge1−Ge3, 59.96(2)° for Ge1−Ge2−Ge3 and 59.94(2)° for Ge1−Ge3−Ge2. The structural features for 15 and 59 are practically the same as those of 55.

The evidence for the existence of the free cyclotrigermanium ion in solution was supported by the NMR spectroscopic data. The \(^1\)H, \(^13\)C and \(^{29}\)Si NMR chemical shifts for the cyclotrigermanium moiety of 15, 57 and 59 in CD\(_2\)Cl\(_2\) are practically the same. For example, the \(^{29}\)Si NMR chemical shifts of 15, 57 and 59 are independent of the counter anion. The \(^{29}\)Si NMR chemical shift of 15 is also essentially the same in different solvents, appearing at \(\delta = 64.0\) in CD\(_2\)Cl\(_2\), \(\delta = 64.2\) in CDCl\(_3\), \(\delta = 64.4\) in toluene-d\(_8\) and \(\delta = 64.5\) in Et\(_2\)O. This independence from both the counter anion and solvent clearly indicates that \((t\text{-}Bu_3SiGe)_3^+\) is a free germyl cation in solution. The large down-field shifted \(^{29}\)Si NMR resonance of \((t\text{-}Bu_3SiGe)_3^+\), relative to that of the precursor 5 (\(\delta = 37.2\) for the \(t\text{-}Bu_3Si\) substituent attached to the saturated Ge atom and 50.1 for the \(t\text{-}Bu_3Si\) group attached to the Ge=Ge double bond)\(^{13}\), is due to the positive charge of the cyclotrigermanium ion.

\[\text{FIGURE 18. ORTEP drawing of } [(t\text{-}Bu_3SiGe)_3^+\cdot\text{TSFPB}^-] 59.\text{ Reproduced by Permission of Wiley-VCH from Reference 67}\]
The positive charge is not localized on the germanium atoms, but is significantly transferred to the silicon centers. The atomic (Mulliken) charges on \((H_3SiGe)_3^+\) according to HF/6-31G* level calculations indicate a delocalization of the positive charge: \(-0.07\) for the ring germanium atoms and \(+0.64\) for the silicon atoms of the SiH3 substituents.

**III. EPILOGUE AND OUTLOOK**

The present review has no pretensions to be a comprehensive one and to cover all the chemistry of small ring systems containing heavier Group 14 elements: this field is quite vast and greatly exceeds the framework of this article. Here we have concentrated on the relatively narrow and rather new field of the unsaturated three-membered rings consisting of heavier Group 14 elements. In organic chemistry, cyclopropene, which is the smallest unsaturated ring system, and its derivatives are among the most important classes of organic compounds due to their enhanced reactivity caused by a great ring strain and existence of the endocyclic C=C double bond. Apparently, the heavy cyclopropene analogues, that is cyclotrимetallenes composed of Si, Ge, Sn and Pb atoms, would occupy a similar important position in the chemistry of Group 14 elements, since their high reactivity is even more pronounced than that of cyclopropene because of the extremely reactive endocyclic metal–metal double bond and the weakness of endocyclic metal–metal single bonds. Even now, cyclotrtrimetallenes, which quite recently were considered to be synthetically inaccessible, can be considered as unusual molecules, and their number is still very limited. The chemistry of such compounds, which often exhibit great differences in the structures, properties and reactivity from their carbon analogues, has started quite recently, and there are still many questions and problems to be solved. Thus, the Pb-containing representative—i.e. cyclotriplumbene—has not yet been prepared. Several possible combinations for the ‘mixed’ cyclotrtrimetallenes can also be imagined as the next target molecules. The reactivity of cyclotrtrimetallenes also needs to be studied in detail; moreover, the first preliminary investigations showed the extremely high synthetic possibilities of such compounds, since very rich chemistry can be developed from them. Thus, one can expect much progress in this ‘hot’ field of Group 14 elements chemistry in the near future, which will have an important impact on our understanding of the nature of bonding and reactivity in systems with elements heavier than carbon.

**IV. ACKNOWLEDGMENT**

We highly appreciate Dr. Masaaki Ichinohe and Mrs. Norihisa Fukaya, Tadahiro Matsuno, Hiroshi Sekiyama and Yutaka Ishida for their invaluable experimental contributions. We wish to thank Professor Shigeru Nagase for the theoretical calculations. This work was supported by a Grant-in-Aid for Scientific Research (Nos. 13029015, 13440185, 12042213) from the Ministry of Education, Science and Culture of Japan, and TARA (Tsukuba Advanced Research Alliance) fund.

**V. REFERENCES**

14. Unsaturated three-membered rings of heavier Group 14 elements

49. N. Fukaya and A. Sekiguchi, unpublished results.
Cage compounds of heavier Group 14 elements

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I. INTRODUCTION

The polycyclic cage compounds of Group 14 elements heavier than carbon (i.e. tetrahedranes, cubanes, prismanes, etc.) have fascinated chemists for a long time because of their unique structures and expected unusual physico-chemical properties and reactivity\(^1\). It was quite reasonable to assume that such exotic compounds could possess properties...
different from their carbon analogues, arising from the highly rigid framework consisting of σ bonds with low ionization potentials. Despite the obviously great synthetic challenge, such strained polyhedranes of Si, Ge and Sn have not been prepared until recently, and were even considered to be synthetically inaccessible. The first breakthrough in their synthesis occurred in the late 80s, when reports on the synthesis of the first octasilacubane\(^2\) and hexagermaprismane\(^3\) were published in the scientific literature. Then, during the last decade, there was dramatic progress in the chemistry of such cage compounds, and many new derivatives have been prepared. To date, two tetrahedranes (one tetrasilatetrahedrane and one tetragermatetrahedrane), four prismanes (one hexasilaprismane, two hexagermaprismanes and one hexastannaprismane) and nine cubanes (five octasilacubanes, three octagermacubanes and one octastannacubane) have been described in the literature. Theoretical calculations\(^4\)–\(^6\) have found that the strain of the cage compounds is significantly decreased by the introduction of electropositive silyl groups. Therefore, in many cases, the successful preparation of the cage molecules has been achieved by using bulky silyl substituents both for the kinetic protection of the strained skeleton and to decrease the ring strain. In the present review we will be concerned mainly with the synthesis of the cage compounds, and the structural and chemical peculiarities arising from their unusual highly strained framework.

II. CAGE COMPOUNDS OF HEAVIER GROUP 14 ELEMENTS: TETRAHEDRANES, PRISMANES, CUBANES

A. Comparative Ring Strain of the Polyhedral Compounds: Theoretical Study

In organic chemistry it is well known that polyhedranes (C\(_{2n}\)H\(_{2n}\)), such as tetrahedranes (\(n = 2\)), prismanes (\(n = 3\)) and cubanes (\(n = 4\)), are highly strained, as their carbon bond angles greatly deviate from the normal tetrahedral value of 109.5°. Since no experimental values are available for the heavier analogues, their strain energies were calculated on the basis of the appropriate homodesmotic reactions\(^7\),\(^8\). Table 1 shows a comparison of the calculated strain energies for the carbon-, silicon-, germanium- and tin-containing polyhedral compounds. The strain energy of tetrasilatetrahedrane is similar to that of tetrahedrane. However, the ring strain of the silicon compounds decreases significantly with increasing number of four-membered rings, while in the case of carbon compounds the tendency is the opposite. It is noteworthy that hexasilaprismane and octasilacubane are less strained than prismane and cubane by 32 and 65 kcal mol\(^{-1}\), respectively. On going from carbon and silicon to germanium and tin atoms, the tendency is the same: in the tetrahedrane molecules there is only a small effect on the relief of strain\(^8\). Apparently, such a phenomenon originates from the high ring strain of the cyclotrimetallanes of Si, Ge and Sn atoms.

<table>
<thead>
<tr>
<th>M(_n)H(_n)</th>
<th>C</th>
<th>Si(^b)</th>
<th>Ge</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedrane (M(_4)H(_4), (T_d))</td>
<td>141.4</td>
<td>140.9</td>
<td>140.3</td>
<td>128.2</td>
</tr>
<tr>
<td>Prismane (M(_6)H(<em>6), (D</em>{3h}))</td>
<td>145.3</td>
<td>113.8</td>
<td>109.4</td>
<td>93.8</td>
</tr>
<tr>
<td>Cubane (M(_8)H(_8), (O_h))</td>
<td>158.6</td>
<td>93.5</td>
<td>86.0</td>
<td>70.1</td>
</tr>
</tbody>
</table>

\(^a\)M\(_n\)H\(_n\) + (3n/2)M\(_2\)H\(_6\) → n(MH\(_3\))\(_3\)MH.
HF/6-31G* level for M = C and Si. HF/DZ(d) level for M = Ge and Sn.
\(^b\)The HF/DZ(d) values are 140.3 (Si\(_4\)H\(_4\)), 118.2 (Si\(_6\)H\(_6\)) and 99.1 (Si\(_8\)H\(_8\)) kcal mol\(^{-1}\). Reproduced by permission of John Wiley & Sons Ltd, from Reference 1d.
which is much larger than that of cyclopropane: cyclotrilsilane (38.9 kcal mol\(^{-1}\))\(^7\), cyclotrigermane (39.4 kcal mol\(^{-1}\))\(^8\), cyclotristannane (36.6 kcal mol\(^{-1}\))\(^8\) vs cyclopropane (28.7 kcal mol\(^{-1}\))\(^7\). However, the strain energies of prismane and cubane molecules containing four-membered rings are further decreased from silicon to germanium and tin compounds. This can be explained by the decrease of the ring strain in the four-membered rings: cyclobutane (26.7 kcal mol\(^{-1}\))\(^7\) > cyclotetrasilane (16.7 kcal mol\(^{-1}\))\(^7\) > cyclotetragermane (15.2 kcal mol\(^{-1}\))\(^8\) > cyclotetrestannane (12.2 kcal mol\(^{-1}\))\(^8\). Thus, there is a general trend of decreasing strain energies of the polyhedral compounds with increasing number of four-membered rings and on going from carbon to tin.

Such a trend is also shown by the larger members of the \([n]\)prismane family (\(M_{2n}H_{2n}\), \(n > 4\)). Figure 1 shows\(^5,9,10\) that the strain energies of persila\([n]\)prismanes (\(Si_{2n}H_{2n}\)) are 53.2 (\(n = 5\)), 70.1 (\(n = 6\)) and 141.0 (\(n = 8\)) kcal mol\(^{-1}\) smaller than those of the corresponding \(C_{2n}H_{2n}\) and even more on going from Si to Ge and Sn. The strain energy decreases when \(n\) increases from 2 to 5, because the number of four-membered rings increases and the bond angles in the \(n\)-membered rings approach the ideal tetrahedral angle of 109.5°. However, the strain sharply increases with \(n > 5\), despite the increasing number of four-membered rings, because of the increasing deviation of the bond angles (120° for \(n = 6\) and 135° for \(n = 8\)) in the \(n\)-membered rings from the tetrahedral angle. Thus, the minimum strain energy was calculated for \(n = 5\). Therefore, it is reasonable to expect a successful synthesis of \([5]\)prismanes, of which the perstanna[5]prismane has already been prepared\(^11\).

The origin of such differences in the ring strain of carbon and its heavy analogues can be reasonably explained by the difference in the hybridization character, since it is known that the heavier atoms have a lower tendency to form sp hybrid orbitals with high p-character, and they tend to maintain the ns\(^2\)np\(^2\) electronic configuration\(^8,9,12\). That

![FIGURE 1. The strain energies of the tetrahedrane and \([n]\)prismane systems (\(M_{2n}H_{2n}\)) calculated at the HF/6-31G\(^*\) level for \(M = C\) and Si and the HF/DZ(d) level for \(M = Ge\) and Sn. Reprinted with permission from Reference 5. Copyright (1995) American Chemical Society](image-url)
makes it favorable for the heavier atoms to form bond angles of ca 90° (that is, to form four-membered rings) and unfavorable to form bond angles of ca 60° (that is, formation of three-membered rings).

Such properties are also reflected in the relative stability of the M₆H₆ valence isomers (Table 2). It is well known that benzene (C₆H₆) is very stable due to cyclic delocalization of its six \( \pi \) electrons (aromatic stabilization), and it is much more stable than other strained valence isomers — Dewar benzene, benzvalene and prismane. However, the tendency is completely reversed in the case of heavier atoms: the isomers with a smaller number of double bonds are more favorable. As a result, the prismane structure becomes much more stable than the benzene structure on going from carbon to tin atoms.

### Table 2. Relative energies (kcal mol\(^{-1}\)) of M₆H₆ valence isomers

<table>
<thead>
<tr>
<th>M</th>
<th>Benzene</th>
<th>Dewar benzene</th>
<th>Benzvalene</th>
<th>Prismane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(D_{6h})</td>
<td>(C_{2v})</td>
<td>(C_{2v})</td>
<td>(D_{3h})</td>
</tr>
<tr>
<td>C(^a)</td>
<td>0.0</td>
<td>81.1</td>
<td>74.9</td>
<td>117.6</td>
</tr>
<tr>
<td>Si(^b)</td>
<td>0.0(0.0)(^c)</td>
<td>4.1</td>
<td>−2.0</td>
<td>−8.1</td>
</tr>
<tr>
<td>Ge(^b)</td>
<td>0.0(−9.1)(^c)</td>
<td>1.8</td>
<td>−1.2</td>
<td>−13.5</td>
</tr>
<tr>
<td>Sn(^b)</td>
<td>0.0(−23.1)(^c)</td>
<td>−6.5</td>
<td>−11.0</td>
<td>−31.3</td>
</tr>
</tbody>
</table>

\(^a\)MP2/6–31G*/HF/6–31G* from Reference 15.\(^a\)

\(^b\)MP2/DZ(d)/HF/DZ(d) from Reference 10.\(^b\)

\(^c\)Values in parentheses are for chair-like puckered structures of \(D_{3d}\) symmetry.\(^c\)

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### B. Tetrahedrane

#### 1. Tetrasilatetrahedrane

The only known example of the tetrasilatetrahedrane molecule, tetrakis(tri-tert-butylsilyl)tetrasilatetrahedrane 1, was reported by Wiberg in 1993 by the reaction of \(t\)-Bu\(_3\)Si–SiBr₂–SiBr₂–Si(Bu-t)\(_3\) with \(t\)-Bu\(_3\)SiNa in THF at \(−20^\circ\)C.\(^{16}\) The details of its synthesis as well as its physico-chemical characteristics are summarized in a recent review\(^{1d}\) and will not be considered in the present article.
2. Tetragermatetrahedrane

The synthesis of the title compound was reported several years later by the same authors, who had previously prepared tetrasilatetrahedrane in a similar way\(^\text{17}\). Thus, \(t\)-Bu\(_3\)Si—GeCl\(_2—\)GeCl\(_2—\)Si(Bu-t)\(_3\), which was prepared by the reaction of GeCl\(_4\) and \(t\)-Bu\(_3\)SiNa in THF at room temperature, was reacted with \(t\)-Bu\(_3\)SiNa in THF at \(-78^\circ\text{C}\). The tetragermatetrahedrane \(2\) was formed in a low yield together with some other products (Scheme 1).

\[
\begin{align*}
\text{GeCl}_2 \cdot \text{dioxane} & \quad \xrightarrow{\text{t-} \text{Bu}_3 \text{SiNa}} \quad \text{THF/RT} \\
\text{Ge} & \quad \text{Si(Bu-t)3} \\
\text{t-Bu}_3 \text{Si} & \quad \text{THF/} \text{78}^\circ\text{C}
\end{align*}
\]

**SCHEME 1**

Tetragermatetrahedrane \(2\) was also prepared by the reaction of dichlorogermylene–dioxane complex GeCl\(_2\)•C\(_4\)H\(_8\)O\(_2\) with \(t\)-Bu\(_3\)SiNa in THF at room temperature (Scheme 1). It is quite interesting that the same reaction, which leads to the tetrakis(tert-butylsilyl)cyclotrigermene at low temperature\(^\text{18}\), in this case results in the formation of a completely different compound (i.e. tetragermatetrahedrane) when performed at room temperature. The tetragermatetrahedrane \(2\) was isolated as intense red crystals, slowly hydrolyzable by water and rapidly oxidizable by air. Compound \(2\) can be reduced with sodium to form a mixture of products, from which \(t\)-Bu\(_3\)SiNa was identified by the trapping reaction with Me\(_3\)SnCl to form \(t\)-Bu\(_3\)Si—SnMe\(_3\).

The crystal structure of \(2\) (which cocrystallizes with the disilane \(t\)-Bu\(_3\)Si—Si(Bu-t)\(_3\)) was determined by X-ray diffraction, which showed the monoclinic unit cell of the crystals with the composition \(2(t\)-Bu\(_3\)Si\(_4\)Ge\(_4\)•(t-Bu\(_3\)Si\(_3\)) containing four molecules of \(2\) and two molecules of \(t\)-Bu\(_3\)Si—Si(Bu-t)\(_3\) (Figure 2). The Ge—Ge (av 2.44 Å) and Si—Ge (2.38 Å) distances are slightly longer than those in the parent H\(_3\)Ge—GeH\(_3\) (2.41 Å) and H\(_3\)Si—GeH\(_3\) (2.36 Å)\(^\text{19}\), respectively.

C. Prismanes

1. Hexasilaprismane

The first and sole example of hexasilaprismane, hexakis(2,6-diisopropylphenyl)hexasilaprismane \(3\), was prepared by Sekiguchi and coworkers in 1993 by the coupling reaction of \((2,6-(i-\text{Pr})_2\text{C}_6\text{H}_3)_2\text{SiCl}_2—\text{SiCl}_2—(2,6-(\text{Pr}-i)_2\text{C}_6\text{H}_3)_2\) with Mg/MgBr\(_2\) in THF at room temperature\(^\text{20}\). The synthesis and properties of hexasilaprismane, and its interesting photochemical isomerization to a hexasila-Dewar benzene, are described in a previous review article\(^\text{14}\).
2. Hexagermaprismanes

The first hexagermaprismane, hexakis[bis(trimethylsilyl)methyl]tetracyclo[2.2.0.0^2,6.0^3,5]hexagermane 4, was reported by Sekiguchi and coworkers in 1989\(^3\), even earlier than the corresponding silicon analogue. Bis(trimethylsilyl)methyl groups were chosen as the appropriate protecting groups, and Li (or Mg) metals as the coupling reagent. Thus, reaction of bis(trimethylsilyl)methyltrichlorogermane with Li in THF at \(-78^\circ\text{C}\) (or Mg in THF at 0°\text{C}) produced the hexagermaprismane 4, which was isolated by column chromatography as yellow-orange crystals in 12% yield in the case of Li (or 24% yield in the case of Mg) (Scheme 2)\(^{1c,5}\).

In the solid state, hexagermaprismane 4 was unexpectedly stable to air and moisture and decomposes only above 200°\text{C}. NMR spectral data fully correspond to a highly symmetrical structure of 4, showing only two singlets in the \(^1\text{H}\) (0.62 and 1.37 ppm) and
13C (4.08 and 29.8 ppm) NMR spectra, and only one signal at $-1.95$ ppm in the $^{29}$Si NMR spectrum. An electronic spectrum revealed an absorption maximum at 280 nm, tailing into the visible region ($ca$ 500 nm). The prismane 4 exhibits thermochromism: it is pale-yellow at $-196^\circ$C and intense orange at $200^\circ$C. Figure 3 shows the UV-Vis spectra of hexagermaprismanes 4 and 5.
FIGURE 3. UV-Vis spectra of hexagermaprismanes 4 and 5 in hexane

The X-ray crystallographic analysis of 4 showed the prismane structure consisting of six germanium atoms with $D_{3h}$ symmetry (Figure 4). The prismane skeleton is constructed from two triangular units [(Ge–Ge bond lengths of 2.578(6)–2.584(6) Å (av. 2.58 Å and Ge–Ge–Ge bond angles of 60.0(2)–60.1(1)° (av. 60°)) and the three rectangles [Ge–Ge bond lengths of 2.516(6)–2.526(6) Å (av. 2.52 Å and Ge–Ge–Ge bond angles of 88.5(2)–91.4(2)° (av. 90°))]. All the Ge–Ge bond lengths are considerably longer than the usual Ge–Ge bond lengths in other polygermanes (2.374–2.465 Å). Surprisingly, the Ge–Ge bond lengths in the triangles are longer than those in the rectangles, although calculations for the C and Si prismanes $^7,^{15,21}$ have predicted the opposite trends, as was found in the structures of the carbon analogues $^{22}$.

The second representative of the hexagermaprismanes, hexakis(2,6-diisopropylphenyl)tetracyclo[2.2.0.0$^{2,6}.0^{3,5}$]hexagermane 5, was synthesized several years later by the same authors by the reductive coupling of the corresponding precursor — (2,6-diisopropylphenyl)trichlorogermane with Mg in THF (Scheme 3) $^{20}$. Similar to the case of hexasilaprismane 3, the $^1$H and $^{13}$C NMR spectra of 5 show two non-equivalent isopropyl groups and aryl protons. From the low-temperature $^1$H NMR spectra, a $\Delta G^\ddagger$ value of 13.1 kcal mol$^{-1}$ for the rotational barrier of the aryl groups was found, which is much smaller than that of hexasilaprismane 3, due to the increased Ge–C$_\text{ar}$ bond length (1.983–1.993 Å, av. 1.988 Å). The hexagermaprismane 5 is less stable than the hexasilaprismane 3 toward atmospheric oxygen.

The choice of the reducing agent is quite important. Thus, reduction of the precursor (2,6-diisopropylphenyl)trichlorogermane with Mg/MgBr$_2$ in THF resulted in the formation of tetrakis(2,6-diisopropylphenyl)digermene $^{21}$ instead of prismane 5.
The crystal structure of 5 is similar to that of prismane 4 (Figure 5). Its structural parameters are listed in Table 3. The prismane skeleton is made from two triangular units [Ge–Ge bond lengths of 2.497–2.507 Å (av. 2.503 Å and Ge–Ge–Ge bond angles of 59.8–60.1° (av. 60.0°)] and the three rectangles [(Ge–Ge bond lengths of 2.465–2.475 Å (av. 2.468 Å) and Ge–Ge–Ge bond angles of 89.0–91.1° (av. 90°)].

As in the case of prismane 4, the cyclopropyl Ge–Ge bond lengths are longer than those in the rectangular units. All the Ge–Ge bond lengths in 5 are elongated compared with the normal ones (2.40 Å), although they are shorter than those in cyclotrigermane (R₂Ge)₃ (R = 2,6-dimethylphenyl: av. 2.541 Å)²⁴. The Ge–Ge bond lengths in 5 are somewhat shorter than those calculated for the parent Ge₆H₆ (2.502 Å for the triangular units and 2.507 Å for the rectangular units)⁸.

Irradiation of the hexagermaprismane 5 with light of 360–380 nm produced new absorption bands at 342, 446 and 560 nm due to the hexagerma-Dewar benzene 6 at low temperature, which seems to be quite similar to the case of hexasilaprismane to hexasil-Dewar benzene isomerization (Scheme 4)¹⁵. Excitation of the new bands with light of wavelength longer than 460 nm led to the regeneration of the starting hexagermaprismane 5. The hexagerma-Dewar benzene 6 also gradually reverted to the starting prismane 5 at temperatures above −160 °C.
3. Hexastannaprismane

The final representative of the prismanes consisting of the heavier Group 14 elements, hexastannaprismane, was synthesized quite recently by Wiberg’s group. The reaction of \( \text{Sn}\left[\text{N(SiMe}_3\right]_2 \) with \( t-\text{Bu}_3\text{SiNa} \) in pentane/tert-butyl methyl ether at \(-78^\circ C \) produced
FIGURE 5. ORTEP drawing of hexagermaprismane 5
TABLE 3. Selected bond lengths and bond angles of hexagermaprismane 5

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gel-Ge2</td>
<td>2.497(1)</td>
</tr>
<tr>
<td>Gel-Ge3</td>
<td>2.507(1)</td>
</tr>
<tr>
<td>Ge2-Ge3</td>
<td>2.505(1)</td>
</tr>
<tr>
<td>Ge1-Ge1'</td>
<td>2.475(1)</td>
</tr>
<tr>
<td>Ge2-Ge3'</td>
<td>2.465(1)</td>
</tr>
<tr>
<td>Ge3-Ge2'</td>
<td>2.465(1)</td>
</tr>
<tr>
<td>Ge-Car</td>
<td>1.983(9)</td>
</tr>
<tr>
<td></td>
<td>1.993(7)</td>
</tr>
<tr>
<td>Ge1-Ge3-Ge3'</td>
<td>89.1(0)</td>
</tr>
<tr>
<td>Ge2-Ge3-Ge2'</td>
<td>90.5(0)</td>
</tr>
<tr>
<td>Ge-Ge-Car</td>
<td>124.4(2)</td>
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<tr>
<td></td>
<td>139.7(2)</td>
</tr>
<tr>
<td>Ge'-Ge-Car</td>
<td>123.7(2)</td>
</tr>
<tr>
<td></td>
<td>130.0(2)</td>
</tr>
</tbody>
</table>

See Figure 5 for designations.

a dark-blue reaction mixture from which dark-violet crystals were precipitated in two days (Scheme 5). These crystals are stable at room temperature in the absence of air and water, and decompose in the presence of organic solvents above 5 °C. Although it was impossible to obtain unambiguous NMR data due to the very low solubility of the compound in THF or toluene, the structure was determined by X-ray diffraction. It was found that the crystals contain hexakis[tri(tert-butyl)silyl]triprismohexastannane 7 (Figure 6) together with hexakis[tri(tert-butyl)silyl]disilane and tert-butyl methyl ether.

The hexastannaprismane 7 comprises a near-equilateral Sn6 prismane framework with almost parallel Sn3 faces that are only slightly twisted away from each other. The three Sn–Sn distances between the Sn3 faces of the Sn6 prismane are 2.91 Å, whereas, within the Sn3 faces, two of the Sn–Sn bonds are also 2.91 Å and the other one is 2.94 Å. They are slightly longer than the sum of the radii of two Sn atoms (2.80 Å)\(^2\), probably due to steric reasons. The average Si–Sn distances are 2.71 Å, which is longer than the sum of the radii (2.57 Å)\(^2\), but similar to the Si–Sn distances in \((t\text{-Bu}_3\text{Si})_2\text{SnCl}_2\) (2.70 Å)\(^2\).

The mechanism of formation of the hexastannaprismane 7 is not evident, although the authors have suggested the initial substitution of the amide groups by \(t\text{-Bu}_3\text{Si}\) groups with formation of the stannylene \((t\text{-Bu}_3\text{Si})_2\text{Sn}^*\), the dimerization of which to form the distannene \((t\text{-Bu}_3\text{Si})_2\text{Sn}=\text{Sn}(\text{Bu}-t)_3\)_2 does not take place due to steric reasons. Apparently, the oligomerization of the stannylene \((t\text{-Bu}_3\text{Si})_2\text{Sn}^*\) proceeds by elimination of the \(t\text{-Bu}_3\text{Si}\) radicals, which subsequently dimerize to form the disilane \(t\text{-Bu}_3\text{Si}=\text{Si}(\text{Bu}-t)_3\).

4. Comparison of the prismane structures

Table 4 summarizes the structural parameters of prismane molecules (\(M_6\text{H}_6; M = C, Si, Ge, Sn\)) together with the calculated values for \(R=H\). The \(M–M\) bonds within and between the three-membered rings are denoted as \(a\) and \(b\), respectively. The calculations predicted that \(a\) is shorter than \(b\) for \(R = H\)\(^7,8\), which is in accordance with the experimental data
15. Cage compounds of heavier Group 14 elements

SCHEME 4

(5)

$h \nu (\lambda = 360-380 \text{ nm})$

$h \nu (\lambda > 460 \text{ nm})$

(6)
$t$-Bu$_3$Si$\cdot$Sn[$N(SiMe_3)_2$]$_2$ $\rightarrow$ $t$-Bu$_3$SiNa
pentane $t$-BuOMe, $-78^\circ$C

Scheme 5

FIGURE 6. ORTEP drawing of hexastannaprismane 7. Reproduced by permission of Wiley-VCH from Reference 25

for prismane$^{28}$ and its derivatives C$_6$R$_6$ (R = Me$^{29}$, SiMe$_3$$^{30}$). The theory shows that the bond length difference between $a$ and $b$ decreases significantly as M becomes heavier. It is interesting that, in contrast to the theoretical calculations, $a$ is longer than $b$ in Si$_6$R$_6$ [R = 2,6-(i-Pr)$_2$C$_6$H$_3$]$^{20}$], Ge$_6$R$_6$ [R = 2,6-(i-Pr)$_2$C$_6$H$_3$]$^{20}$, R = CH(SiMe$_3$)$_2$$^3$] and Sn$_6$R$_6$ (R = $t$-Bu$_3$Si$^{25}$).
TABLE 4. Structural parameters of prismanes comprising Group 14 elements

<table>
<thead>
<tr>
<th>M</th>
<th>R</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>H</td>
<td>1.507</td>
<td>1.549</td>
<td>Calcd.(^a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.500</td>
<td>1.585</td>
<td>ED(^b)</td>
</tr>
<tr>
<td></td>
<td>Me</td>
<td>1.540</td>
<td>1.551</td>
<td>ED(^c)</td>
</tr>
<tr>
<td></td>
<td>SiMe(_3)</td>
<td>1.510</td>
<td>1.582</td>
<td>XRD(^d)</td>
</tr>
<tr>
<td>Si</td>
<td>H</td>
<td>2.359</td>
<td>2.375</td>
<td>Calcd.(^a)</td>
</tr>
<tr>
<td></td>
<td>i-Pr</td>
<td>2.380</td>
<td>2.373</td>
<td>XRD(^e)</td>
</tr>
<tr>
<td></td>
<td>i-Pr</td>
<td>(2.374–2.387)</td>
<td>(2.365–2.389)</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>H</td>
<td>2.502</td>
<td>2.507</td>
<td>Calcd.(^f)</td>
</tr>
<tr>
<td></td>
<td>i-Pr</td>
<td>2.503</td>
<td>2.468</td>
<td>XRD(^e)</td>
</tr>
<tr>
<td></td>
<td>i-Pr</td>
<td>(2.497–2.507)</td>
<td>(2.465–2.475)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SiMe(_3)</td>
<td>2.580</td>
<td>2.522</td>
<td>XRD(^e)</td>
</tr>
<tr>
<td></td>
<td>SiMe(_3)</td>
<td>(2.578–2.584)</td>
<td>(2.516–2.526)</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>Si(Bu-(t)) (_3)</td>
<td>2.92</td>
<td>2.91</td>
<td>XRD(^h)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2.91–2.94)</td>
<td>(2.91)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)From Reference 7.
\(^b\)From Reference 28.
\(^c\)From Reference 29.
\(^d\)From Reference 30.
\(^e\)From Reference 20.
\(^f\)From Reference 8.
\(^g\)From Reference 3.
\(^h\)From Reference 25.

D. Cubanes

1. Octasilacubanes

Octasilacubanes seem to be the most widely studied cage compounds, several examples of their reactivity having been described. To date, five examples of the octasilacubanes have been reported in the literature\(^{1d,2,31–36}\). Their synthesis, as well as structural parameters and reactivity, were summarized in a recent review\(^{1d}\).

2. Octagermacubanes

To date, three examples of octagermacubanes have been described in the literature. For all of them, the crystal structures were determined by X-ray crystallography. The
Scheme 6

\[
\text{Mg/MgBr}_2 \xrightarrow{\text{THF}} \text{GeGePh} \xrightarrow{\text{cis-cis-trans}} \text{HCl/AlCl}_3 \xrightarrow{\text{benzene}} \text{trans-trans-GeGeCl} \xrightarrow{\text{THF}} \text{Mg/MgBr}_2
\]
first two octagermacubanes were reported by Sekiguchi and coworkers in 1992. For the preparation of alkyl substituted octagermacubane, 1,2,3,4-tetrachloro-1,2,3,4-tetrakis(1-ethyl-1-methylpropyl)cyclotetragermane \( \text{8} \) was selected as a precursor (Scheme 6). To design this compound, condensation of dichloro(1-ethyl-1-methylpropyl)phenylgermane with Mg/MgBr\(_2\) in THF was performed to give a mixture of isomeric cyclotetragermanes in 72\% yield. These last compounds were reacted with gaseous HCl in the presence of AlCl\(_3\) in benzene with the formation of \( \text{8} \) in a \textit{trans-trans-trans} configuration in 45\% yield. The octakis(1-ethyl-1-methylpropyl)pentacyclo[4.2.0.0\(_2\),5.0\(_3\),8.0\(_4\),7]octagermane \( \text{9} \) was obtained by the coupling reaction of \( \text{8} \) with Mg/MgBr\(_2\) in THF in 16\% yield as yellow crystals with a melting point above 215 °C (Scheme 6). Figure 7 shows the UV-Vis spectra of octagermacubane \( \text{9} \) and \( \text{10} \).

The \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra correspond well to the structure, showing only signals belonging to alkyl substituents. The UV-Vis spectrum of \( \text{9} \) showed an absorption maximum at 240 nm (\( \varepsilon = 48700 \)) tailing to the visible region (Figure 7). In the solid state the cubane \( \text{9} \) was relatively stable to moisture and air. The same compound \( \text{9} \) can also be obtained by a direct coupling of (1-ethyl-1-methylpropyl)trichlorogermaine with Mg/MgBr\(_2\) in THF in 3\% yield. Despite the low yield, such a method has the advantage of a simple one-pot synthesis.

The aryl-substituted octagermacubane, octakis(2,6-diethylphenyl)pentacyclo[4.2.0.0\(_2\),5.0\(_3\),8.0\(_4\),7]octagermane \( \text{10} \), was synthesized by the dehalogenative coupling of (2,6-diethylphenyl)trichlorogermaine with Mg/MgBr\(_2\) in THF in 1\% yield as yellow crystals (Scheme 7). This compound was found to be less stable to atmospheric moisture and
air, which is evidence for the lower steric bulkiness of 2,6-diethylphenyl substituents compared with that of the 1-ethyl-1-methylpropyl groups.

For the mechanism of the formation of cubane molecule 9, the cyclotetr germene 11 was proposed as the reactive intermediate\textsuperscript{1c}, which can dimerize in a [2 + 2] cycloaddition manner to form \textit{syn} and \textit{anti} dimers 12 and 13 (Scheme 8). The former (12) would produce the octagermacubane 9, whereas the latter (13) produces ladder-type polygermanes 14.
FIGURE 8. ORTEP drawing of octagermacubane 10

TABLE 5. Selected bond lengths and bond angles of octagermacubane 10

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge1-Ge2 2.478(1)</td>
<td>Ge2-Ge1-Ge4 90.6(0)</td>
</tr>
<tr>
<td>Ge2-Ge3 2.486(1)</td>
<td>Ge2-Ge1-Ge4' 90.3(0)</td>
</tr>
<tr>
<td>Ge3-Ge4 2.503(1)</td>
<td>Ge4-Ge1-Ge4' 90.3(0)</td>
</tr>
<tr>
<td>Ge4-Ge1 2.492(1)</td>
<td>Ge1-Ge2-Ge3 89.9(0)</td>
</tr>
<tr>
<td>Ge1-Ge4' 2.500(1)</td>
<td>Ge1-Ge2-Ge3' 90.3(0)</td>
</tr>
<tr>
<td>Ge2-Ge3' 2.482(1)</td>
<td>Ge3-Ge2-Ge3' 88.9(0)</td>
</tr>
<tr>
<td>Ge-Car 1.976(9)</td>
<td>Ge2-Ge3-Ge4 90.2(0)</td>
</tr>
<tr>
<td>1.997(9)</td>
<td>Ge2-Ge3-Ge2' 91.1(0)</td>
</tr>
<tr>
<td></td>
<td>Ge4-Ge3-Ge2' 90.1(0)</td>
</tr>
<tr>
<td></td>
<td>Ge1-Ge4-Ge3 89.2(0)</td>
</tr>
<tr>
<td></td>
<td>Ge1-Ge4-Ge1' 89.2(0)</td>
</tr>
<tr>
<td></td>
<td>Ge3-Ge4-Ge1' 89.3(0)</td>
</tr>
<tr>
<td></td>
<td>Ge-Ge-Car 120.3(2)</td>
</tr>
<tr>
<td></td>
<td>129.7(2)</td>
</tr>
</tbody>
</table>

*aSee Figure 8 for designations.

The crystal structure of 10 was established by X-ray diffraction to show an almost perfect cubic framework (Figure 8). Its structural parameters are listed in Table 5. The Ge–Ge bond lengths are 2.478–2.503 Å (av. 2.490 Å), which is close to, but slightly shorter than, that of the 2.527 Å calculated for Ge₈H₈. The Ge–Ge–Ge bond angles are 88.9–91.1° (av. 90.0°). The exocyclic Ge–C_car bonds (1.982 Å) are slightly elongated compared with the normal Ge–C_ar bond lengths (1.95 Å). Due to steric reasons, the Ge–Ge–C_ar bond angles (av. 124.6°) are expanded. The cubic crystal structure was also found for the octagermacubane 9 with Ge–Ge bond lengths of 2.534 Å (av.) and Ge–Ge–Ge bond angles of 90.0° (av.).
The last representative of octagermacubanes, octakis(1,1,2-trimethylpropyl)pentacyclo[4.2.0.0²,5.0³,8.0⁴,7]octagermane 15, was reported quite recently by Matsumoto’s group.38 The synthetic strategy for its preparation was essentially the same, as described above. Thus, (1,1,2-trimethylpropyl)trichlorogermane was reacted with Mg/MgBr₂ in THF at room temperature to form octagermacubane 15 in 3% yield as yellow crystals (Scheme 9). The structure of 15 was established on the basis of spectral data. Thus, the ¹H and ¹³C NMR spectra were fully consistent with the high symmetry of the molecule, revealing three resonances in the ¹H NMR and four in the ¹³C NMR spectra, indicating the equivalence of all substituents.

\[
\begin{align*}
\text{(Me₂CHCMe₂)GeCl₃} & \xrightarrow{\text{Mg/MgBr₂}} \text{THF/RT} \\
\text{(15)} & \quad R = \text{CMe₂CHMe₂}
\end{align*}
\]

**SCHEME 9**

The crystal structure of 15 was determined by X-ray analysis, which displayed the cubic skeleton of 15 with Ge—Ge bond lengths of 2.494–2.540 Å (av. 2.516 Å), which are slightly longer than those of the above-mentioned octagermacubane 10 (av. 2.490 Å)²¹ (Figure 9). The Ge—Ge—Ge bond angles lie between 88.0 and 91.9° (av. 90.0°). The exocyclic Ge—C bonds are slightly elongated (2.037–2.056 Å, av. 2.046 Å) in comparison with the octagermacubane 10 (av. 1.982 Å)²¹.

The highly strained Ge₈ framework of 15 causes interesting electronic properties. Thus, the oxidation potential of 15 (0.22 V) is much lower than that of the corresponding octasilacubane with the same substituents (0.43 V). This suggests that the HOMO of 15 lies at a higher level than that of the octasilacubane. However, in the UV-Vis spectrum of 15 there is a hypsochromic shift in comparison with octasilacubane (236 nm vs 252 nm). Such a hypsochromic shift is likely due to the greater energy separation between the HOMO and LUMO, presumably because of the high-lying LUMO in 15. Such a suggestion was supported by the electron transmission spectroscopy study of oligogermaines, which found that the LUMO (σ*) of Me₃GeGeMe₃ shifts by 0.30 eV to higher energy in comparison with σ* of Me₃SiSiMe₃.

Due to the low oxidation potential, cubane 15 is reactive toward electrophiles. Thus, chlorination of 15 with PCl₅ in benzene at room temperature finally gave the mixture of endo,exo- and exo,exo-4,8-dichlorooctakis(1,1,2-trimethylpropyl)tetracyclo[3.3.0.0²,7.0³,6]octagermanes 16 in 7 and 37% yield, respectively (Scheme 10).³⁸ The absence of the endo,endo-isomer could be explained by the exclusive generation of the intermediate 17. The lower steric hindrance of the exo-isomer is most likely responsible for the higher yield of exo,exo-16. The frameworks of type 16 have been reported previously by Sekiguchi and coworkers (t-Bu₈Ge₈Cl₂)⁴⁰ and Weidenbruch and coworkers (t-Bu₈Ge₈Br₂)⁴¹, who...
prepared these compounds by the reductive coupling of the tert-butyl substituted halogermanes with lithium naphthalenide. Treatment of compound 16 with sodium in toluene at 120 °C regenerated the starting octagermacubane 15 in 50% yield.

3. Octastannacubane

There is only one precedent for the preparation of octastannacubane reported by Sita and Kinoshita in 1990\textsuperscript{42}. The thermolysis of hexakis(2,6-diethylphenyl)cyclotristannane at 200–220 °C produced the deep red octastannacubane 18 together with the blue-violet pentastanna[1.1.1]propellane 19\textsuperscript{43}. Both compounds have been isolated by chromatography on silica gel (Scheme 11). Finally, the octastannacubane 18 was purified by recrystallization from pentane in 0.76% yield. The spectral data of 18 support the Sn\textsubscript{8}R\textsubscript{8} structure. Thus, the \(^1\)H NMR spectrum showed the equivalence of all substituents on the NMR time scale with four resonances for Et and aryl protons. In contrast to other known polycyclic polystannanes\textsuperscript{43,44} there is only a small rotational barrier about the Sn–C\textsubscript{aryl} bonds in 18, which implies lower steric congestion among the substituents. The \(^{119}\)Sn NMR spectrum revealed only one resonance at +44.3 ppm with two pairs of satellites \([\(1^J(\text{Sn}^{119}–\text{Sn}^{117}) = 1576 \text{ Hz} \text{ and } 2^J(\text{Sn}^{119}–\text{Sn}^{117}) = 1345 \text{ Hz}\)]\). The red crystals of 18 exhibit thermochromic properties: they become pale yellow at −196 °C. In the presence of air the toluene solutions of 18 decolorize in a few minutes. The UV-Vis spectrum of

FIGURE 9. ORTEP drawing of octagermacubane 15. Reproduced by permission of the Chemical Society of Japan from Reference 38.
SCHEME 10

(15) R = CMe$_2$CHMe$_2$

(16) PCl$_5$ benzene

(17) fast

exo, exo

endo, exo

benzene
(18) Sn Sn or Ph₂CO

200−220°C

(19) +

(20)

SCHEME 11
18 in hexane exhibits no absorption maxima in the region 360–900 nm \( \lambda_{\text{max}} = 275 \text{ nm} \) (\( \varepsilon = 112000 \)), 320 nm (sh) (32000), 450 nm (sh) (2000)).

The X-ray analysis confirmed the cubic structure of 18 with Sn–Sn bond lengths of 2.839(2)–2.864(2) Å and all Sn–Sn–Sn bond angles nearly 90° (Figure 10). These structural parameters are in close agreement with those calculated for the parent Sn\(_8\)H\(_8\) octastannacubane (Sn–Sn bond length 2.887 Å and Sn–Sn–Sn bond angles 90°)\(^8\).

The mechanism of the formation of cubane 18 is not clear, although the authors have discussed the possible intermediate species RSn, which can be generated by the disproportionation \( 2R_2Sn \rightarrow RSn + R_3Sn^* \). A similar disproportionation of stannylene [(Me\(_3\)Si)\(_2\)CH]\(_2\)Sn has been observed under photolysis\(^{45}\). Such RSn species then undergo rapid oligomerization to form a family of \((RSn)_n\) compounds, of which the octastannacubane molecule is either the thermodynamically or kinetically favored member. A similar mechanism for the formation of cyclopolystannanes \((R_2Sn)_n\) by the oligomerization of transient stannylenes R\(_2\)Sn has been proposed previously\(^{46,47}\).

\[\text{FIGURE 10. ORTEP drawing of octastannacubane 18. Reprinted with permission from Reference 43. Copyright (1989) American Chemical Society}\]
It is interesting that the thermolysis of cyclotristannane in the presence of benzophenone increased the yield of octastannacubane 18 to 3.6%, probably due to complexation of the intermediate R₂Sn species by benzophenone. Except for the previously reported octastannacubane 18 and pentastanna[1.1.1]propellane 19, decakis(2,6-diethylphenyl)descastannana[5]prismane 20 was also formed (Scheme 11). The structure of the [5]prismane 20 was also established by X-ray diffraction, showing that the Sn–Sn bond lengths of 20 (av. 2.856 Å) are essentially the same as those of 18 (av. 2.854 Å).

4. Comparison of the cubane structures

Table 6 shows a comparison of the geometries [both experimental (X-ray) and calculated] of the cubane (C₈H₈)₄₈ and heavy cubane molecules M₈R₈ (M = Si, Ge, Sn; R = 2,6-Et₂C₆H₃). The M–M–M bond angles in M₈R₈ range from 89 to 91°, indicating the almost perfect cubic skeleton for these structures. The M–M bond lengths of 2.399 Å for Si, 2.490 Å for Ge and 2.854 Å for Sn are in good agreement with the calculated values of 2.382 Å for Si, 2.527 Å for Ge and 2.887 Å for Sn. The range of the M–M–C_ar bond angles increases in the order: 121–128° for Si, <120–130° for Ge, <117–133° for Sn. This implies a decrease in the steric congestion between the neighboring groups due to the elongation of the M–C_ar bond from silicon to tin: 1.911 Å for Si, <1.982 Å for Ge, <2.193 Å for Sn.

III. CONCLUSIONS AND OUTLOOK

The cage compounds of heavier Group 14 elements, which quite recently were considered as exotic molecules, now constitute an important class of organometallic compounds. Their specific structural and chemical characteristics, which are sometimes completely different from those of their carbon analogues, cause a permanent and increasing interest.

TABLE 6. Structural parameters of cubanes comprising Group 14 elements

<table>
<thead>
<tr>
<th></th>
<th>C₈H₈ a</th>
<th>Si₈R₈ b</th>
<th>Ge₈R₈ b</th>
<th>Sn₈R₈ c</th>
</tr>
</thead>
<tbody>
<tr>
<td>M–M (Å)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-ray</td>
<td>1.551</td>
<td>2.399</td>
<td>2.490</td>
<td>2.854</td>
</tr>
<tr>
<td></td>
<td>(1.549–1.553)</td>
<td>(2.384–2.411)</td>
<td>(2.478–2.503)</td>
<td>(2.839–2.864)</td>
</tr>
<tr>
<td>Calculated d</td>
<td>1.559</td>
<td>2.382</td>
<td>2.527</td>
<td>2.887</td>
</tr>
<tr>
<td>M–Car (Å)</td>
<td>1.06 (av.)</td>
<td>1.911 (av.)</td>
<td>1.982 (av.)</td>
<td>2.193 (av.)</td>
</tr>
<tr>
<td>M–M–M (deg)</td>
<td>89.3–90.5</td>
<td>88.9–91.1</td>
<td>88.9–91.1</td>
<td>89.1–91.1</td>
</tr>
<tr>
<td>M–M–Car (deg)</td>
<td>123–127</td>
<td>121–128</td>
<td>120–130</td>
<td>117–133</td>
</tr>
</tbody>
</table>

a From Reference 48.
b From Reference 31.
c From Reference 42.
d From Reference 8. Reproduced by permission of John Wiley & Sons Ltd, from Reference 1d
for researchers. Despite the great achievements of the last decade, there are still many synthetic challenges in the field of cage compounds. Thus, tetrastannatetrahedrane and all Pb-containing polyhedral compounds are still waiting to be prepared; undoubtedly, their unusual elegant design and potentially interesting properties will stimulate chemists to find methods for their synthesis. The reactivity of the cage compounds is also open for detailed investigation, since one can expect a very interesting chemistry in such highly strained molecules. The evident importance of such problems allows us to hope for significant progress in this field in the near future.

Quite recently after submission of this manuscript the remarkable paper describing the second example of octastannacubane compound was reported by Power and Eichler. This new octastannacubane $\text{Sn}_8(2,6-(2,4,6-\text{Me}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3)_4$ was prepared by a coupling reaction of the aryltin halide $\text{Sn}(\mu-\text{Cl})(2,6-(2,4,6-\text{Me}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3)_2$ with potassium in THF. X-ray analysis showed a highly distorted cubane structure, in which only four of the tin atoms carry substituents and the other four tin atoms are unsubstituted. the Sn–Sn distances fall in the range 2.853(2)–3.107(2) Å, which is usual for the $\text{Sn}_n\text{R}_n$ clusters.

IV. ACKNOWLEDGMENT

We thank Professors Hideki Sakurai and Shigeru Nagase for helpful discussions and useful advice. We are also grateful to C. Kabuto, T. Yatabe and H. Naito for their experimental contributions. This work was supported by a Grant-in-Aid for Scientific Research (Nos. 13029015, 13440185, 12042213) from the Ministry of Education, Science and Culture of Japan, and TARA (Tsukuba Advanced Research Alliance) Fund.

V. REFERENCES

1. For reviews on the cage compounds of the heavier Group 14 elements, see:
CHAPTER 16

Hypervalent compounds of organic germanium, tin and lead derivatives

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I. LIST OF ABBREVIATIONS

The following abbreviations are used in addition to the well-known abbreviations, which are listed at the beginning of each volume.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AO</td>
<td>atomic orbital</td>
</tr>
<tr>
<td>BDT</td>
<td>benzene-1,2-dithiolate</td>
</tr>
<tr>
<td>Phen</td>
<td>1,10-phenanthroline</td>
</tr>
<tr>
<td>NMI</td>
<td>1-methylimidazole</td>
</tr>
<tr>
<td>Oh</td>
<td>octahedral</td>
</tr>
<tr>
<td>( \sigma^- )</td>
<td>( SC_6H_4S^- )</td>
</tr>
</tbody>
</table>
II. INTRODUCTION AND OUTLINE

A. Introduction

The extensive investigations of five- and six-coordinated heavy group 14 elements, especially tin, are due to the work of the last two decades. The large number of publications, annual reviews and surveys are devoted to separate aspects of the chemistry of these compounds and concern mostly extra-coordinate species (see, for example, reviews and monographs dedicated to organogermanium\(^1,2\), organotin\(^3–5\) and organolead\(^6,7\) compounds and references cited therein). The inter- and intramolecular D → M donor–acceptor bonds are common characteristics especially for tin(IV) compounds\(^4,5,8,9\). Up to now the number of hypervalent organic compounds of group 14 elements given in the Cambridge Structural Database is 104 (Ge), 1473 (Sn) and 52 (Pb)\(^10\).

The increasing interest in extra-coordinate derivatives of group 14 elements is caused by their structural peculiarities, their high reactivity and also by the possibility of using them for studying dynamic processes and modeling the pathway of nucleophilic substitution reactions at the central atoms. However, only a few publications deal with a model of hypervalency.

The purpose of the present chapter is to review the investigations dealing with the synthesis, structure and reactivity of hypervalent germanium, tin and lead compounds. The structures and properties of these compounds still remain a challenge. Many novel and unusual structures were elucidated by the X-ray diffraction technique.

In this chapter we discuss the chemistry of germanium, tin and lead species in which at least one organic group is bonded to carbon. Similar silicon compounds will sometimes be discussed for comparison. Synthetic details will be mentioned mostly for the compounds recently reported. Species without any M–carbon bond will also be described.

B. Outline

According to the formalism of Akiba\(^11\) hypervalent compounds are compounds of the main group elements (\(sp\) elements: Groups 1, 2, 13–18) those contain a number (\(N\)) of formally assignable electrons of more than the octet in a valence shell directly
associated with the central atom (X) which is directly bound with a number \((L)\) of ligands (substituents). The \(N\-M\-L\) designation is rather convenient for the classification of hypervalent structures. A trigonal bipyramid (TBP) or, more rarely, a square pyramid (SP) as well as an octahedral (Oh) arrangement of the metal atom are typical for germanium, tin and lead in pentacoordinate 10-M-5 and hexacoordinate 12-M-6 compounds, respectively.

The pronounced acceptor ability of the tetravalent germanium, tin and lead atoms, as well as the similar structures of compounds of other group 14–18 elements containing a penta- and hexacoordinate central atom, are usually interpreted (by analogy with transition metals) by assuming that the bonding process involves not only s and p AOs but also the vacant d AOs localized within the valence shell (the d orbital concept)\(^{12–14}\). The group 14 atoms (Ge, Sn and Pb) have five vacant nd AOs, the participation of which can in principle lead to penta- and hexacoordinate states. It was stated, however, that d AOs of these elements were so diffuse that they could not participate in the bonding\(^{15–18}\).

Another concept of hypervalent bonding suggests representation of the structures of penta- and hexacoordinate species without substantial contribution from nd orbitals. This concept is based on the idea of a three-center four-electron (3c-4e) bonding\(^ {19–21}\) for orbital-deficient compounds and was presented in a generalized form by Musher in 1969: ‘Hypervalent molecules are ions or molecules of the elements of Groups 15–18 bearing more electrons than the octet (nine or more) within a valence shell’\(^ {22}\). Hypervalent bonds in high-coordinate group 14 compounds differ from similar bonds of sulfur, phosphorus and chlorine derivatives, since the lone electron pair in this case is supplied by the ligand. According to Musher’s classification\(^ {22}\), considering 10-M-5 and 12-M-6, hypervalent compounds of germanium, tin and lead contain hypervalent bonding of the second kind (HV\(\text{II}\)), in which the central atom has no ns\(^2\) lone pair.

This model implies that the TBP M atom could use its nsp\(^2\) orbitals for bonding with the equatorial ligands to form two-center bonds, and its np\(_z\) orbital could be involved in the interaction with an appropriate orbital of the axial substituent X and a lone electron pair of the donor atom to form a hypervalent, 3c-4e bond in the axial moiety D \(\rightarrow\) M–X. The simplest MO diagram of a 3c-4e bond may be represented by three molecular orbitals: bonding (b), nonbonding (nb) and antibonding (ab) (Scheme 1).

The following conditions for the formation of hypervalent bonds have been stated\(^ {22,23}\):

1. These bonds can be formed when ligands are more electronegative than the central M atom.

2. The most electronegative substituents of those surrounding the M atom participate in a hypervalent bond and tend to occupy the axial positions in a trigonal-bipyramidal molecule.

3. The M–X bond lengths in penta- and hexacoordinate compounds are longer than those in similar tetrahedral molecules.

Hypervalent bonds in hexacoordinate compounds are formed in a similar fashion: the four equatorial M–X bonds (two 3c-4e bonding) in Oh are longer and more polar than the two axial bonds.
SCHEME 1. The simplest MO diagram of a 3c-4e bonding in hypervalent D → M–X fragment

In connection with the use of the hypervalent concept as an explanation of mutual cis/trans-influence in penta- and hexacoordinated compounds of group 14 elements, the experimental\textsuperscript{24–29} and theoretical\textsuperscript{30,31} works and references cited therein should be consulted.

In spite of some critical remarks\textsuperscript{32,33}, the hypervalent model is successfully used in interpreting the results of physicochemical investigations\textsuperscript{34–36}. For discussion on using the term ‘hypercoordinate’ instead of ‘hypervalent’, see Reference 37.

The development of the hypervalency concept was discussed in general\textsuperscript{11}. This model was concerned with the group 14 elements\textsuperscript{38}. The ability of the tin atom to expand the coordination sphere in organotin compounds was established in the early 1960s, when an oligomeric structure was suggested for trimethyltin fluoride\textsuperscript{39} and trimethyltin carboxylates\textsuperscript{40} on the basis of IR data. It should be pointed out that the trimethyltin chloride–pyridine adduct was the first pentacoordinate organotin compound structurally characterized by X-ray diffraction in 1963\textsuperscript{41}.

In contrast to silicon, for which the number of known compounds has grown rapidly over the last 15 years\textsuperscript{36,42}, little has been cited in the literature concerning the hypervalency of germanium\textsuperscript{1,8}, despite the fact that Ge exhibits a greater hypervalency than Si.

<table>
<thead>
<tr>
<th>M</th>
<th>Ge(IV)\textsuperscript{a}</th>
<th>Sn(IV)\textsuperscript{b}</th>
<th>Pb(IV)\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Sigma(r_{\text{cov}})$</td>
<td>$\Sigma(r_{\text{vdv}})$</td>
<td>$\Sigma(r_{\text{cov}})$</td>
</tr>
<tr>
<td>M−N</td>
<td>1.957</td>
<td>3.44</td>
<td>2.154</td>
</tr>
<tr>
<td>M−P</td>
<td>2.330</td>
<td>3.38</td>
<td>2.527</td>
</tr>
<tr>
<td>M−O</td>
<td>1.925</td>
<td>3.67</td>
<td>2.122</td>
</tr>
<tr>
<td>M−S</td>
<td>2.272</td>
<td>3.78</td>
<td>2.469</td>
</tr>
<tr>
<td>M−Se</td>
<td>2.390</td>
<td>3.88</td>
<td>2.587</td>
</tr>
<tr>
<td>M−F</td>
<td>1.904</td>
<td>3.38</td>
<td>2.101</td>
</tr>
<tr>
<td>M−Cl</td>
<td>2.217</td>
<td>3.73</td>
<td>2.414</td>
</tr>
<tr>
<td>M−Br</td>
<td>2.365</td>
<td>3.85</td>
<td>2.562</td>
</tr>
<tr>
<td>M−I</td>
<td>2.556</td>
<td>4.02</td>
<td>2.753</td>
</tr>
</tbody>
</table>

\textsuperscript{a}$r_{\text{cov}} = 1.223$ Å\textsuperscript{45} and $r_{\text{vdv}} = 2.15$ Å\textsuperscript{46}. The latter value was obtained from reliable van der Waals radius for Si (2.10 Å\textsuperscript{46}) and taking into account the difference between the covalent radii of Si (1.169 Å\textsuperscript{45}) and Ge. ($r_{\text{vdv}} = 2.11$ Å was obtained by Boyd\textsuperscript{47}.)

\textsuperscript{b}$r_{\text{cov}} = 1.42$ Å\textsuperscript{45} and $r_{\text{vdv}} = 2.17$ Å\textsuperscript{46}. ($r_{\text{vdv}} = 2.15$ Å was obtained by Boyd\textsuperscript{47}.)

\textsuperscript{c}$r_{\text{cov}} = 1.48$ Å\textsuperscript{45} and $r_{\text{vdv}} = 2.02$ Å\textsuperscript{46}.
Hypervalent compounds are common in the case of lead, rather than the tetrahedral ones\textsuperscript{7,8,43}. However, the coordination chemistry of hypervalent lead compounds has been much less studied than that of hypervalent organotin compounds, probably due to the well-known high toxicity of organolead derivatives. The progressive lowering of the three-center interaction for the group 14 column of the Periodic Table and the marked drop for lead can be accounted for in terms of the relativistic effect\textsuperscript{44}.

In the following sections we shall compare the bond lengths in hypervalent compounds to those of their 'standard' tetravalent derivatives as well as the sum of van der Waals radii of the corresponding atoms. These data are summarized in Table 1 and will not be mentioned further in the text discussing interatomic distances.

The various donor–acceptor complexes of carbene analogues $R_2M$: ($X_2M \rightarrow M'$ and $D \rightarrow MX_2$, $M = \text{Ge, Sn and Pb}$; $M' = \text{transition metal, D} = \text{Lewis base}$) and doubly bonded germanium, tin and lead derivatives ($D \rightarrow X_2M = Z, Z = MX_2, CR_2, O, NR$ etc.) are not considered in this review.

### III. SELF-ASSOCIATES

The intermolecular complexes of germanium(IV), tin(IV) and lead(IV) organohalides and tetrahalides with halide ions and neutral N-, O-, S- or P-donors, including electron donor solvents, have been well known for a long time. An analysis of the data on their stability was well documented in the literature\textsuperscript{8,26,48–56}. The presence of the electronegative substituents is essential for the formation of such complexes. Their stabilities decrease on increasing the number and the size of alkyl substituents at the central atom, as well as on increasing the size of the halogens. Lewis acidity increases in the sequence $\text{Si} < \text{Ge} \ll \text{Sn} < \text{Pb}$ and the largest change takes place on going from germanium to tin\textsuperscript{57,58}. Based on the enthalpies and equilibrium constants, compounds $R_2SnX_2$, $RGeX_3$ and $SiX_4$ ($R = \text{Alk, Ar}; X = \text{Hal}$) are closely related in their ability to form complexes with halide ions and neutral donors\textsuperscript{57–63}.

The stoichiometry of the complexes formed depends on the nature of organometallic halides. With monodentate ligands, triorganohalides form 1 : 1 complexes containing a pentacoordinated central atom. Diorganodihalides, organotrihalides and tetrahalides as a rule form 1 : 2 complexes with hexacoordinate central atom and less often pentacoordinate complexes.

The reviews mentioned above tabulate the data on the complexes discussed above, and this information is not repeated here. For completion, we discuss a few examples and compare some of the properties of inter- and intramolecular complexes.

Neutral compounds of heavy group 14 elements having donor atoms in monodentate ligands can be tetrahedral in the solution. However, in this case the environment for the element in the solid state can be five-coordinate due to hypervalent bridges. Self-association can be also observed for pentacoordinate species when the donor atom forms a unidentate bridge across the six-coordinate centers. The self-association is also characteristic of anionic species (Sections IV.A and IX.A). For a tin atom the intermolecular coordination is observed very frequently\textsuperscript{64}. As a rule it results in a polymeric structure mainly via the oxygen atom\textsuperscript{65}. However, dimers and other simple cyclic hypervalent structures are formed only seldom.

#### A. $N \rightarrow M$ Coordination

The relative ability of group 14 atoms to increase the coordination number up to five is clearly shown by comparing crystal structures of such compounds as $Me_3MCN$ ($M = \text{Si, Ge and Sn}$). The minimal intermolecular contact between $M$ and $N$ atoms for silicon
(3.66 Å) corresponds to the sum of van der Waals radii and the silicon atom coordination is close to tetrahedral. For germanium, the N → Ge distance (3.57 Å) is closer than the sum of van der Waals radii and the silicon atom coordination is close to tetrahedral. In Me₃SnCN, the tin atom is in a TBP environment with three equatorial methyl groups and equally distant (2.49 Å) axial cyanide groups giving rise to the formation of a linear polymeric array by hypervalent bonding. Et₃SnCN has a similar structure.

The coordination environment of germanium in Me₂Ge(CN)₂ is close to tetrahedral; however, the intermolecular N → Ge distances of 3.84 Å indicate a weak association. In Me₂Ge(CN)₂, the angle between equatorial methyl groups is 114°. In Me₃SnCN, the tin atoms are in a TBP environment with three equatorial methyl groups and equally distant (2.49 Å) axial cyanide groups giving rise to the formation of a linear polymeric array by hypervalent bonding. Et₃SnCN has a similar structure.

There is a gradual decrease in the N → Sn distances in going from the exact trigonal-bipyramidal geometry at tin for (CH₃)₃SnN₃ to tetrahedral in (t-Bu)₃SnN₃ (Table 2). However, Me₃SnN₃ (a one-dimensional zigzag polymer attained by 1,1-azide hypervalent bridges) has an N → Sn bond length of 2.386 Å, which is longer than the Sn–N distances in monomeric (t-Bu)₃SnN₃ (2.101 Å) (Table 2) and (t-Bu)₂Sn(N₃)₂ (2.156, 2.141 Å). For triphenyl tin azide, there are two different five-coordinate tin environments formed by 1,3-azide hypervalent bridges giving rise to two different (Ph₃SnN₃)ₙ polymer chains. One has almost planar Ph₃Sn units, while the other shows geometry close to tetrahedral. Thus, triphenyltin azide appears to be along a structural continuum from tetrahedral silicon molecule Ph₃SiN₃ to polymeric lead azide Ph₃PbN₃.

The azide Me₃PbN₃ forms a linear chain polymer with a μ²-N atom symmetrically hypervalent bridging the pentacoordinate lead centers (N–Pb 2.54 Å). The N–Pb–N angle (178.6°) deviates only slightly from the ideal value of 180°. The carbodiimide Me₃SnNCNSnMe₃ forms an infinite helical network, too.

Chloro(diethylamino)dimethyltin consists of discrete dimer molecules, with Sn atoms linked by bridging diethylamino groups. The coordination geometry about the metal atom is a distorted trigonal bipyramid with two C atoms and one N atom in the equatorial plane, and Cl and the second N atom in the axial hypervalent bonding.

Though the crystal structure of monomeric 1-(Ph₃SnCH₂)-1,2,4-triazole contains a tetrahedral tin atom with very weak intramolecular N² → Sn distance 3.000 Å, the molecular structure of 1-(BrPh₂SnCH₂)-1,2,4-triazole consists of two independent cyclic dimers (10-membered cycles), formed by N⁴ → Sn coordinations. Parameters for hypervalent fragments of TBP tin atoms: N⁴ → Sn = 2.463 and 2.474 Å, Sn–Br = 2.633 and 2.641 Å, N⁴ → Sn–Br = 170.5 and 171.8°. On replacing the Br atom by I, the 1-(Ph₂SnCH₂)-1,2,4-triazole obtained is a tetrameric cyclic species (20-membered ring), arising from N⁴ → Sn interactions. There are two distinct trigonal-bipyramidal

<p>| Table 2. Selected bond distances and angles of the N → SnR₃–N hypervalent unit in triorganotin azides |
|---------------------------------|-----------|-----|-----|-----|-----|-----|</p>
<table>
<thead>
<tr>
<th>Compound</th>
<th>N → Sn(Å)</th>
<th>Sn–N(Å)</th>
<th>Σ(C–Sn–C)(deg)</th>
<th>N–Sn–C°(deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₃SnN₃</td>
<td>2.386</td>
<td>2.386</td>
<td>360.1</td>
<td>90.0</td>
<td>72</td>
</tr>
<tr>
<td>Ph₃SnN₃</td>
<td>2.565</td>
<td>2.210</td>
<td>355.1</td>
<td>95.0</td>
<td>73</td>
</tr>
<tr>
<td>(t-Bu)₃SnN₃</td>
<td>2.861</td>
<td>2.162</td>
<td>353.5</td>
<td>98.5</td>
<td>74</td>
</tr>
<tr>
<td>(t-Bu)₃SnN₃</td>
<td>—</td>
<td>2.101</td>
<td>347.0</td>
<td>101.5</td>
<td>74</td>
</tr>
</tbody>
</table>

*a* Average value.
*b* Two independent molecules.
*c* Tetracoordinate.
tin environments per tetramer with hypervalent fragments: N$_4$ → Sn = 2.36 and 2.45 Å, Sn–I = 2.944 and 2.856 Å, N$_4$ → Sn–I = 174.1 and 171.8°.81.

Attempts to prepare 1 : 1 and 1 : 2 adducts of SnPh$_2$Cl$_2$ with pyrazine (Pyz) by varying the acid-to-base ratio leads exclusively to the formation of an adduct having the bulk composition SnPh$_2$Cl$_2$ · 0.75 Pyz. It has a structure composed of layers in which zigzag polymeric chains, (SnPh$_2$Cl$_2$ · Pyz)$_n$, with six-coordinate tin, alternate with layers containing noninteracting molecules of (SnPh$_2$Cl$_2$)$_2$ · Pyz with five-coordinate tin.82 The data for the hypervalent fragments are: N → Sn = 2.783, 2.961 Å, Sn–Cl = 2.404, 2.379 Å and N → Sn–Cl = 166.7° and 166.2°.

Whereas germanes Ge(NSNR)$_4$ (R = t-Bu, TMS) are monomeric in solution, the $^{119}$Sn NMR data suggest that stannane Sn(NSNBu-t)$_4$ (4) and analogous bis- and tris(sulfurdiimido)tin compounds are associated in solution. The $\delta^{119}$Sn value (−624.0 ppm) of 4 falls in the typical range for hexacoordinated tin atoms.85,86 The structure in the solid state must be similar to that in solution, since the solid state $^{119}$Sn
CP/MAS NMR spectrum reveals an isotropic $\delta^{119}\text{Sn}$ value of $-604.0$ ppm\textsuperscript{83}. The increase of the coordination number at the tin atom in 4 is caused by intermolecular association via the free electron pairs at the nitrogen atoms of the hypervalent $\text{N} \rightarrow \text{Sn} - \text{N}$ systems.

\begin{equation}
\begin{array}{c}
\text{NSNBu-}t \\
\text{Sn} \quad \text{NSNBu-}t \\
\text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \\
\text{NSNBu-}t \\
\end{array}
\end{equation}


B. O $\rightarrow$ M Coordination

The tendency for tetrahedral main-group 14 elements to expand the coordination sphere enhances on increasing the nuclear number. Whereas silanole molecules are incorporated in associates by hydrogen bonding, for germanoles an intermolecular O $\rightarrow$ Ge coordination is also characteristic\textsuperscript{87}.

The presence of oxygen donor atoms in monodentate ligands promotes higher coordination numbers of group 14 elements, often leading to stabilization of associates in the solid state. Usually, organotin hydroxides are associated by strong intermolecular O $\rightarrow$ Sn bond and diverse oligomeric and polymeric structures are known\textsuperscript{88–90}. The triorganotin hydroxides Et$_3$SnOH\textsuperscript{91} and Ph$_3$SnOH\textsuperscript{92} crystallize in a zigzag chain structure with the tin atoms being pentacoordinated. The hydroxide groups are located in the axial positions and the hypervalent fragments O $\rightarrow$ Sn are slightly unsymmetrical with Sn–O distances ranging from 2.15 to 2.29 Å. In contrast, the sterically overcrowded [(t-Bu)$_2$Sn(OH)X]\textsubscript{2} (X = F, Cl, Br\textsuperscript{93} and OH\textsuperscript{94}) adopt a dimeric structure and trimesityltin hydroxide\textsuperscript{95} is monomeric in the solid state and the Sn–O bond length amounts to 1.999 Å.

Multinuclear solid- and solution-state NMR investigations of monomer HO(CH$_2$)$_n$SnCl$_3$ ($n = 3–5$) revealed a coordination behavior depending on both the length of the alkyl chain and the solvent. In a noncoordinating solvent, the compounds with three and four carbon atoms between the tin and the hydroxy group ($n = 3, 4$) show exclusively intramolecular HO $\rightarrow$ Sn coordination, resulting in five- and six-membered ring structures, respectively (Section VII.A). With five carbon atoms ($n = 5$), the corresponding intramolecular coordination leads to an unstable seven-membered ring, resulting in intermolecular coordination in the solid state, which is too strong for a CD$_2$Cl$_2$ solvent to break\textsuperscript{96}. The crystal structure of the ($n = 5$) alcohol reveals a polymeric structure that arises from significant intermolecular HO $\rightarrow$ Sn interactions of 2.356 Å. The tin atom is five-coordinate and exists in distorted trigonal-bipyramidal geometry with the oxygen and one of the chlorine atoms defining the axial hypervalent positions\textsuperscript{96}.

The structures of tin alkoxides Sn(OR)$_4$ (R = alkyl, aryl) were extensively investigated and were the subject of a recent review\textsuperscript{97}. As an important conclusion it was pointed out that the degree of association within these compounds decreases with an increasing steric demand of the alkoxy ligands; e.g. Sn(BOBu-$_t$)$_4$\textsuperscript{98,99} is a monomer whereas [Sn(OPr-$_t$)$_4$ $\cdot$ i-PrOH]\textsuperscript{98,100} is a dimer.

In contrast, structural information on organotin alkoxides R$_n$Sn(OR$^1$)$_{4-n}$ (R, R$^1$ = alkyl, aryl; $n = 1–3$) are rather limited. In the structure of Me$_2$SnOMe, almost planar trimethyltin groups are linked by two methoxy ligands forming infinite one-dimensional zigzag chains with nearly ideally trigonal-bipyramidal coordinated tin atoms (cf 5)\textsuperscript{101}. In [Ph$_3$SnOBu-$_t$ $\cdot$ i-BuOH] the tin atom exhibits a distorted trigonal
bipyramidal configuration 6 (O → Sn–O 173.5°) with the isobutoxy ligand being more strongly bonded to tin (2.066 Å) than isobutanol (2.549 Å)\(^{102}\). Isopropyltin triisopropylate contains a dimer 7 with both tin atoms possessing an almost ideal trigonal bipyramidal configuration\(^{103}\).

Organotin carboxylates have been the subject of numerous investigations and more than 400 X-ray crystal structure analyses have been reported to date. Some representative examples of the simplest coordinated organotin carboxylates can adopt one of the two idealized structure types: as intramolecularly bidentate giving rise to a distorted trigonal-bipyramidal coordination geometry (Sections VII.A and X.B.2a), and as a linear polymer formed by unsymmetrical bridging carboxylate groups connecting TBP configurated tin centers with two oxygens in the axial positions. The ideal tetragonal structure of triorganotin carboxylates without secondary interactions was only observed with aromatic carboxylic acids or with bulky substituents at tin. The structural chemistry of organotin carboxylates was thoroughly reviewed by Tiekink\(^ {104}\) and Jurkschat\(^ {65}\).

Reaction of \((n\text{-Bu})_2SnO\) with thiophene glyoxylic acid yields the tetrabutylbis(thiophene glyoxylate)distannoxane which crystallizes as the distannoxane dimer \([((n\text{-Bu})_2SnO_2CC(O)C_4H_3S)_2O]_2\). Determination of the crystal structure of the compound reveals the presence of two different environments for tin and two distinct carboxylate groups; one of them bonds to the six-coordinate tin atom via a carboxylate and keto oxygen atom to form a five-membered chelate ring, whereas the other carboxylate group forms a unidentate bridge (via one oxygen atom only) across the six-coordinate and five-coordinate tin centers\(^ {64}\).

The trimethyltin thiophene-2-carboxylate\(^ {105}\) propagates by glides to give rise to zigzag chains. The furan-2-carboxylate\(^ {106}\) and substituted benzoates\(^ {107}\) propagate by twofold screw axes to form stretched helical chains. Trimethyltin acetate and trimethyltin trifluoroacetate\(^ {108}\) propagate by glides to give rise to zigzag chains. The intramolecular and intermolecular O → Pb distances in trimethyllead acetate amount to 2.327 and 2.555 Å\(^ {109}\).

In solution, the tin acetates CH\(_3\)COO(CH\(_2\))\(_n\)SnCl\(_3\) (\(n = 3–5\))\(^ {110}\) exist as a mixture of a monomer with intramolecular coordination (Section VII.A) and an oligomer with intermolecular coordination in fast equilibrium on the \(^1H\), \(^{13}C\) and \(^{119}Sn\) NMR time
scales. The oligomer is the cyclodimer with carbonyl coordination, as found in an X-ray diffraction analysis of the \((n = 4)\) ester\(^{110}\).

The \(^{119}\)Sn cross polarization-magic angle spinning NMR spectrum of bis[1,3-bis(3-oxapentamethylene carbamoylthioacetato)-1,1,3,3-tetraethyl-1,3-distannoxane] consists of two resonances (\(\delta = -152, -202\) ppm), implying the existence of two five-coordinate tin sites in the centrosymmetric dimer. The crystal structure shows two tin atoms in \(cis\)-\(C_2\), trigonal-bipyramidal coordination\(^{111}\). The \([N,N\text{-dimethylthiocarbamoylthio})\) acetato\\(\text{trimethyltin}\)\(^{112}\) forms a polymer by translations and forms more of a zigzag than a helical chain.

Organotin compounds with intermolecular S\(=\)O \(\rightarrow\) Sn or Se\(=\)O \(\rightarrow\) Sn interactions are relatively rare and only a few single-crystal X-ray crystal structure analyses have been reported. Early examples of coordination are the trimethyltin sulfinites \(\text{Me}_3\text{SnO}_2\text{SR} (R = \text{Me, CH}_2\text{C}≡\text{CH})^{113–115}\) and the corresponding selenates \(\text{R}_3\text{SnO}_2\text{SeR} (R = \text{Me, Ph})^{116–117}\).

The tin sulfite \(\text{Ph}_3\text{SnO-}\text{S(O)-OSnPh}_3\) is monomeric in solution but forms polymeric chains in the solid state with both tetra- and pentacoordinate tin atoms\(^{118}\). In the case of the pentacoordinate tin atoms forming polymeric chains, the axial O \(\rightarrow\) Sn–O angle is 176.9° and the axial bonds are 2.264 and 2.252 Å, which are significantly longer than the sum of covalent radii. These crystal structures are very similar to that of \(\text{Me}_3\text{SnO-}\text{Se(O)-OSnMe}_3\)\(^{119}\) which, however, crystallizes with one equivalent of water\(^{119}\). The crystal structure of \(\text{Ph}_3\text{SnOSO}_2\text{SnPh}_3\) resembles that of the carbonates \(\text{R}_3\text{SnO-}\text{C(O)-OSnR}_3\) with respect to the presence of both tetra- and pentacoordinate tin atoms, and polymeric chains are formed by pentacoordination of tin atoms through O \(\rightarrow\) Sn–O linkages\(^{120}\).

The triorganotin phosphinates \(\text{Me}_3\text{SnO}_2\text{PMe}_2\)\(^{121}\), \(\text{Me}_3\text{SnO}_2\text{PCl}_2\)\(^{121}\) and \(\text{Bu}_3\text{SnO}_2\text{PPh}_2\)\(^{122}\) self-assemble in the solid state to give polymeric helical chain structures with pentacoordinated tin atoms. In contrast, dithiophosphorus acid derivatives show a higher tendency to function as chelating rather than bridging ligands\(^{123,124}\).

The crystal structure of the complex of diphenyltin dichloride with propylenediphosphonate consists of polymer chains with bridging bidentate ligands and an octahedral tin environment containing two types of phosphoryl fragments\(^{125–127}\). All of the \(\text{R}_2\text{SnX}_2\) adducts have \(\text{trans-R}_2\text{SnX}_2\text{O}_2\) geometries of octahedral tin coordination. The main Sn–Cl and Sn–O bond distances in octahedral coordination of polymeric diphosphoryl complexes of organotin halides are comparable. The C–Sn–C angles are significantly smaller (154–164°) than 180°.

Attempts to prepare organotin derivatives of phosphorus acids usually resulted in amorphous powders unsuitable for X-ray diffraction\(^{123}\). However, the crystal structure analysis of one representative, namely \((\text{Me}_2\text{Sn})_3(\text{PO}_3)_2·8\text{H}_2\text{O}\), was reported\(^{128}\). The organotin phosphate is built up by fused eight-membered Sn\(_2\)O\(_4\)P\(_2\) rings with alternating \(\text{Me}_2\text{Sn}\) and \(\text{Sn}-\text{O}\) bond distances in octahedral coordination of polymeric diphosphoryl complexes of organotin halides are comparable. The C–Sn–C angles are significantly smaller (154–164°) than 180°.

Compounds \(8\)\(^{129}\) and \(9\)\(^{130}\) are associated as dimers via O \(\rightarrow\) Sn interactions: there are intermolecular O \(\rightarrow\) Sn distances (2.327 and 2.587 Å) approximately \(\text{trans}\) to \(S^2\) (angle 150.6°) and N (angle 146.92°) with a symmetrical distannoxane Sn\(_2\)O\(_2\) unit. In addition, there are intramolecular O \(\rightarrow\) Sn bonds (2.679 Å with HOCH\(2\)CH\(_2\)S ligands in \(8\)) and transannular N \(\rightarrow\) Sn bonds (2.224 Å in \(9\)) and the tin coordination is raised to 6. Only one signal at 28.7 ppm is observed in the \(^{119}\)Sn NMR spectrum of \(8\), which is within the range for the four-coordinated tin nucleus. Therefore, the structure of \(8\) in solution is
different from that observed in the solid state and there are no intermolecular \( O \rightarrow Sn \) interactions in solution\(^{129}\).

The reaction of the dimethyltin(IV) cation with pyridoxine [3-hydroxy-4,5-bis(hydroxymethyl)-2-methylpyridine, PN] has been investigated in ethanol–water (80 : 20 v/v) containing \( NO_3^- \), \( NO_3^- \) and \( Cl^- \), \( NO_3^- \) and \( MeCO_2^- \) or \( Cl^- \) and \( MeCO_2^- \) ions in various mole ratios\(^{131}\). In each dimeric unit of 10 and 11 (Table 3) the tin atom is coordinated to two methyl groups, the phenolic O atom, the O atoms of two deprotonated \( CH_2OH \) groups and the O atom of a nondeprotonated \( CH_2OH \) group. In 10 the units are connected in a polymeric structure via the O of a deprotonated \( CH_2OH \) group of each PN–H. In compound 11 the coordination polyhedron of the tin atom is completed within the dimeric unit by water molecules which thus prevent the polymerization found in 10. The C–Sn–C angle is slightly wider in 11 (159.9°) than in 10 (143.8°), probably because the O → Sn distance of 2.466 Å in 11 is much shorter than the O → Sn distance of 2.802 Å in 10. In 12 the crystal contains dimeric \([SnMe_2(H_2O)(PN-2H)]_2\) units in which the dideprotonated ligand coordinates as in 10 and water.

The \( R_2(X)SnOSn(X)R_2 \) species associates have structure considerably more confusing (monomers have appeared only for the compound with \( R = 2,4,6\)-tris(trifluoromethyl) phenyl and \( X = Cl\))\(^{132}\). A characteristic feature of symmetric tetraorganodistannoxanes in the solid state is their dimerization, resulting in the so-called ladder-type arrangement, which contains a central planar Sn2O2 four-membered ring. The \([(t-Bu)_2(F)SnOSn(F)(Bu-t)]_2\) (13)\(^{133}\) and \([(R_2ClSn)_2O)_2\] (\( R = Me, i-Pr, Ph\))\(^{134}\) exhibit a centrosymmetric dimer with a typical ladder-type arrangement. In 13 the terminal Sn$^2-F^5$ distance
(1.981 Å) is almost identical to single bond length whereas \( {\text{F}}^a \rightarrow \text{Sn}^2 \) and \( \text{Sn}^1 \rightarrow {\text{F}}^a \) distances are much longer (2.196 Å and 2.177 Å, respectively). The \( {\text{F}}^b \rightarrow \text{Sn}^1 \) distance of 3.656 Å is too large to be considered as an interaction.

In solution, \textbf{13} exhibits a unique valence tautomerism as evidenced by \( ^{19}\text{F} \) and \( ^{119}\text{Sn} \) NMR spectroscopy; for example the \( ^1J({^{117/119}\text{Sn}}-{^{19}\text{F}}) = 2442/2335 \) Hz satellites are
16. Hypervalent compounds of organic germanium, tin and lead derivatives

TABLE 3. Selected bond distances and angles of the bridge hypervalent unit for pyridoxine (PN) tin dimers

<table>
<thead>
<tr>
<th>N</th>
<th>Compound</th>
<th>O → Sn (Å)</th>
<th>Sn–O (Å)</th>
<th>O → Sn–O (deg)</th>
<th>C–Sn–C (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>[SnMe₂(PN−H)]NO₃ ⋅ 2H₂O</td>
<td>2.802</td>
<td>2.063</td>
<td>160.6</td>
<td>143.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.291</td>
<td>2.104</td>
<td>153.2</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>[SnMe₂(H₂O)(PN−H)]Cl ⋅ H₂O</td>
<td>2.466</td>
<td>2.116</td>
<td>162.1</td>
<td>159.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.203</td>
<td>2.179</td>
<td>154.7</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>[SnMe₂(H₂O)(PN−2H)] ⋅ 0.5H₂O</td>
<td>2.963</td>
<td>2.046</td>
<td>164.0</td>
<td>142.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.268</td>
<td>2.087</td>
<td>154.7</td>
<td></td>
</tr>
</tbody>
</table>

averaged couplings for the Sn²–Fᵃ and Sn²–Fᵇ bond pairs. The two smaller non-averaged couplings of 874/834 Hz and 743/709 Hz are assigned to the pairs Sn¹–Fᵃ and Sn¹–Fᵇ, respectively. These and other data are explained by the equilibrium between the valence tautomers with the averaged structure 13a as a transition state. The valence tautomer interconversion of 13 represents a unique example where, for the first time, the ‘motion of electron density’ in a hypervalent system becomes visible by NMR spectroscopy.

Of the [R₂(Cl)SnOSn(Cl)R₁₂]₂-type compounds 14–16, selected interatomic Sn–Cl distances for 15 are listed in Table 4.

TABLE 4. The Sn–Cl bond distances in [R₂(Cl)SnOSn(Cl)R₁₂]₂

<table>
<thead>
<tr>
<th>R</th>
<th>R¹</th>
<th>Cl₂ → Sn¹(Å)</th>
<th>Sn¹–Cl¹(Å)</th>
<th>Cl¹ → Sn²(Å)</th>
<th>Sn²–Cl²(Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>Me</td>
<td>3.409</td>
<td>2.702</td>
<td>2.789</td>
<td>2.445</td>
<td>134</td>
</tr>
<tr>
<td>i-Pr</td>
<td>i-Pr</td>
<td>3.473</td>
<td>2.675</td>
<td>2.803</td>
<td>2.462</td>
<td>135</td>
</tr>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>3.355</td>
<td>2.688</td>
<td>2.697</td>
<td>2.430</td>
<td>136</td>
</tr>
<tr>
<td>Me</td>
<td>t-Bu</td>
<td>3.126</td>
<td>2.802</td>
<td>2.675</td>
<td>2.516</td>
<td>137</td>
</tr>
<tr>
<td>n-Bu</td>
<td>t-Bu</td>
<td>3.013</td>
<td>2.907</td>
<td>2.598</td>
<td>2.574</td>
<td>137</td>
</tr>
</tbody>
</table>
There is a substantial difference between the structures found for the symmetric and asymmetric \((R \neq R^1)\) compounds. In the symmetric compounds \((14)\) one Cl atom forms a symmetric bridge and the other is essentially terminal. This has the consequence that in the symmetric \([(R_2SnCl)_2O]_2\) species both Sn atoms are five-coordinate and trigonal-bipyramidal. However, in the asymmetric compounds \((15)\) both Cl atoms are involved in weak, but significant interactions with the endocyclic Sn atom. Ladder compounds containing \(t\)-Bu substituents at tin may be isolated in the solid state as discrete molecular species \([((t\text{-}Bu)_2(Cl)SnOSn(Cl)R_2)]_2\), which may be regarded as the 1 : 2 adduct \([(t\text{-}Bu)_2SnCl_2(R_2SnO)(t\text{-}Bu)_2SnCl_2)]_2\) \((16)\). In solution this adduct is labile and undergoes some dissociation, whose extent depends on the nature of the R group.

Attempts to form a ladder species, \([(t\text{-}Bu)_2SnCl_2)((t\text{-}Bu)_2SnO)(t\text{-}Bu)_2SnCl_2]\), where all four tin atoms carry \(t\)-Bu substituents, were unsuccessful. Formation of that ladder species would require the tin atoms in the central \((t\text{-}Bu)_2SnO_2\) moiety to be able to become six-coordinate. Apparently, the \(t\)-Bu groups reduce the Lewis acidity at tin or they are sterically overcrowded to such an extent that six-coordination is not possible. Instead, there is evidence for the 1 : 1 adduct \([(t\text{-}Bu)_2SnCl_2)((t\text{-}Bu)_2SnO)]_2\), in which the tin atoms are all five-coordinate.

The formation of a ladder-type 1 : 2 associate, which contains a central planar Sn\(_2\)O\(_2\) four-membered ring (e.g. \((17)\)), and more complete symmetric species\(^{140-146}\) are often observed for diorganotin alkoxides.

The dihalogenated 1,2,5-oxaphosphastannolane dimerizes as a result of an intermolecular O \(\rightarrow\) Sn coordination to give a diastereomeric mixture\(^{147}\); the structure of one of them \((18)\) is shown. As a result of both inter- and intramolecular interactions the coordination
16. Hypervalent compounds of organic germanium, tin and lead derivatives

(17)

(18)

(19)
TABLE 5. Selected structural parameters for lead polymers with O → PbR₃X ligand framework

<table>
<thead>
<tr>
<th>Compound</th>
<th>O → Pb (Å)</th>
<th>Pb–X (Å)</th>
<th>O → Pb–X (deg)</th>
<th>Σ</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Me₃Pb(H₂O)NC]ₙₜ b</td>
<td>2.679</td>
<td>2.323</td>
<td>174.4</td>
<td>358.3</td>
<td>148</td>
</tr>
<tr>
<td>[Me₃Pb(H₂O)NC]ₙₜ c</td>
<td>2.658</td>
<td>2.345</td>
<td>175.0</td>
<td>359.0</td>
<td>148</td>
</tr>
<tr>
<td>[Me₃PbOCO-2-Fu]ₙ</td>
<td>2.534</td>
<td>2.353</td>
<td>169.4</td>
<td>359.2</td>
<td>149</td>
</tr>
<tr>
<td>[Me₃PbOAc]ₙ</td>
<td>2.44</td>
<td>2.37</td>
<td>176.3</td>
<td>359.8</td>
<td>109</td>
</tr>
<tr>
<td>[Ph₃PbOH]ₙ</td>
<td>2.44</td>
<td>2.37</td>
<td>176.3</td>
<td>359.8</td>
<td>92</td>
</tr>
<tr>
<td>[Ph₃PbOC₆H₃-5-F-4-NO]ₙ</td>
<td>2.423</td>
<td>2.506</td>
<td>169.3</td>
<td>360.0</td>
<td>151</td>
</tr>
</tbody>
</table>

a The sum of the CPbC equatorial angles.
b Fragment of catena-(hexakis(µ₂-cyano)-diaqua-dodecamethyl-tetralead ruthenium).
c Fragment of catena-(hexakis(µ₂-cyano)-diaqua-dodecamethyliron-tetralead).

dimetallic structure 18 can be described as distorted octahedra with trans-angles of 173.9° for O → Sn−Cl and 161.78° for O → Sn−O. The almost equal intermolecular dative O → Sn and covalent Sn−O bond lengths of 2.140 Å and 2.147 Å, respectively, are shorter than the intramolecular O → Sn distance of 2.204 Å147.

Only few examples of self-organized organolead compounds with oxygen-based donors were reported to date (Table 5). Lead hydroxide Ph₃PbOH92 is isostructural with its tin analogue and forms zigzag chains in which planar Ph₃Pb fragments are linked by hydroxide groups. In the unsymmetrical O → Pb−O fragment the oxygen–lead bond lengths amount to 2.44 and 2.37 Å.

Catena-[µ₂-acetoxy]-acetoxydiphenyllead(IV) (19) is among the few structurally characterized hypervalent hexacoordinate organolead acetates. The latter forms a polymer via intermolecular O → Pb interactions152.

C. Hal → M Coordination

In the condensed phase Me₃SiF molecules show no intermolecular interactions, while the same germanium derivatives are associated as a dimer due to intermolecular F → Ge87 coordination. According to the tendency for tetrahedral main-group 14 elements to expand the coordination sphere, organotin fluorides show a strong tendency to associate in the solid state and even in triorganotin fluorides the tin atom is five-coordinate153,154. A common feature of this class of compounds in the solid state is coordination expansion of the tin atom due to hypervalent interaction, which in turn often results in formation of polymeric materials.

Trimethylfluorostannane is probably a chain-type polymer155 containing five-coordinate tin. Solid state ¹¹⁹Sn NMR studies have confirmed five coordination for Me₃SnF, as well as for (i-Bu)₃SnF and Ph₃SnF66. Two identical Sn−F distances of 2.146 Å for the hypervalent fragment F → Sn−F in the axial positions of a symmetrical trigonal bipyramid was observed for Ph₃SnF156. For the unsymmetrically substituted triorganotin fluoride Me₂PhSnF157 the tin fluoride adopts a structure with only slightly different Sn−F distances of 2.179 and 2.162 Å and F → Sn−F angle of 179.4°. An unsymmetrical structure with Sn−F distances of 2.051 and 2.303 Å was reported for the sterically overcrowded (c-Hex)₃SnF158. For comparison, the Sn−F single bond distance in monomeric [(SiMe₃)₃C]₂PbSnF₁₅₉ and Mes₃SnF₉₅ is 1.96 Å in the solid state and it contains four-coordinate tin, presumably because the bulky organyl substituent prevents hypervalent bridging.
In contrast, difluorostannanes \( \text{R}_2\text{SnF}_2 \) (\( \text{R} = \text{Me}, \text{n-Bu}, \text{Ph} \)) show strong intermolecular \( \text{F} \rightarrow \text{Sn} - \text{F} \) hypervalent bridges and consequently are almost insoluble in organic solvents\(^{66}\). The poor solubility of organylfluorostannanes has largely restricted their study to investigations of solid compounds. For example, \( \text{Me}_2\text{SnF}_2 \) is a sheetlike polymer\(^{160}\) containing six-coordinate tin. Vibrational and \(^{119}\text{Sn} \) Mössbauer spectroscopies imply that \( \text{MeSnF}_3 \) contains both bridging and terminal fluorides such that the tin is six-coordinate\(^{161}\).

Although \( \text{Cl} \rightarrow \text{Sn} \) bonds are weaker than \( \text{F} \rightarrow \text{Sn} \) bonds they are strong enough to give hypervalent association of triorganotin chlorides in the solid state\(^{5,90,162,163}\). An example of \( \text{Sn}_3\text{Cl} \) crystallizing as a linear chain polymer, having one short \( \text{Sn} - \text{Cl} \) distance of \( 2.387 \, \text{Å} \), and one long \( \text{Cl} \rightarrow \text{Sn} \) distance of \( 3.531 \, \text{Å} \), was observed\(^{164}\). \( \text{Me}_3\text{SnCl} \)\(^{162,163}\) forms a zigzag chain, with \( \text{Sn} - \text{Cl} \) distances of \( 2.430 \, \text{Å} \) and \( 3.269 \, \text{Å} \), and \( \text{Sn} - \text{Cl} \) angle of \( 150.5^\circ \). In contrast, \( \text{Ph}_3\text{SnCl} \)\(^{165}\) does not self-associate in the solid state and consists of discrete tetrahedral molecules.

Compounds with the general formula \( \text{R}_2\text{SnCl}_2 \) are commonly found to dimerize via hypervalent \( \text{Cl} \rightarrow \text{Sn} - \text{Cl} \) bridges\(^{166-170}\). It is significant that the intermolecular \( \text{Cl} \rightarrow \text{Sn} \) interactions of \( 3.54 \, \text{Å} \) (\( \text{R} = \text{Me}^{171} \)), \( 3.483 \, \text{Å} \) (\( \text{Et}^{172} \)), \( 3.308 \, \text{Å} \) (\( \text{i-Pr}^{173} \)), \( 3.514 \, \text{Å} \) (\( \text{n-Bu}^{174} \)), \( 3.770 \, \text{Å} \) (\( \text{Ph}^{175} \)), \( 3.332 \, \text{Å} \) (\( \text{E}_{\text{t}}^{176} \)), \( 3.482 \, \text{Å} \) [\( \text{Ph(Me)SnCl}_2 \)]\(^{177}\) are less than the sum of van der Waals radii. It is noteworthy that there are no intermolecular \( \text{Cl} \cdots \text{Sn} \) contacts > \( 4.0 \, \text{Å} \) in two compounds, i.e. when \( \text{R} = 2\text{-PhC}_6\text{H}_4^{178} \) and \( \text{R} = \text{t-Bu}^{173} \) which contain the most bulky tin-bound substituents of the compounds listed above.

Hypervalent \( \text{Cl} \rightarrow \text{Sn} - \text{Cl} \) bridges are also typical for pentacoordinate tin atoms. For example, the crystal structure of \( \text{MeOOCCH}_2\text{CH(COOMe)CH}_2\text{Sn(S}_2\text{CNEt}_2)\text{Cl}_2 \)\(^{168,179}\) and \( \text{MeSn(Ar)Cl}_2 \)\(^{170}\) comprise dimeric pairs of molecules bridged by weak intermolecular \( \text{Cl} \rightarrow \text{Sn} \) interactions. The \( \text{Cl} \rightarrow \text{Sn} \) distances in \( 20 \) (\( 2.475 \, \text{Å}^{179} \)), \( 21 \) (average \( 3.869 \, \text{Å}^{170} \)) and in \( \text{MeSn(Ar)Cl}_2 \) (\( \text{Ar} = 3\text{-methyl-4-nitropyridine-N-oxide} \)) (\( 3.934 \, \text{Å}^{180} \)) are longer than in most comparable structures\(^{168,169,181}\). The \(^{119}\text{Sn} \) NMR resonance (\( -285.7 \, \text{ppm} \)) for \( 21 \) suggests that it possesses a five-coordinate structure in solution\(^{170}\).

The structure of \( \text{MeOOCCH}_2\text{CH(COOMe)CH}_2\text{Sn(S}_2\text{CNEt}_2)\text{Cl}_2 \), the only other previously characterized \( \text{RSn(S}_2\text{CNEt}_2)\text{Cl}_2 \) compound, is very different from that of \( 21 \) as the \( \text{MeOOCCH}_2\text{CH(COOMe)CH}_2 \)- ligand is bidentate, giving rise to a monomeric, six-coordinate structure (Section X.B) in which there are no \( \text{Cl} \cdots \text{Sn} \) bridges\(^{182}\).

Compound \( 22 \) exhibits a distorted trigonal-bipyramidal geometry at both Sn atoms. The intermolecular \( \text{Cl} \rightarrow \text{Sn} \) bond of \( 3.116 \, \text{Å} \) is considerably longer than the axial \( \text{Sn}^2 - \text{Cl} \) bond (\( 2.420 \, \text{Å} \)), which in turn is longer than the equatorial \( \text{Sn}^2 - \text{Cl} \) bond (\( 2.370 \, \text{Å} \))\(^{183}\). In contrast, the bromodimethyl(\( N\text{-methylpyrroolidin-2-one-O} \)tin(IV)-di-\( \mu \)-bromo-bromodimethylin(IV), \( 23 \), contains two Sn atoms in the asymmetric unit, the Sn\(^1\) complexed by \( N\text{-methylpyrroolidin-2-one} \)exhibiting a hexacoordinated arrangement while Sn\(^2\) is pentacoordinated with hypervalent fragments possessing the following parameters: \( \text{Br} \rightarrow \text{Sn}^1 = 3.584 \, \text{Å}, \, \text{Sn}^1 - \text{Br} = 2.508 \, \text{Å}, \, \text{Br} \rightarrow \text{Sn}^1 - \text{Br} = 178.0^\circ \) and \( \text{Br} \rightarrow \text{Sn}^2 = 3.712 \, \text{Å}, \, \text{Sn}^2 - \text{Br} = 2.506 \, \text{Å}, \, \text{Br} \rightarrow \text{Sn}^2 - \text{Br} = 169.7^\circ \)\(^{184}\).

Triorganolead halides are usually associated in the solid state, which was confirmed by X-ray crystallography\(^{185-188}\). Usually, the lead atom is pentacoordinated with the halogen atoms located at the axial positions of a trigonal bipyramid, forming infinite chains with unsymmetrical \( \text{X} \rightarrow \text{Pb} - \text{X} \) links. The two lead–halide distances in a given compound differ significantly. Thus in \( \text{Me}_3\text{PbI} \) the lead–iodine distances amount to \( 3.038 \) and \( 3.360 \, \text{Å} \)\(^{186}\), whereas the lead–bromine distances are \( 2.852 \) and \( 3.106 \, \text{Å} \) in \( \text{Ph}_3\text{PbBr}^{185} \), and \( 2.885 \) and \( 2.985 \, \text{Å} \) in \( \text{BnPh}_2\text{PbBr}^{187} \). All structures reported show a linear \( \text{X} \rightarrow \text{Pb} - \text{X} \) fragment\(^{185,186}\).
The Pb—Br bond (2.696 Å) has been shortened relative to the terminal bond (2.852 Å) and the bridging (3.106 Å) Pb—Br bonds in the parent Lewis acid, which adopts a helical chain structure\textsuperscript{189}. The molecule Ph\textsubscript{2}PbCl\textsubscript{2}\textsuperscript{190} forms chains in which an octahedral Pb atom is linked by Cl bridges.
D. Other X → M Coordination

For hypervalent compounds the S → Sn interactions are less known than O → Sn ones. Generally, a tin center in an unassociated diorganotin dithiolate is coordinatively unsaturated and will coordinate, at least in the solid state, with available internal or external donor centers, unless other factors, such as steric hindrance, are operating. For solid diorganotin 1,2-ethanedi(thiolates), R₂Sn(EDT), only thiolato S atoms are available for intermolecular hypervalent coordination, with the formation of SSnSSn rings. The number and strength of the S → Sn interactions depend on the R group, e.g. the intermolecular S → Sn bond length in pentacoordinate Me₂Sn(EDT) is 3.18 Å, and in hexacoordinate Bu₂Sn(EDT) 3.69 Å. There is a single long intermolecular S···Sn separation of 3.885 Å in Ph₂Sn(EDT), which is within the sum of the van der Waals radii of Sn and S.

The compound (t-Bu)₂Sn(DMIT) is unassociated. The tin center in solid PhMeSn(DMIT) (24a) is five-coordinate with a trigonal-bipyramidal geometry: the molecules are linked into spiral chains via intermolecular S(thione) → Sn interactions (Table 6). This was confirmed by the single δ¹¹⁹Sn value (94.9 ppm) in the solid state ¹¹⁹Sn NMR spectrum.

![Diagram of compounds](image)

Compound Me₂Sn(DMIT) (24b) and orthorhombic Et₂Sn(DMIT) (24c) are linked into chains as a result of intermolecular S(thione) → Sn interactions. The tin centers are pentacoordinate with distorted TBP geometries. The intermolecular S → Sn bonds of 3.001 and 2.960 Å in the two independent molecules of 24b, and 3.008 Å in 24c at 150 K (3.037 Å at 298 K), are considerably longer than the covalent Sn bonds to the dithiolato Sax andSeq atoms between 2.440 and 2.523 Å (Table 5). As expected, the axial dithiolato — tin bond of 2.523 Å is longer than the equatorial bond, 2.459 Å. The distortions from ideal trigonal-bipyramidal arrays in 24a–c are not the result of the presence of the chelate, since the chelate bite angles are near 90° in all cases.
TABLE 6. Selected bond distances and angles for pentacoordinate associated diorganotin dithiolate 24

<table>
<thead>
<tr>
<th>N</th>
<th>Compound</th>
<th>T (K)</th>
<th>S → Sn (Å)</th>
<th>Sn−Sax (Å)</th>
<th>Sn−Seq (deg)</th>
<th>S → Sn−Sax (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>24a</td>
<td>PhMeSn(DMIT)</td>
<td>—</td>
<td>3.139</td>
<td>2.487</td>
<td>2.437</td>
<td>161.53</td>
<td>197</td>
</tr>
<tr>
<td>24b</td>
<td>Me₂Sn(DMIT)</td>
<td>150</td>
<td>3.001</td>
<td>2.518</td>
<td>2.440</td>
<td>165.61</td>
<td>198</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.960</td>
<td>2.521</td>
<td>2.457</td>
<td>167.57</td>
<td></td>
</tr>
<tr>
<td>24c</td>
<td>Ortho-Et₂Sn(DMIT)</td>
<td>298</td>
<td>3.037</td>
<td>2.513</td>
<td>2.436</td>
<td>159.53</td>
<td>198</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150</td>
<td>3.008</td>
<td>2.523</td>
<td>2.459</td>
<td>158.26</td>
<td></td>
</tr>
</tbody>
</table>

*aTwo different crystalline phases of Et₂Sn(DMIT) have been obtained: slow recrystallization from acetone produced an orthorhombic form, ortho-Et₂Sn(DMIT), 24c, while recrystallization from aqueous MeOH gave a monoclinic form, mono-Et₂Sn(DMIT), 25b.*

TABLE 7. Selected bond distances and angles for hexacoordinate associated diorganotin dithiolate 25

<table>
<thead>
<tr>
<th>N</th>
<th>Compound</th>
<th>E → Sn (Å)</th>
<th>Sn−E (Å)</th>
<th>E → Sn−E (deg)</th>
<th>C−Sn−C (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>25a</td>
<td>Me₂Sn(DMIO)</td>
<td>2.654a</td>
<td>2.487a</td>
<td>126.46a</td>
<td>124.2</td>
<td>191</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.649b</td>
<td>2.440b</td>
<td>154.10b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25b</td>
<td>Mono-Et₂Sn(DMIT)c</td>
<td>3.567, 3.620</td>
<td>2.460, 2.449</td>
<td>154.43, 150.40</td>
<td>126.3</td>
<td>198</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.555, 3.929</td>
<td>2.458, 2.447</td>
<td>155.29, 151.31</td>
<td>119.5</td>
<td></td>
</tr>
</tbody>
</table>

*aE = O.  
bE = S.  
cTwo independent molecules; see footnote in Table 6.*

In the case of Me₂Sn(DMIO) (25a) intermolecular associations involve both a carbonyl O and a thiolato S atom and a six-coordinate tin (Table 7), and again a SSnSn ring is formed 191.

The two independent molecules of monoclinic Et₂Sn(DMIT) 25b have quite different arrangements: tin atoms in molecule A (Table 7) form two relatively weak intermolecular thione S → Sn bonds of 3.567 and 3.620 Å, with the formation of sheets, while those in molecule B form a similar bond, S → Sn = 3.555 Å to give chains, with a much longer contact, S···Sn = 3.927 Å to another chain. The latter is only ca 0.03 Å less than the van der Waals radii sum for Sn and S (Table 1).

The geometries in the six-coordinate species, 25a and 25b, are also far from regular: even a severely distorted octahedral description appears inappropriate. The DMIO derivative, 25a, forms a honeycomb network due to a combination of S → Sn and O → Sn intermolecular interactions and the rings are formed from six molecules 191.

Examples of association resulting from intermolecular sulfur → organolead hypervalent interactions are rare and compounds such as Me₃PbSMe and Ph₃PbSPh are monomeric in the solid state 199. The cyclic diorganodithiolate 2,2-diphienyl-1,3,2-dithiaplumbolan 200 self-assembles in the solid state via intermolecular sulfur → tin interactions into a one-dimensional polymeric array. The intramolecular S → Pb bond lengths amount to 2.52 and 2.49 Å, and the intermolecular S → Pb distances are 3.55 Å.

Hypervalent compounds with coordinative phosphorus → tin bonds are rare. An intermolecular P → Sn coordination in Me₂ClSnCH₂CH₂PPh₂ and its bromo-substituted analogue was suggested based on NMR and ¹¹⁹Sn Mössbauer spectroscopic data 201,202. The X-ray crystal structure analyses showed pentacoordinate tin atoms with the phosphorus and the chlorine atoms located in axial positions 203. The P → Sn distance amounts to
IV. PENTACOORDINATE ANIONIC COMPOUNDS

A. Intermolecular Complexes

1. Tetraorganotin and tetra- and triorganogermainium derivatives

Tetraorganogermanes, -stannanes and -plumbanes bearing four M–C bonds and having no donor atoms in the organic moiety have been known to be usually reluctant to form pentacoordinate anionic complexes\textsuperscript{1,4,6.8.205}. However, in the case of the lithium—tin exchange reaction, NMR evidence for the formation of the intermediate species Me\textsubscript{5}Sn– and Ph\textsubscript{5}Sn– was presented\textsuperscript{206}. With the highly electronegative trifluoromethyl group as a substituent at germanium, the Lewis acid character of this atom is conserved. As a result, the reactions of (CF\textsubscript{3})\textsubscript{n}GeX\textsubscript{4–n} (X = Hal, n = 1–4) with fluoride ions (as KF, NaF or NH\textsubscript{4}F) in aqueous or acetonitrile solutions give pentacoordinate and hexacoordinate anionic complexes\textsuperscript{207,208}. Bulky CF\textsubscript{3} groups decrease the germanium capacity for hexacoordination. Consequently, octahedral fluorine complexes have been observed upon fluoride addition to CF\textsubscript{3}GeF\textsubscript{3} or (CF\textsubscript{3})\textsubscript{2}GeF\textsubscript{2}, whereas the derivatives containing four or three CF\textsubscript{3} groups yield mostly pentacoordinated monoanions \textsuperscript{26} and \textsuperscript{27} (equations 1 and 2).

\[
\begin{align*}
\text{CF}_3\text{Ge}^{+} + \text{F}^- & \rightarrow \text{CF}_3\text{GeF}^- \quad (26) \\
\text{H}_2\text{O}, \text{F}^- \rightarrow \text{CF}_3\text{GeF}^- & \rightarrow \text{CF}_3\text{GeF}_{2}^{2-} \quad (27)
\end{align*}
\]

\[
\begin{align*}
\text{CF}_3\text{GeCl}^{+} + \text{F}^- & \rightarrow \text{CF}_3\text{GeF}^- \rightarrow \text{CF}_3\text{GeF}_{2}^{2-} \quad (28)
\end{align*}
\]

In aprotic solvents, however, both (CF\textsubscript{3})\textsubscript{4}Ge and (CF\textsubscript{3})\textsubscript{3}GeCl react with excess of fluoride ion to give octahedral species \textsuperscript{28} and \textsuperscript{29} which are stable only in the absence of moisture\textsuperscript{208}. According to \textsuperscript{19}F NMR spectroscopy, the monoanions \textsuperscript{26} and \textsuperscript{27} have in solution the TBP structures, with the fluorine atoms occupying the apical positions. The structure of anion \textsuperscript{27} in the complex [Me\textsubscript{4}N][((CF\textsubscript{3})\textsubscript{3}GeF\textsubscript{2})], obtained by treatment of Na[(CF\textsubscript{3})\textsubscript{3}GeF\textsubscript{2}] with Me\textsubscript{4}NCl in ethanol, provides an example for the almost ideal TBP structure (F–Ge–F 177.4°) with three equatorial trifluoromethyl groups\textsuperscript{208}. The axial Ge–F bonds (1.81 Å) are significantly longer as compared to those determined for the tetrahedral derivatives (1.74 Å in Me\textsubscript{2}GeF\textsubscript{3}\textsuperscript{9}), whereas the averaged equatorial C–Ge distance (1.98 Å) is not essentially different from that of 1.99 Å in (CF\textsubscript{3})\textsubscript{4}Ge\textsuperscript{9}.

2. Triorganostannates

The data on stable pentacoordinate anionic organylhalo-germaine and -lead complexes with halide ions are rather limited, in particular on those where the structure was determined by X-ray investigation (see the reviews\textsuperscript{7,8} and references cited therein). On the contrary, the strong Lewis acidity of organylhalostannanes toward halide ion has been the subject of study for many years\textsuperscript{8,209,210}. Moreover, the pentacoordinate anionic tin complexes have attracted attention in recent years as reagents for selective organic syntheses\textsuperscript{211,212}, as well as in host–guest chemistry\textsuperscript{213–217} and as soluble organotin halides for biocides\textsuperscript{8}.

3.065 Å, which is comparable to the P → Sn distance of 3.078 Å in the monomeric, intramolecularly coordinated Me\textsubscript{2}ClSnCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}PPhBu-\textsubscript{t}\textsuperscript{204}. 
The reaction is reversible (equation 3, step a) and, furthermore, a mixture of stannate complexes may undergo disproportionation to establish an equilibrium between homo- and mixed-ligand compounds (equation 3, step b). Moreover, the aryloxy mixed ligand stannates 36–38 are more stable than a 1 : 1 mixture of the corresponding dichloro- and bis(aryloxy)-stannates. Thus, the stability of the TAS stannates with TBP structures is highly affected by the nature of the equatorial organic groups and apical heteroatom substituents.

\[
R_3SnX + TAS^+ Y^- \xrightleftharpoons[\text{a}]{\text{b}} [R_3SnXY]^- \xrightleftharpoons[\text{b(X \neq Y)}]{1/2} 1/2[R_3SnX_2]^- + 1/2[R_3SnY_2]^- \xrightleftharpoons[\text{b(X \neq Y)}]{1/2} R_3SnX + TAS^+ Y^- (36–38)
\]

As judged by NMR investigation, hexacoordinate Sn complexes are not formed by the addition of excess chloride, arylxide or HMPA to the pentacoordinate complexes 30a–32a, 33–35 226.

Analogously, attempts to prepare stable adducts from the reaction of stannates Ph₃SnF₂⁻ or Ph₃Sn(F)Cl⁻ with F⁻, Et₄NCl, HMPA or DMSO were also unsuccessful. However, small changes in the chemical shifts and coupling constants detected by the addition of fluoride ion or DMSO to Ph₃SnF₂⁻ were interpreted as due to the formation of small amounts of the six-coordinate adducts 218.

Nucleophic addition of halides or cyanide to Me₃SnCl leads to a series of salts 30b–d, 39a, 39b and 40 containing trimethyltin anions with a variety of cations (equation 4) 219.

Tetraalkyammonium stannates 30c and 39a obtained in CH₂Cl₂ or CH₃CN solution in 62–71% yield are susceptible to hydrolysis. The more stable potassium 18-crown-6 stannates 30d, 39b and 40, handled for a prolonged time in air, were prepared in quantitative yields in toluene solution.
In some cases anionic complexes can be obtained by the interaction of triorganylhalostannanes with neutral donors. For example, the reaction of Me₃SnBr with HMPA led to formation of the complex [Me₃SnBr₂][Me₃Sn(HMPA)₂] (41) in which both the cation and the anion contain TBP tin atoms.

While stable neutral five-coordinate adducts (Ar₃SnX·L; X = N₃, NCO, NCS; L = various O- and N-donor ligands) are well known (Section V.B), some aliphatic amines react with Ph₃SnN₃ to form the anionic complexes 42a–d, presumably due to the water present in the incompletely dried solvent or ligand (equation 5).

\[
2\text{Ph}_3\text{SnN}_3 + \text{L(H}_2\text{O}) \rightarrow [\text{Ph}_3\text{Sn(N}_3)_2]^- (\text{LH})^+ + \text{Ph}_3\text{SnOH}'
\]

The similar anionic complex [Ph₃Sn(NCS)₂][L₂H] (43a) (L = 1-(salicylideneimino)-2-methoxybenzene) was obtained by the reaction of Ph₃SnNCS and the corresponding ligand (1 : 2) in 95% ethanol. Another case of Ph₃Sn(NCS)₂⁻ formation in the salt [Ph₃Sn(NCS)₂][Et₄N] (43b) was observed on work-up of a reaction mixture derived from the sequential addition to [(PhCO)₂C₃S₅] (dibenzoyl-DIMT) of NaOMe, Ph₂Sn(NCS)₂ and Et₄NBr.

Recently, a series of trifluoroacetates (44a–c) have been described. Unlike other triorganotin carboxylates such as the acetates, which display no discernible Lewis acceptor properties, triorganotin trifluoroacetates form pentacoordinate complexes with neutral and anionic donors. Consequently, the interaction of trifluoroacetic acid, a molar equivalent of di-2-pyridylamine (DPA) yielded stannate 44c instead of the desirable neutral complex. Analogous reaction using a molar equivalent each of trifluoroacetic acid and chlorodifluoroacetic acid gave the mixed stannate [Ph₃Sn(OCOCF₃)(OCOCF₂Cl)][DPAH] (45) as one of the products. The latter is the first example of a triorganostannate having two different carboxylato groups covalently bonded to tin. A similar synthesis of coumarin-3-carboxylato stannate 46 involves the reaction of tetramethylammonium hydroxide, coumarin-3-carboxylic acid and Ph₃SnOH in 1 : 2 : 1 ratio in ethanol.

Some reports demonstrate the utility of the hypervalent species [R₃SnF₂]⁻ as useful reagents and intermediates. In particular, the crystalline stannate [Ph₃SnF₂][Bu₄N] (47) is relatively stable up to 210 °C and is not hygroscopic or undergoes hydration. Recently, its availability as a fluorinating agent was shown for the transformation of PhCH₂Br into PhCH₂F₂ and of gem-bistriflates RCH(OTf)₂ (R = Alk, Ar) into the mono-fluorides RCH(OTf)F₂ and the di-fluorides RCHF₂. Difluoroenoxyisilanes are produced in high yield by catalytic activation of a mixture of CF₃SiMe₃ and an acylsilane by using 47. In turn, enoxysilanes may be effectively alkylated by alkyl bromides in...
the presence of \textsuperscript{47}\textsuperscript{211}. Analogously, the reaction of alkenyl triflates with \textsuperscript{47} catalyzed by Pd(PPh\textsubscript{3})\textsubscript{4} affords regio- and stereospecifically the corresponding alkenylbenzene in excellent yields\textsuperscript{247}. Sulfuration of \textsuperscript{47} with elemental sulfur gives a simple and practical methodology for generating C−S bonds under almost neutral conditions and, in particular, the disulfide PhSSPh was obtained in a quantitative yield\textsuperscript{212}.

\textit{b. Crystal structures.} X-ray crystallographic structures of the pentacoordinate triorgano-stannate complexes \textsuperscript{30d–h}, \textsuperscript{31b}, \textsuperscript{32b–d}, \textsuperscript{33}, \textsuperscript{38}, \textsuperscript{41}, \textsuperscript{42a–c}, \textsuperscript{43a,b}, \textsuperscript{44a–c}, \textsuperscript{45}, \textsuperscript{46}, \textsuperscript{48–52}, including zwitterionic stannates (Section IV.A.6) have been reported. Tables 8–10 list the principal structural parameters for anions \textsuperscript{R\textsubscript{3}SnX\textsubscript{2}}\textsuperscript{−} and \textsuperscript{R\textsubscript{3}SnXY}\textsuperscript{−} in the homo- and mixed-ligand complexes discussed above, which are generally composed of discrete cations and anions. These anions possess a near-TBP arrangement with the organic and electronegative groups occupying the equatorial and apical positions, respectively. In the case of homo-ligand halide complexes (Table 8), near-regular TBP was found for large cations, in particular [K(18-crown-6)]\textsuperscript{+}, {[(Ph\textsubscript{3}PAu)\textsubscript{2}S]\textsubscript{2}Au}\textsuperscript{+} (complexes \textsuperscript{30d}\textsuperscript{219} and \textsuperscript{30h}\textsuperscript{248}, respectively).

Equal anions Ph\textsubscript{3}Sn(NCS)\textsubscript{2}\textsuperscript{−} in both described isothiocyanato complexes \textsuperscript{43a}\textsuperscript{230} and \textsuperscript{43b}\textsuperscript{231} have an almost ideal TBP arrangement about the tin atom regardless of the counterion (Table 9). The TBP structure of the anion Ph\textsubscript{3}Sn(N\textsubscript{3})\textsubscript{2}\textsuperscript{−} in the complex \textsuperscript{42c}\textsuperscript{225} is also close to ideal. In contrast, the axial azide groups in the stannates \textsuperscript{42a} and \textsuperscript{42b} are not equivalent (Table 10), showing that one azide group is acting as a weaker ligand than the other\textsuperscript{229}. This effect is clearly due to the hydrogen bonding in which this weaker donor azide group is involved.

The essentially linear geometry of the X−Sn−X or X−Sn−Y fragment and the significant lengthening of the X−Sn and Y−Sn bonds are consistent with the hypervalent nature of the apical bonds. The Sn−C bond lengths (2.11−2.15 Å) are close to those of the corresponding tetrahedral derivatives with the exceptions of compounds \textsuperscript{30h}\textsuperscript{248}, \textsuperscript{31b}\textsuperscript{221} and \textsuperscript{32d}\textsuperscript{221}, in which these distances are 2.212, 2.235 and 2.193 Å, respectively (Table 8).
The structure of the chlorine-cyanide stannate 39b is unusual in that the strongly nucleophilic cyanide would exhibit N-bonded coordination to Sn rather than a C-bonded orientation. 219

In the case of homo-ligand dihalide complexes, Sn–Hal distances lie generally in the range of 2.57–2.69 Å for dichlorides and 2.73–2.79 Å for dibromides, and the relative lengthenings of these bonds are almost equal (11.5 and 11.3%). Analogously, the Sn–N bond lengths in the anion [Ph3Sn(N3)]− of the complexes 42a–c are longer as compared to those in t-Bu3SnN3 (2.103 Å)26 containing a tetrahedral tin atom. It is noteworthy that in the stannate 42c, in which the Sn–N bonds are equal, their values are intermediate between those found for asymmetric bonding in the protonated derivatives 42a,b. An unusually long Sn–F bond length was found259 for Me3SnF2−. However, this value is associated with the Sn–Cl bonds in Me3SnCl2−. 260

### TABLE 8. X-ray data for pentacoordinate anions R3SnHal2−

<table>
<thead>
<tr>
<th>Complex</th>
<th>Sn–Hal (Å)</th>
<th>Sn–C (Å)b</th>
<th>Hal–Sn–Hal (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Me3SnCl2]−[K(18-crown-6)]+ (30d)</td>
<td>2.618</td>
<td>2.110</td>
<td>179.4</td>
<td>219</td>
</tr>
<tr>
<td>[Me3SnCl2]−[(Me3Sn)2NH2]+ (30e)</td>
<td>2.656, 2.662</td>
<td>2.112</td>
<td>175.5</td>
<td>228</td>
</tr>
<tr>
<td>[Me3SnCl2]−[Mo3(η5-C5H5)3S]+ (30f)</td>
<td>2.572, 2.696</td>
<td>2.12</td>
<td>—</td>
<td>249</td>
</tr>
</tbody>
</table>

2[Me3SnCl2]−[Cat]2+ (30g)

[Me3SnCl2]−[((Ph3PAu)2S]2Au)+ (30h) | 2.622 | 2.212 | 178.7 | 248

Bu3SnCl2−[Ph3PCH2Ph] + (31b) | 2.573, 2.689 | 2.235 | 179.4 | 221 |
| Ph3SnCl2−[Me4N]+ (32b) | 2.598 | 2.139 | 177.1 | 250 |
| Ph3SnCl2−[DPAH]+ (32c) | 2.623 | 2.135 | 172.4 | 232 |
| Ph3SnCl2−[Ph3AsCH2COPh]− (32d) | 2.580, 2.601 | 2.193 | 177.5 | 221 |
| Me3SnBr2−[Me3Sn(HMPA)2]+ (41) | 2.776, 2.781 | — | 179.2 | 227 |
| Ph3SnBr2−[Et4N]+ (48) | 2.751, 2.791 | 2.149 | 175.2 | 251 |
| [(p-MeSC6H4)3SnBr2]−[Et4N]+ (49) | 2.731, 2.782 | 2.145 | 175.4 | 251 |

a For comparison: Ph3SnF, TBP, Sn–F, 2.114 Å.156; Ph3SnCl, tetrahedral (T), Sn−Cl, 2.353, 2.374 Å (two independent molecules)165; Ph3SnBr, T, 2.491, 2500 Å (two independent molecules)189; (PhCH2)3SnCl, T, 2.387 Å.164.
b Average value.
c Cat = 1.4-(Me2Sn)2[2,3,5,6-(Me2NC6H4)2]C6.

### TABLE 9. X-ray data for pentacoordinate anions R3SnX2− with ligands containing N or O coordinating atoms

<table>
<thead>
<tr>
<th>Complex</th>
<th>Sn–X (Å)</th>
<th>C–Sn (Å)c</th>
<th>X–Sn–X (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph3Sn(N3)2−[Ph4As]+ (42c)</td>
<td>2.279, 2.282</td>
<td>2.148</td>
<td>178.6</td>
<td>225</td>
</tr>
<tr>
<td>Ph3Sn(NCS)2−[Cat]+ (43a)</td>
<td>2.290</td>
<td>2.126</td>
<td>176.8</td>
<td>230</td>
</tr>
<tr>
<td>Ph3Sn(NCS)2−[Et4N]+ (43b)</td>
<td>2.268</td>
<td>2.134</td>
<td>179.6</td>
<td>231</td>
</tr>
<tr>
<td>Me3Sn(OC6H5Me2-2,6)2−[TAS]+ (33)</td>
<td>2.212, 2.225</td>
<td>2.130</td>
<td>180.0</td>
<td>226</td>
</tr>
<tr>
<td>[(c-C6H11)2Sn(OCOCF3)2]−[DPAH]+ (44a)</td>
<td>2.312</td>
<td>2.135</td>
<td>177.6</td>
<td>232</td>
</tr>
<tr>
<td>Ph3Sn(OCOCF3)2−[Me4N]+ (44b)</td>
<td>2.219, 2.255</td>
<td>2.135</td>
<td>175.1</td>
<td>234</td>
</tr>
<tr>
<td>Ph3Sn(OCOCF3)2−[DPAH]+ (44c)</td>
<td>2.201, 2.252</td>
<td>2.136</td>
<td>178.6</td>
<td>233</td>
</tr>
<tr>
<td>Ph3Sn(C10H8O2)2−[Me4N]+ (46)</td>
<td>2.231</td>
<td>2.123</td>
<td>167.1</td>
<td>236</td>
</tr>
<tr>
<td>Ph3Sn(OONO2)2−[Cat]3+ (50)</td>
<td>2.240, 2.276</td>
<td>2.124</td>
<td>171.8</td>
<td>252</td>
</tr>
</tbody>
</table>

a Average value.
b 2-MeOC6H4NH=CHC6H4OH-2'.
c bis(coumarin-3-carboxylato).
d (Ph2PCH2=CHPPPh2)2Ag.
TABLE 10. X-ray data for pentacoordinate anions $R_3SnXY^-$ with mixed ligands containing essential H-bonding as well as zwitterionic structure

<table>
<thead>
<tr>
<th>Complex</th>
<th>Sn–X (Å)</th>
<th>Sn–Y (Å)</th>
<th>C–Sn (Å)</th>
<th>$\Delta Sn$ (Å)</th>
<th>X–Sn–Y (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ph}_3\text{SnCl(OAr)}]^- [\text{TAS}]^+$ (38)</td>
<td>2.693$^b$</td>
<td>2.102$^c$</td>
<td>2.141$^d$</td>
<td>0.10$^d$</td>
<td>177.1</td>
<td>226</td>
</tr>
<tr>
<td>$[\text{Me}_3\text{Sn(Cl)(CN)}][-\text{K(18-crown-6)}]^+$ (39b)</td>
<td>2.73$^b$</td>
<td>2.654$^e$</td>
<td>2.128$^f$</td>
<td>0.07$^f$</td>
<td>177.3</td>
<td>219</td>
</tr>
<tr>
<td>$[\text{Ph}_3\text{Sn(OOCF}_3\text{)(OCOCF}_2\text{Cl)}]^-$</td>
<td>2.207$^g$</td>
<td>2.294$^h$</td>
<td>2.130$^i$</td>
<td>—</td>
<td>179.9</td>
<td>233</td>
</tr>
<tr>
<td>$[\text{Me}_3\text{SnCl}_2^-][\text{TMPH}]^+$ (51)</td>
<td>2.453$^j$</td>
<td>3.035$^k$</td>
<td>2.122$^l$</td>
<td>0.26$^l$</td>
<td>179.2</td>
<td>223</td>
</tr>
<tr>
<td>$[\text{Ph}_3\text{Sn(N}_3\text{)}_2^-][\text{PipH}_2]^+$ (42a)</td>
<td>2.216</td>
<td>2.396$^m$</td>
<td>2.133$^n$</td>
<td>0.10$^n$</td>
<td>178.4</td>
<td>229</td>
</tr>
<tr>
<td>$[\text{Ph}_3\text{Sn(N}_3\text{)}_2^-][\text{QNH}]^+$ (42b)$^j$</td>
<td>2.226$^j$</td>
<td>2.372$^j$</td>
<td>2.135$^j$</td>
<td>0.05$^j$</td>
<td>177.5</td>
<td>229</td>
</tr>
<tr>
<td>$\text{R}_1\text{OSnPh}_3\text{Cl}$ (69a)$^k$</td>
<td>2.536$^b$</td>
<td>2.301$^c$</td>
<td>2.127$^d$</td>
<td>0.10$^d$</td>
<td>176.9</td>
<td>253</td>
</tr>
<tr>
<td>$\text{R}_2\text{OSnPh}_3\text{NCS}$ (69b)</td>
<td>2.281$^c$</td>
<td>2.229$^e$</td>
<td>2.115$^f$</td>
<td>0.05$^f$</td>
<td>178.0</td>
<td>254</td>
</tr>
<tr>
<td>$2\text{-C}_5\text{H}_4\text{NHCOOSnPh}_3\text{Cl}$ (69c)</td>
<td>2.515$^b$</td>
<td>2.347$^c$</td>
<td>2.135$^d$</td>
<td>0.13$^d$</td>
<td>172.8</td>
<td>255</td>
</tr>
<tr>
<td>$2\text{-C}_5\text{H}_4\text{NHCOOSnPh}_3\text{NCS}$ (69d)</td>
<td>2.285$^c$</td>
<td>2.221$^e$</td>
<td>2.115$^f$</td>
<td>0.01$^f$</td>
<td>175.9</td>
<td>256</td>
</tr>
<tr>
<td>$\text{Bn}_3\text{Sn(Cl)(OCOCF}_3\text{CH}_2\text{PPh}_3\text{Cl}$ (69e)</td>
<td>2.591$^b$</td>
<td>2.253$^c$</td>
<td>2.143$^c$</td>
<td>0.02$^c$</td>
<td>173.1</td>
<td>257</td>
</tr>
<tr>
<td>$\text{r-Bu}_3\text{Sn(CH}_2\text{PPh}_3\text{)}_2\text{F}_2\cdot\text{BF}_3$ (69f)</td>
<td>2.782$^b$</td>
<td>2.027$^c$</td>
<td>—</td>
<td>0.35$^c$</td>
<td>170.1</td>
<td>258</td>
</tr>
<tr>
<td>$\text{r-Bu}_3\text{SnCl(=CH}_2\text{PPh}_3\text{)}_2\cdot\text{BF}_3$ (69g)</td>
<td>2.853$^b$</td>
<td>1.972$^c$</td>
<td>—</td>
<td>0.32$^c$</td>
<td>176.6</td>
<td>258</td>
</tr>
</tbody>
</table>

$^a$Average value.
$^b$Sn–Cl.
$^c$Sn–O.
$^d$Toward the O atom.
$^e$Sn–N.
$^f$Toward the N atom.
$^g$Sn–O(COCF$_3$).
$^h$Sn–O(OCOF$_2$Cl).
$^i$Toward the ligand without an additional coordination bond.
$^j$Two anions in unit.
$^k$R$_1$OH = 2-(3′-methylphenyliminomethyl)phenol-O.
$^l$R$_2$OH = 1-(4′-methylphenyliminomethyl)-2-naphthol-O.

The Sn–O distances in the homo-ligand oxystannates 33, 44a–c and 50 (Table 9) increase in the order of ligands OAr < OCOCF$_3$ < ONO$_2$, which is parallel to the decrease in their basicity and donor ability.

The mixed-ligand stannates (Table 10) are especially of interest in the context of the mutual influence of the apical ligands in the hypervalency theory, first developed by Musher. In these compounds the bond lengths with apical ligands differ considerably from those of the corresponding homo-ligand stannate complexes. Whereas in homo-ligand stannates (Table 8) the lengths of the Sn–X bonds are generally nearly equal, in the oxy-chloro stannate 30c, for example, the Sn–O bond is 5% shorter than in the dioxy compound 8 and the Sn–Cl bond is ca 4% longer than in triphenyltin complexes 32b–d. Thus, the tin atom is located 0.10 Å out of the plane formed by the three carbon atoms ($\Delta Sn$) in the direction of the aryloxy oxygen. Hence, the aryloxy anion is a strong donor with respect to the tin as compared with chloride ion. Analogously, the latter is a weak donor in comparison with cyanide ion ($\Delta Sn$ 0.07 Å). These X-ray data are in agreement with the solution behavior of the mixed-ligand complexes 36–38, where chloride ion (but not phenoxy ion) is split of preferentially, as well as with the fact that chlorine in Me$_3$SnCl can be displaced by the aryloxy group to form Me$_3$SnOAr but the oxygen ligand in Me$_3$SnOAr is not displaced by chloride under these conditions.
The difference in Sn–X bond distances in some homo-ligand complexes, in particular 42a,b and [Me₃SnCl₂][TMPH] (51), which are also included in Table 10, reflects the influence of hydrogen bonding between one of the ligands and a cation. In these cases, a hydrogen-bonded ligand acts as a weaker donor, and the tin atom is displaced from the equatorial plane to the direction of the ligand without hydrogen bond 229. In this connection, of particular interest is the stannate 51, in which the anion is distorted halfway between idealized four- and five-coordinate geometries (ΔSn 0.26 Å) 223.

The variation in the parameter ΔSn and the mutual changes in the axial bond lengths discussed above can be referred to in connection with a model for the S_N 2 reaction coordinate for substitution at tin. Following a Burgi–Dunitz-type analysis of crystal structures 261–263 for chloro stannate complexes, in which only the second axial ligand is changed, a series of the hydrogen-bonded stannates represents an early step in the reaction (Scheme 2). The case of X = Cl represents a symmetrical, near-TBP midway state for the reaction. For the oxy-chloro and cyano-chloro stannates the progress of the reaction is more advanced: the corresponding nucleophiles have essentially displaced the chlorine, which remains weakly coordinated, with the pyramidal inversion of the tin center.

\[
\text{X} \quad \text{Sn} \quad \text{Cl} \quad \text{X} \quad \text{Sn} \quad \text{Cl} \quad \text{X} \quad \text{Sn} \\
\text{X = Cl(...H), F, Cl} \quad \text{X = Cl} \quad \text{X = OAr, CN} \\
(42a,b, 51) \quad (30d,g,h, 32b,c) \quad (38, 39b)
\]

SCHEME 2. Simulated S_N 2 reaction coordinate: the variation of ΔSn as a function of X in chloro stannates

A qualitative MO description of the homo- and mixed-stannate anions in terms of frontier orbitals supported by the structures of the known stannates is given by Suzuki and coworkers 226. According to the hypervalency theory 19,22,264–266, pentacoordinate triorganostannates bearing two electronegative substituents have a hypervalent nature. The central tin atom has three sp² orbitals forming the equatorial bonds and a p orbital. The latter is available for creating the apical bonds with three-center, four-electron configurations and, because the HOMO is derived from a nonbonding MO, the electronegative groups are utilized to form such bonds. This approach is particularly compatible with the observation of a pronounced effect of the two axial ligands on each other and the overall stability of the hypervalent complexes.

c. NMR spectroscopy. NMR data reveal the hypervalent nature of the homo- and mixed triorganostannates with TBP structures 219,266,267. The 119Sn chemical shifts and the one-bond carbon–tin coupling constants, 1^J(119Sn−13C), are summarized in Table 11. Changes in the coordination number at tin have a dramatic effect on the shielding and a wide range of 119Sn values are observed from the relatively deshielded Me₃SnCl (δ¹¹⁹Sn = 154.3 ppm, c-C₆H₁₂ 271), Ph₃SnCl (δ¹¹⁹Sn = −48 ppm, CDCl₃ 272) or (n-Bu)₃SnOPh (δ¹¹⁹Sn = 105 ppm, pure 273) to the more shielded anionic species.

The NMR data (δ¹¹⁹Sn and 1^J(¹¹⁹Sn−¹³C)) for stannates 30, 33, 36, 39, 40 219,226 suggest that exchange phenomena occur in solution according to equations 4 and 5. The value of δ¹¹⁹Sn for these equilibria depends on the nature of the equatorial organic groups and the apical heteroatom substituents, the cation M⁺ and the temperature. The influence of hydrogen bonding in solution is reflected in a markedly downfield shift
**TABLE 11.** Selected $^{119}$Sn NMR data for pentacoordinate organotin anions at ambient temperature$^{a}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta^{119}$Sn (ppm)</th>
<th>$^{1}J^{(119}$Sn−$^{13}$C) (Hz))</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Me$_3$SnCl$_2$]$^-$[TAS]$^+$ (30a)</td>
<td>(559)</td>
<td>CD$_2$CN</td>
<td>226</td>
<td></td>
</tr>
<tr>
<td>[Me$_3$SnCl$_2$]$^-$[Bu$_4$N]$^+$ (30c)</td>
<td>-22.1 (522)</td>
<td>CDCl$_3$</td>
<td>219</td>
<td></td>
</tr>
<tr>
<td>[Me$_3$SnCl$_2$]$^-$[K(18-crown-6)]$^+$ (30d)</td>
<td>-6.7 (507)</td>
<td>CDCl$_3$</td>
<td>219</td>
<td></td>
</tr>
<tr>
<td>[Me$_3$Sn(OAr)$_2$]$^-$[TAS]$^+$ (33)</td>
<td>(606)</td>
<td>CD$_2$CN</td>
<td>226</td>
<td></td>
</tr>
<tr>
<td>[Me$_3$SnCl(OAr)]$^-$[TAS]$^+$ (36)</td>
<td>(572)</td>
<td>CD$_2$CN</td>
<td>226</td>
<td></td>
</tr>
<tr>
<td>[Me$_3$SnCl(CN)]$^-$[Et$_4$N]$^+$ (39a)</td>
<td>-149.0 (509)</td>
<td>CD$_3$CN</td>
<td>219</td>
<td></td>
</tr>
<tr>
<td>[Me$_3$SnCl(CN)]$^-$[K(18-crown-6)]$^+$ (39b)</td>
<td>-166.9 (538)</td>
<td>CDCl$_3$</td>
<td>219</td>
<td></td>
</tr>
<tr>
<td>[Ph$_3$SnCl(F)]$^-$[K(18-crown-6)]$^+$ (40)</td>
<td>6.09 (508)</td>
<td>CDCl$_3$</td>
<td>219</td>
<td></td>
</tr>
<tr>
<td>[Ph$_3$SnF$_2$]$^-$[Bu$_4$N]$^+$ (47)</td>
<td>-345.9, -160.9 (2010)$^b$</td>
<td>CD$_2$Cl$_2$</td>
<td>218</td>
<td></td>
</tr>
<tr>
<td>[Ph$_3$SnCl$_2$]$^-$[Et$_4$N]$^+$</td>
<td>-253.7</td>
<td>CDCl$_3$</td>
<td>218</td>
<td></td>
</tr>
<tr>
<td>[Ph$_3$SnBr$_3$]$^-$[Bu$_4$N]$^+$</td>
<td>-233</td>
<td>CD$_3$CN</td>
<td>205</td>
<td></td>
</tr>
<tr>
<td>[Ph$_3$SnFCl]$^-$[Et$_4$N]$^+$</td>
<td>-293, -159 (1916)$^b$</td>
<td>CDCl$_3$</td>
<td>218</td>
<td></td>
</tr>
<tr>
<td>[Me$_3$SnCl$_2$]$^-$[TMPH]$^+$ (51)</td>
<td>153.7 (400)</td>
<td>CDCl$_3$</td>
<td>223</td>
<td></td>
</tr>
<tr>
<td>[(Ph$_2$SN)$_2$CH$_2$F]$^-$[Bu$_4$N]$^+$</td>
<td>-184.8, -172.1 (2178),$^b$</td>
<td>CH$_2$Cl$_2$</td>
<td>238</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-97.4 (879)$^d$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[ClSn(CH$_2$)$_6$]$_3$SnCl.F$^-$[Bu$_4$N]$^+$ (52a)</td>
<td>-6.5 (1100)</td>
<td>CDCl$_3$</td>
<td>213</td>
<td></td>
</tr>
<tr>
<td>[(Ph$_2$Sn(CH$_2$)$_2$.Y$^-$)[(Ph$_3$P)$_2$N]$^+$</td>
<td>-128.3 (619)</td>
<td>CDCl$_3$</td>
<td>269</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(52d, X = Y = Cl)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-138.3, -155.4 (1912)$^b$</td>
<td>CD$_2$Cl$_2$</td>
<td>215</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(52k, X = Y = F)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-126.8 (1172)$^d$</td>
<td>CD$_2$Cl$_2$</td>
<td>215</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-100.8, -137.1 (1108)$^d$</td>
<td>CD$_2$Cl$_2$</td>
<td>215</td>
<td></td>
</tr>
<tr>
<td>[ClSn[(CH$_2$)$_3$]$_3$SnCl]$^-$[Ph$_3$PCH$_2$Ph]$^+$ (52l)</td>
<td>27$^f$</td>
<td>CDCl$_3$</td>
<td>213</td>
<td></td>
</tr>
<tr>
<td>[(Ph$_2$FSn(CH$_2$)$_2$.SnPh.F$^-$[Bu$_4$N]$^+$ (54b)</td>
<td>-62.9</td>
<td>CD$_2$Cl$_2$</td>
<td>214</td>
<td></td>
</tr>
<tr>
<td>[Ph$_2$SnF$_3$]$^-$[Bu$_4$N]$^+$</td>
<td>-402 (2310, 2250)$^e$</td>
<td>CH$_2$Cl$_2$</td>
<td>237</td>
<td></td>
</tr>
<tr>
<td>[Ph$_2$SnCl$_3$]$^-$[Ph$_4$PCH$_2$]$^+$</td>
<td>-258</td>
<td>CH$_2$Cl$_2$</td>
<td>205</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-250</td>
<td>CH$_2$Cl$_2$</td>
<td>237</td>
<td></td>
</tr>
<tr>
<td>[Me$_2$SnBr$_3$]$^-$[Et$_4$N]$^+$</td>
<td>-118.8</td>
<td>CDCl$_3$</td>
<td>270</td>
<td></td>
</tr>
<tr>
<td>[Me$_2$SnBr$_3$]$^-$[Bu$_4$N]$^+$</td>
<td>-148</td>
<td>CH$_2$Cl$_2$</td>
<td>205</td>
<td></td>
</tr>
<tr>
<td>[Ph$_3$SnBr$_3$]$^-$[Bu$_4$N]$^+$</td>
<td>-293</td>
<td>CH$_2$Cl$_2$</td>
<td>205</td>
<td></td>
</tr>
</tbody>
</table>

$^{a}$For comparison, $\delta^{119}$Sn values for some 4-coordinated tin compounds ($-100^\circ$C, CH$_2$Cl$_2$) are$^{223}$:

(Ph$_2$ClSn)$_2$CH$_2$, 21.0 ppm; (Ph$_2$BrSn)$_2$CH$_2$, 3.2; (Ph$_2$ClSn)(CH$_2$)$_2$, 1.8; (Ph$_2$Sn)(CH$_2$)$_2$, 40.4;

(Ph$_2$ClSn)($CH_2$)$_3$, 10.3; Me$_3$SnCl, 165.7 ppm $^{1}J^{(119}$Sn−$^{13}$C) = 397 Hz, 30$^\circ$C, CDCl$_3$)$^{233}$;

Me$_2$SO$_4$CH$_3$, 2.6. $^{1}J^{(119}$Sn−$^{13}$C) = 421 Hz (30$^\circ$C, CD$_3$CN)$^{226}$.

$^{b}$$\delta^{19}$F$_{Fac}$($^{1}J^{(119}$Sn−$^{19}$F)$_{Fac}$).

$^{c}$At $-80^\circ$C.

$^{d}$$\delta^{19}$F$_{Fbr}$($^{1}J^{(119}$Sn−$^{19}$F)$_{Fbr}$).

$^{e}$At $-70^\circ$C.

$^{f}$Average value.

$^{g}$$J^{(119}$Sn−$^{13}$C).

$\delta^{119}$Sn = 153.7 ppm for 51$^{223}$ as compared to the other general pentacoordinate stannanes (Table 11). The tin chemical shifts for 51 are strongly temperature-dependent. At the low-temperature limit the structure of the tin anion could be described as distorted halfway between idealized four- and five-coordinate geometries (Scheme 2).

Solid state CP/MAS $^{119}$Sn NMR spectra are fully in accord with these changes in the anions. The $^{119}$Sn resonance shifts upfield in the solid state versus that in solution by ca
50 ppm, e.g. from $-6.5$ to $-50$ ppm for $[\text{ClSn}((\text{CH}_2)_6)_3\text{SnCl} \cdot \text{F}] [n\text{-Bu}_4\text{N}]$ ($52a$) and from $-149.0$ to $-204.4$ ppm for $[\text{Me}_3\text{SnCl}((\text{CN})][\text{Et}_4\text{N}]$ ($39a$).

$^{19}$F and $^{119}$Sn variable-temperature NMR studies of $[\text{Bu}_3\text{Sn}_2][\text{Bu}_4\text{N}]$ show the presence of two distinct tributyltin species in equilibrium, the $\text{trans-Bu}_3\text{SnF}_2^{-}$ and $\text{trans-}([\text{Bu}_3\text{SnF}_2]_2\text{F}^{-}$ anions.

As shown by $^{19}$F and $^{119}$Sn NMR spectroscopies, fluorine exchange in the $\text{Ph}_3\text{SnX} - \text{Ph}_3\text{SnFX}^{-}$ system ($X = \text{F, Cl}$) occurs between four- and five-coordinated tin complexes, presumably via fluorine- and chlorine-bridged intermediates, while phenyl–tin bonds were not cleaved during any of the ligand-exchange processes. The proposed mechanism (equation 6), including bridged intermediates of the type $53$, is in agreement with the fact that purified $\text{Ph}_3\text{SnF}_2^{-}$, containing no $\text{Ph}_3\text{SnF}$, does not undergo fluorine exchange. This result eliminates simple ionization of $\text{Ph}_3\text{SnF}_2^{-}$ and the loss of $\text{F}^{-}$ as a mechanism for the fluorine exchange.

\[
\begin{align*}
\text{Ph} & \quad \text{Sn} \quad X + \quad \left[ \begin{array}{c}
\text{Ph} \\
\text{Sn} \\
\text{X} \\
\text{Ph}
\end{array} \right] \\
\text{Ph} & \quad \text{Sn} \quad \text{F} \quad \text{Ph} \\
\text{X} & \quad \text{Sn} \quad \text{Ph} \quad \text{Ph}
\end{align*}
\]

$X = \text{F, Cl}$

In connection with equation 6, the fact that the five-coordinated 1 : 1 adducts $\text{Ph}_3\text{SnF} \cdot \text{HMPA}$, $\text{Ph}_3\text{SnF} \cdot \text{DMSO}$ and $\text{Ph}_3\text{SnFCl}^{-}$ undergo rapid fluorine exchange and disappearance of $\text{Sn} - \text{F}$ coupling suggests that partial dissociation of adducts to give the four-coordinated tin species is taking place. Moreover, an addition of a large excess of HMPA, DMSO or $\text{Cl}^{-}$ to the corresponding adducts stops the fluorine exchange in these adducts owing to a decrease in the concentration of the four-coordinated species by the action of the excess Lewis base.

The results are relevant to the mechanism of the isomerization and racemization of triorganotin halides, which may include the selective cleavage of the bridging halogen bonds in unsymmetrical intermediates $\text{X} - \text{SnR}_3 - \text{Y} - \text{SnR}_3 - \text{D}$ ($\text{D} = \text{donor}$) like $53$.

### 3. Bridged triorganostannates

Recently, the complexation ability of organotin compounds containing two or more tin atoms bridged through carbon as multifunctional Lewis acids toward halide ion in host–guest chemistry were investigated intensively. Commonly, the reaction of bis(halodiphenylstannyl)alkanes ($\text{Ph}_2\text{XSn}((\text{CH}_2)_n)(\text{CH}_2)_n(X = \text{F, Cl, Br, I}; n = 1 - 3)$ and halide ions $Y^{-}$ ($Y = \text{F, Cl, Br}$) as the corresponding ammonium salts in dichloromethane solution led to anionic 1 : 1 adducts $[\text{Ph}_2\text{XSn}((\text{CH}_2)_n) \cdot Y]^{-}$ ($52b$, $n = 1, X = Y$); $52c$, $n = 1, X \neq Y (Y = \text{F})$; $52d$, $n = 2$; $52e$, $n = 3$) containing bridged halogen and two pentacoordinated tin atoms. $\text{Me}_2\text{ClSn}((\text{CMe}_2)_2 \cdot \text{F}^{-}$ ($52f$) was prepared in a similar way. The bis(halodiphenylstannyl)alkanes always preferentially chelate fluoride ion over chloride or bromide, and in the case of $X \neq Y$ ($Y = \text{F}$), fluoride ion is bridged in the final adducts. Methylene-bridged 1 : 1 adducts $52b$ ($X = \text{Y} = \text{F, Cl, Br}$) and $52e$ ($X = \text{Cl, Br}; Y = \text{F}$) eventually react with the additional fluoride ion (but not chloride or bromide ion) to give the 1 : 2 tetrafluoro adduct $[\text{Ph}_2\text{F}_2\text{Sn}((\text{CMe}_2)_2]^{-}$ ($52g$) (Scheme 3). Ethylene-bridged 1 : 1 adducts $52d$ ($X = \text{Y}$) appear to be particularly stable and do not react with halide ions (only the bridged chlorine is exchanged by fluorine). In contrast, for propylene-bridged adducts $52e$ ($X = \text{Y} = \text{F, Cl}$) the exchange occurs as well as an
SCHEME 3. Principal reaction scheme for the formation of methylene-bridged adducts
interaction with both fluoride and chloride ion resulting in the formation of 1 : 2 adducts 52h. All the 1 : 2 adducts include two pentacoordinate tin atoms.

![Diagram](image)

The principal products of the reaction between bis(halodiphenylstannyl)alkanes and halide ions as well as some intermediate species were identified by \(^{119}\text{Sn}\) and \(^{19}\text{F}\) spectroscopies. The ammonium salts \([^\text{[(Ph}_{2}\text{XSn)}_{2}\text{CH}_2\cdot F\text{][Et}_4\text{N}] (52b, X = F; 52c, X = Cl, Br, I, [\text{[(Ph}_{2}\text{XSnCH}_2)]_{2}\cdot F\text{][Et}_4\text{N}] (52d, X = F, Cl) as well as [\text{[(Me}_{2}\text{ClSn)}_{2}\text{CMe}_2\cdot F\text{][Et}_4\text{N}] (52f) were isolated. The salt \([^\text{[(Ph}_{2}\text{ClSnCH}_2)]_{2}\cdot Cl\text{][}\text{(Ph}_3\text{P)}_{2}\text{N}] (52d, X = Y = Cl) was also isolated.\text{^269}]

More recently, \(o\)-bis(haloorganostannyl)benzenes were found to be powerful bidentate Lewis acids toward halide ions\textsuperscript{215}. Treatment of \(o\)-C\(_6\)H\(_4\)(SnMe\(_2\)X)\(_2\), \(X = \text{Cl, F} (52i\text{ and } 52j)\) with 1 molar equivalent of the halide ion afforded the corresponding anionic 1 : 1 complexes 52k, \(X = Y = \text{F, M = Et}_4\text{N, K \cdot 18-crown-6; X = Y = Cl, M = (Ph}_3\text{P)}_{2}\text{N; X = Cl, Y = F, M = Et}_4\text{, K \cdot dibenzo-18-crown-6} (\text{equation 7).}

![Diagram](image)

No dianionic 1 : 2 adducts were observed even with excess of halide ions. As in the case of the bis(chlorodiphenylstannyl)alkanes\textsuperscript{238}, the affinity of 52i to fluoride is greater than that toward chloride. This suggests, in particular, \textit{in situ} formation of the fluoride complexes \([o\text{-C}_6\text{H}_4(\text{SnMe}_2\text{Cl})\cdot F][\text{M}] (M = (\text{Ph}_3\text{P)}_{2}\text{N, Bu}_4\text{N}) by the reaction of the chloride complex 52k, X = Y = Cl, M = (Ph\(_3\text{P)}_{2}\text{N with KF in CH}_2\text{Cl}_2 as well as by the reaction of 52i with [Ph\(_3\text{SnF}_2]^-\text{[Bu}_4\text{N]}^+ (47) in the same solvent.
These results are in agreement with the data\textsuperscript{213} that the anion in the complex \{ClSn[(CH\textsubscript{2})\textsubscript{8}SnCl\textsubscript{2}][Ph\textsubscript{3}PCH\textsubscript{2}P\textsubscript{3}] (52i)\} is a stannate-stannane species wherein one of the Lewis acidic tin atoms binds the chloride strongly, and the other interacts weakly with the chloride. At the same time, the anion in the complex \{ClSn[(CH\textsubscript{2})\textsubscript{6}SnCl·F][Bu\textsubscript{4}N] (52a)\} is a bis-hemistannate species wherein one of the Lewis acidic tin atoms binds simultaneously the guest fluoride.

Information on the related complexation ability of organotin chlorides was provided by the \textsuperscript{119}Sn NMR investigations of equimolar amounts mixtures of [Ph\textsubscript{3}P=N=NPh\textsubscript{3}]\textsuperscript{+}Cl\textsuperscript{−} and two or three corresponding organotin compounds\textsuperscript{215}. The following qualitative sequence for the affinity of organotin chlorides as hosts toward chloride ions was obtained: Ph\textsubscript{3}SnCl ≪ Ph\textsubscript{2}SnCl\textsubscript{2} ≪ (Ph\textsubscript{2}ClSnCH\textsubscript{2})\textsubscript{2} ≈ (Ph\textsubscript{2}ClSn)\textsubscript{2}CH\textsubscript{2} ≈ o-C\textsubscript{6}H\textsubscript{4}(SnMe\textsubscript{2}Cl)\textsubscript{2} (52i) ≪ (PhCl\textsubscript{2}Sn)\textsubscript{2}CH\textsubscript{2} ≈ o-C\textsubscript{6}H\textsubscript{4}(SnMeCl\textsubscript{2})\textsubscript{2}. The sequence shows that the bidentate ditin species are more efficient in comparison with the monotin derivatives and that the stability of the adducts formed is apparently affected not only by the Lewis acidity of the two tin centers but is also assisted by formation of particularly stable five-membered chelate rings.

Another case of bridging reported recently is in the series of anionic adducts 54–56 with methylene-bridged tri- and tetra-tin framework\textsuperscript{214}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Chemical structures of the anionic adducts 54–56.}
\end{figure}

They were synthesized by the reaction of halides with the corresponding tri- or tetranuclear tin compounds, (XPh\textsubscript{2}SnCH\textsubscript{2})\textsubscript{2}SnPX and (XPh\textsubscript{2}SnCH\textsubscript{2}SnPhX)\textsubscript{2}CH\textsubscript{2} (X = F, Cl). The structure of 54c was proved by X-ray crystallography, and variable-temperature \textsuperscript{119}Sn and \textsuperscript{19}F NMR studies indicate that the structure observed for the anion in 54c in the solid state is retained in solution. Analogously, NMR spectral data suggest the structure of the trinuclear adducts 54a, 54b, 55 and the tetranuclear tin chloride complex 56. In contrast, \textsuperscript{119}Sn and \textsuperscript{19}F NMR data show that the tetranuclear tin fluoride reacts with fluoride ion to give a stable 1 : 2 adduct 57. Its structure in solution was postulated\textsuperscript{214} on the basis that more electronegative fluorine atoms would occupy axial positions in TBP geometries at five-coordinate tin atoms.
TABLE 12. Selected structural parameters for bridged pentacoordinate anionic stannates\(^a\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sn−X(_{br}) (b) (Å)</th>
<th>Sn−Y(_t) (c) (Å)</th>
<th>X−Sn−Y (d) (deg)</th>
<th>ΔSn(_{d}^d) (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(Ph(_2)FSn)(_2)CH(_2) · F(_b)](^−) [Et(_4)N](^+) ((57))</td>
<td>2.249</td>
<td>1.995</td>
<td>176.3</td>
<td>0.22</td>
<td>238</td>
</tr>
<tr>
<td>[(Me(_2)ClSn)(_2)CM(_2) · F(_b)](^−) [Et(_4)N](^+)</td>
<td>2.212</td>
<td>2.572</td>
<td>175.2</td>
<td>0.17</td>
<td>277</td>
</tr>
<tr>
<td>[(Ph(_2)BrSn)(_2)CH(_2) · F(_b)](^−) [Et(_4)N](^+)</td>
<td>2.212</td>
<td>2.593</td>
<td>174.8</td>
<td>0.15</td>
<td>277</td>
</tr>
<tr>
<td>[(Ph(_2)Sn)(_2)CH(_2) · F(_b)](^−) [Et(_4)N](^+)</td>
<td>2.248</td>
<td>2.856</td>
<td>169.6</td>
<td>0.22</td>
<td>238</td>
</tr>
<tr>
<td>[(Ph(_2)ClSnCH(_2)](_2) · F(_b)](^−) [Et(_4)N](^+)</td>
<td>2.197</td>
<td>2.504</td>
<td>174.5</td>
<td>0.12</td>
<td>238</td>
</tr>
<tr>
<td>[(Ph(_2)ClSnCH(_2)](_2) · Cl(_b)](^−) [(Ph(_3)P)(_2)](^+)</td>
<td>2.829</td>
<td>2.475</td>
<td>175.1</td>
<td>—</td>
<td>269</td>
</tr>
<tr>
<td>[(o-C(_6)H(_4)(Me(_2)ClSn)(_2) · Cl(_b)](^−) [(Ph(_3)P)(_2)](^+)</td>
<td>2.699</td>
<td>2.534</td>
<td>172.6</td>
<td>0.12</td>
<td>269</td>
</tr>
<tr>
<td>[ClSn((\text{CH}_2)_6)](_3)SnCl · F(_b)](^−) [Bu(_4)N](^+)</td>
<td>2.128</td>
<td>2.661</td>
<td>173.5</td>
<td>0.06</td>
<td>213</td>
</tr>
<tr>
<td>[ClSn((\text{CH}_2)_8)](_3)SnCl · F(_b)](^−) [Bu(_4)N](^+)</td>
<td>2.126</td>
<td>2.568</td>
<td>174.4</td>
<td>0.05</td>
<td>213</td>
</tr>
<tr>
<td>[(Ph(_2)FSnCH(_2)](_2)SnPhF · F(<em>b)](^−) [Ph(<em>3)PCH(<em>2)Ph] (\text{K} \cdot \text{C}</em>{20}\text{H}</em>{24}\text{O}</em>{6})</td>
<td>2.342</td>
<td>2.020</td>
<td>175.7</td>
<td>0.23</td>
<td>214</td>
</tr>
<tr>
<td>[K · C(<em>{12})H(<em>24)O(<em>6)] (\text{K} \cdot \text{C}</em>{20}\text{H}</em>{24}\text{O}</em>{6})</td>
<td>2.154</td>
<td>2.154</td>
<td>177.1</td>
<td>0.00</td>
<td>213</td>
</tr>
</tbody>
</table>

\(^a\)For two tin atoms.
\(^b\)Bridged halogen.
\(^c\)Terminal halogen atom.
\(^d\)Toward the terminal halogen atom.
\(^e\)Toward the bridged halogen atom.
\(^f\)For the terminal tin atom.
\(^g\)For the internal tin atom.

Some of the crystallographic data for anions in bridged di- and tri-tin complexes \(52\) \(52b\), \(52c\), \(52d\), \(52f\), \(52k\), \(52l\) and \(54\) are collected in Table 12. With the possible exception of the anion \{ClSn[(CH\(_2\)_8]_3SnCl\(_2\)\}\(^−\) in salt \(52\) \(213\), all anions have distorted TBP geometries around the tin atoms with the equatorial plane being defined by the carbon atoms in each case. The Sn−Hal\(_{br}\) and Sn(2)−Hal\(_{br}\) (br = bridge) distances are generally not equal, resulting in the formation of a skewed rombus for the anions with a central four-membered ring. Each of the Sn atoms in ditin complexes lies out of the trigonal plane defined by the three carbon atoms.
in the directions of the terminal halogen atom. Thus, the latter is a stronger donor atom as compared with a bridged halogen. The structures of the anions discussed represent an early step in the SN2 reaction coordinate for substitution of a halogen at tin by added halide ion (Scheme 2).

The availability of several closely related structures enables systematic comparison of their derived interatomic parameters. In the case of the anions 52b, X = F, 52c, X = Br, I and 52f comprising a central four-membered ring, the distortion of the axial Fbr–Sn–Hal angles increases in the sequence F ⩽ Cl < Br < I. The average differences between the Sn–Hal(terminal) bond length and the ‘standard’ value determined for tetrahedral derivatives follow the sequence F ≪ Br ≈ I < Cl. Consequently, in the case of terminal F atoms, the Sn–Fbr(terminal) distance is the shortest in accordance with the high affinity of fluoride to tin as compared to the other halides. Moreover, in the anion of the complex 52d, X = Cl, Y = F with less strained central five-membered ring, the Sn–Fbr distance is shorter than that in the anions containing four-membered rings, and the fluorine bridge is symmetrical.

In contrast to the anion of the complex 52d, X = Cl2, in the analogous trichloride anions of complexes 52k, X = Y = Cl, M = (Ph3P)2N215 and 52d (X = Y = Cl)269 the Sn(1)ClSn(2) bridge is slightly asymmetric. Consequently, the Sn(1)–Clbr and Sn(2)–Clbr distances are not equal (Table 12). In comparison with the latter compounds, the anion of the complex 52k, X = Cl, Y = F, M = K · dibenzo-18-crown-6215 shows a greater asymmetry due to the interaction between K+ and one of the terminal chlorine atoms.

A peculiarity of the anion structure in the tritin complex 54c214 is that the central tin atom does not deviate from the equatorial plane defined by the carbon atoms. The Sn(central)–Fbr–Sn(terminal) fragment is more asymmetrical than in the related bridged fragment in 52b, X = F.

Solid state CP/MAS 119Sn NMR spectra are in good agreement with the molecular structures of bridged stannates discussed above. In particular, the spectrum of the F-bridged complex 52a comprises a doublet centered at δ = −50 ppm and F coupling constant of 1120 Hz, while for the stannane-stannate complex 52l, the upfield signal is assigned to the stannate tin (−24 ppm) and the downfield signal (+128 ppm) to the stannane tin213. Variable-temperature 119Sn and 19F NMR spectra of the trifluorides [(Ph2FSn)2(CH2)n · F]−Bu4N+ (n = 1–3) indicate an intramolecular exchange of the terminal and chelate fluorine atoms resulting from rupture of Sn–F (bridged bond) and rotation about a Sn–C bond in the methylene bridge (as shown for n = 1 in equation 8)238.

\[
\begin{align*}
\text{Ph} & \qquad \text{Sn} & \qquad \text{Sn} & \qquad \text{Ph} \\
\text{F} & \quad \text{F} & \quad \text{F} & \quad \text{F} \\
\text{Ph} & \quad \text{Ph} & \quad \text{Ph} & \quad \text{Ph}
\end{align*}
\]

The energy barrier for the endocyclic Sn–C bond rotation is higher for the trifluoride with n = 2 than for the anion with n = 1, indicating that the five-membered SnFSnCC ring is more stable than the four-membered SnFSnC ring. These results correlate well with earlier data on exchange processes in complexes 52l and 52a, for which the activation energies are 5.3 and 2.9 kcal mol−1, respectively213.

4. Diorganostannates

The interaction of diorganotin dihalides with halide ions (usually as the ammonium or potassium salts) can lead to the formation (equation 9; either X = Y or Y ≠ X) of
either trihalodiorganostannate or tetrahalodiorganostannate salts. The structure of the complexes isolated depends on the ratio of reagents, the nature of the halide, the cation, the ligands at tin and the solvent.

\[
\begin{align*}
R_2SnX_2 + Y^- & \rightarrow R_2SnX_2Y^- \quad (58a) \ R = Me \\
R_2SnX_2 + 2Y^- & \rightarrow R_2SnX_2Y_2^{2-} \quad (59a) \ R = Me
\end{align*}
\]

The trend for the formation of the monoanions increases from the lighter halogens to the heavier halogens. Thus, the reaction of an aqueous solution of Me_2SnF_2 with NH_4F in a 1 : 2 molar ratio gives both [Me_2SnF_3][NH_4] and [Me_2SnF_4][NH_4]^2, while the same reaction in a 1 : 3 molar ratio yields only the latter. However, the reaction between Me_2SnBr_2 and Alk_4NBr yielding the monoanionic complexes [Me_2SnBr_3][Alk_4N] (58a, Alk = Me, Et) is independent of molar ratio in water (58a, Alk = Et; 1 : 1 or 1 : 2 molar ratio of reagents) and in ethanol (58a, Alk = Et; 1 : 1). The reaction of Me_2SnBr_2 with Et_4NBr in CHCl_3/hexane mixture, in 1 : 2 molar ratio, unlike the above reaction in water, gives dianionic complex [Me_2SnBr_4][Et_4N]^2 (59a), which is independent of molar ratio in water (58a, Alk = Et) and therefore low solvation enthalpies would favour the formation of 59a. Consequently, when the reaction is performed in a highly solvating solvent such as water, pentacoordinate complex 58a, Alk = Et crystallizes. However, in solvents with a lower solvating capacity like the CHCl_3/hexane mixture, hexacoordinate complex 59a is formed.

Earlier attempts to isolate the anionic iodide complexes Me_2SnI_3^- and Me_2SnI_4^- had failed. Moreover, it was recently shown that the previously reported [Me_2SnI_4][Bu_4N]^2 is actually a 1 : 1 mixture of [Bu_4N] and [Me_2SnI_3][Bu_4N]. The pure salts [R_2SnI_3][Bu_4N] (R = Me, Ph) were obtained by a stoichiometric reaction of R_2SnI_2 with Bu_4NI in CH_2Cl_2 in the absence of light. A TBP arrangement for the R_2SnI_3^- anions was proved by IR, Raman and ^119Sn Mössbauer spectroscopies and by X-ray powder diffraction data.

Like stannates R_2SnX_2^- discussed above, diorganotrihalostannates R_2SnX_3^- can be obtained by the interaction of the corresponding organotin halides with neutral donors. Hence the reaction of Ph_2SnCl_2 with 8-methoxyquinoline (L) in cyclohexane gives the pentacoordinate [Ph_2SnCl_3][LH] (60) and the hexacoordinate tin complex [Ph_2SnCl_4][LH]^2 (61) as well as dimeric distannoxane [Ph_2SnCl_2]_2O_2. The latter is a product of a partial hydrolysis of Ph_2SnCl_2 due to the presence of water in the solvent. The anion Ph_2SnCl_3^- of 60 disproportionated into Ph_2SnCl_2 and [Ph_2SnCl_4]^2 upon heating in chloroform. Consequently, the formation of the latter is due to the disproportionation reaction (equation 10) rather than to addition of chloride ion to Ph_2SnCl_3^-.

\[
2Ph_2SnCl_3^- \rightleftharpoons Ph_2SnCl_2 + Ph_2SnCl_4^{2-} \quad (10)
\]

The formation of pentacoordinated stannates 62a and 62b has been detected in the hydrolysis of the organotin halide complexes with phosphoryl ligands containing aliphatic amino group in the ligand. The tentative reaction scheme is shown in equation 11.

The first tin hydride complex [Bu_2SnI_2H][Li] was recently synthesized. The observed upfield ^119Sn chemical shift (~177.9 ppm in THF-d_8) and spin–spin coupling constants [^1J(^119Sn^–^13C) 498 Hz, ^1J(^119Sn^–^1H) 2318 Hz] as compared with those for Bu_2SnIH (~76.3 ppm, 408 and 2060 Hz, respectively) strongly indicate the formation of a pentacoordinated tin complex.
The X-ray crystallographic structures of a number of diorganotrihalostannate complexes were briefly analyzed. A significant structural diversity of the anions was found. The fluoro-anion in the complex [Me₄Sn₂F₅][Et₄N] displays linear, fluoride-bridged units resulting in a six-coordinate tin. The dinegatively charged chloro-anion Me₆Sn₃Cl₈²⁻, which can be considered as the adduct Me₂SnCl₂ · 2Me₂SnCl₃⁻, includes three hexacoordinated tin atoms, as well as distorted TBP with an additional Cl → Sn contact near the equatorial plane of the bipyramid in dimers, having coordination environment of two tin atoms that can be classified as a distorted octahedron. Principal geometric parameters of these anions are given in Table 13.

Bond distances between tin atom and the two axial chlorine atoms in the isolated TBP anions 63 are significantly longer (2.52–2.62 Å) than the equatorial Sn–Cl bond (2.32–2.40 Å).

In accordance with the theory of hypervalent bonds, the CSnC angle constricts and the lengths of equatorial and terminal axial bonds Sn–Cl diverge with the reduction of the secondary Cl → Sn interaction. An interesting feature of some structures [see entries 6, 8, and 8 (62a) in Table 13] is that the axial Sn–Cl bond not involved in the secondary Cl → Sn interaction is longer than the other axial bond, probably due to specific interactions between the terminal chlorine atom and cation (hydrogen bonds in entries 6 and 8 and Cl···S contacts in entry 7). It is still unclear why some diorganotrichlorostannates exist as dimeric anions while others do not. Nevertheless, it is noteworthy that there are no examples of hydrogen-bonded anion-cation pairs among the structures containing isolated anions and all phenyltin derivatives (entries 11–13) form isolated anions. As for alkyl derivatives, the diversity of tin coordination polyhedra suggests that both edge-sharing octahedron and isolated TBP possess similar energies, hence relatively weak crystal packing forces control the choice between these forms.

An X-ray crystallographic study of 58a, Alk = Me (entry 14) revealed the first example of a TBP structure containing an R₂SnBr₃⁻ anion. In contrast to the structures observed for Me₂SnCl₃⁻ anions that are generally associated as dimers, the Me₂SnBr₃⁻ anion is...
16. Hypervalent compounds of organic germanium, tin and lead derivatives

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compounda</th>
<th>Sn–Xax (b) (Å)</th>
<th>Sn–Xeq (Å)</th>
<th>X → Snf (Å)</th>
<th>CSnC (deg)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Me₄Sn₂Cl₆]²⁺</td>
<td>2.836, 2.523</td>
<td>2.472</td>
<td>2.899</td>
<td>166.6</td>
<td>285</td>
</tr>
<tr>
<td>2</td>
<td>[Me₄Sn₂Cl₆]²⁺</td>
<td>2.623, 2.575</td>
<td>2.406</td>
<td>3.259</td>
<td>156</td>
<td>286</td>
</tr>
<tr>
<td>3</td>
<td>[Me₄Sn₂Cl₆]²⁺</td>
<td>2.759, 2.488</td>
<td>2.440</td>
<td>2.944</td>
<td>165.2</td>
<td>286</td>
</tr>
<tr>
<td>4</td>
<td>[Me₄Sn₂Cl₆]²⁺</td>
<td>2.773, 2.491</td>
<td>2.405</td>
<td>3.205</td>
<td>159.5</td>
<td>287</td>
</tr>
<tr>
<td>5</td>
<td>[Me₄Sn₂Cl₆]²⁺</td>
<td>2.687, 2.564</td>
<td>2.432</td>
<td>3.370</td>
<td>154.2</td>
<td>288</td>
</tr>
<tr>
<td>6</td>
<td>[Me₄Sn₂Cl₆]²⁺</td>
<td>2.560, 2.585</td>
<td>2.407</td>
<td>3.486</td>
<td>152.2</td>
<td>289</td>
</tr>
<tr>
<td>7</td>
<td>[Me₄Sn₂Cl₆]²⁺</td>
<td>2.589, 2.649</td>
<td>2.381</td>
<td>3.585</td>
<td>142.1</td>
<td>290</td>
</tr>
<tr>
<td>8</td>
<td>Bu₄SnCl₂</td>
<td>2.494, 2.766</td>
<td>2.361</td>
<td>3.824</td>
<td>138</td>
<td>282</td>
</tr>
<tr>
<td>9</td>
<td>[Me₄SnCl₃]⁻⁺ (Catb)⁺</td>
<td>2.526, 2.565</td>
<td>2.323</td>
<td>&gt;4.75</td>
<td>140.7</td>
<td>291</td>
</tr>
<tr>
<td>10</td>
<td>[Et₂SnCl₃]⁻⁺ (Catb)⁺⁺ · 3Cl⁻</td>
<td>2.622, 2.622</td>
<td>2.343</td>
<td>&gt;5.0</td>
<td>141.1</td>
<td>292</td>
</tr>
<tr>
<td>11</td>
<td>[Ph₂SnCl₃]⁻⁺ (Catb)⁺⁺ (62b)</td>
<td>2.528, 2.545</td>
<td>2.353</td>
<td>&gt;5.0</td>
<td>123.9</td>
<td>282</td>
</tr>
<tr>
<td>12</td>
<td>[Ph₂SnCl₃]⁻⁺ (Et₂N)⁺</td>
<td>2.517, 2.531</td>
<td>2.378</td>
<td>&gt;6</td>
<td>127.5</td>
<td>293</td>
</tr>
<tr>
<td>13</td>
<td>[Ph₂SnCl₃]⁻⁺ (Catb)⁺⁺ (60)</td>
<td>2.546, 2.528</td>
<td>2.401</td>
<td>&gt;6</td>
<td>135.8</td>
<td>281</td>
</tr>
<tr>
<td>14</td>
<td>[Me₂SnBr₃]⁻⁺ (Me₄N)⁺ (85a, Alk = Me)</td>
<td>2.734, 2.734</td>
<td>2.498</td>
<td>&gt;4.2</td>
<td>133.2</td>
<td>270</td>
</tr>
<tr>
<td>15</td>
<td>[MeSnCl₄]⁻⁺ (Ph₄As)⁺⁺</td>
<td>2.492, 2.273</td>
<td>&gt;6</td>
<td>104.9⁶ (174.6)⁶</td>
<td>294</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>[Me₂SnCl₄]⁻⁺ (Catb)⁺⁺</td>
<td>2.486, 2.455</td>
<td>2.334</td>
<td>—</td>
<td>118.1⁶</td>
<td>295</td>
</tr>
<tr>
<td>17</td>
<td>[Cl₄Sn(CH₂)₄SnCl₄]²⁻ (2BnPPH₃)⁺⁺ (67c)</td>
<td>2.463, 2.543</td>
<td>2.343</td>
<td>—</td>
<td>106.7⁶</td>
<td>296</td>
</tr>
<tr>
<td>18</td>
<td>[SnCl₅]⁻⁺ (Catb)⁺⁺ (13b)⁺⁺</td>
<td>2.560, 2.366</td>
<td>2.367</td>
<td>2.628</td>
<td>173.2⁸</td>
<td>248b</td>
</tr>
<tr>
<td>19</td>
<td>[SnCl₅]⁻⁺ (Catb)⁺⁺ (13b)⁺⁺</td>
<td>2.340, 2.390b</td>
<td>2.320b</td>
<td>&gt;4.4j</td>
<td>125.6k</td>
<td>297</td>
</tr>
<tr>
<td>20</td>
<td>[SnCl₅]⁻⁺ (Ph₄P)⁺⁺</td>
<td>2.391, 2.293b</td>
<td>&gt;5.1</td>
<td>123.1f (176.0)j</td>
<td>298</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>[SnBr₅]⁻⁺ (Catb)⁺⁺</td>
<td>2.561m</td>
<td>2.993m</td>
<td>—</td>
<td>(174.8)l</td>
<td>295</td>
</tr>
</tbody>
</table>

aCations:
Cat¹ = N-(2-methoxy-1-naphthylidene)-3-methoxyanilinium;
Cat² = (η⁴-cycloocta-1,5-diene)-(σ¹, η⁴-2,6-diallylpyridine-N)-rhodium(I) · CH₂Cl₂;
Cat³ = cis-[(Z)-azathien]-1-yl-S¹, N⁴-bis(triethylphosphine)-platinum(II);
Cat⁴ = tetrathiafulvalenium;
Cat⁵ = 8-methoxyquinolinium;
Cat⁶ = dibenzotetrafulvalenium;
Cat⁷ = bis[di(i-propyl)phosphoryl]-(dimethylammonium)methane;
Cat⁸ = 2,2',2''-terpyridyl(dimethyl)chlorotin(IV);
Cat⁹ = bis(diethyl-bis(2,6-diacylpyridine-bis(isomicotinoylhydrazone))-tin;
Cat¹⁰ = N-(diethylphosphoryl)methyl]-piperidinium;
Cat¹¹ = Cl₂MeSn[HC(PyrMe₂-3,5)₃](Pyr = pyrazole);
Cat¹² = [2-(2-acetoxy-5-methylphenyl)-4,6-dimethyl-1-benzopyranium;
Cat¹³ = dicarbonyl-cyclopentadienyl-triphenylphosphine(trichloro-tin(IV))-manganese(III);
Cat¹⁴ = Br₂Sn[HC(PyrMe₂-3,4,5)₃];

bFor dimeric anions, the first value corresponds to the bond involved in the secondary interaction, and the second to the terminal axial bond.
cSecondary contact.
dTwo crystallographically independent discrete anions.
eHal₂SnHal₂c.
fHal₃SnHal₃c.
gThe angle between the trans chlorine atoms at 2.369 and 2.365 Å.
hThe Cl₃SnCl₃c angle is 176.3°.
iCl²eq–Sn.
jNearest contact of the tin atom with chlorine in the cation is 3.981 Å.
kThe Cl²eqSnCl²eq angle; the bond lengths Cl²eq–Sn and Cl³eq–Sn are 2.317 and 2.325 Å.
lThe Cl²eqSnCl³eq angle; the bond lengths Cl²eq(Cl³eq)–Sn are both 2.339 Å.
mAverage value.

TABLE 13. Comparison of the principal geometric parameters for isolated R₂SnX₃⁻ and dimeric [R₄Sn₂X₆]²⁻ anions.
monomeric. The TBP structure of the Me$_2$SnBr$_3$\(^-\) anion in complex 58b was proved by IR, Raman and $^{119}$Sn Mössbauer and MAS NMR spectrosocopies in the solid state, and by $^{119}$Sn NMR spectroscopy in solution (Table 11)\(^{270}\).

The dinegatively charged anion 65 obtained as its 2-aminopyrimidinium salt, by the reaction of Ph$_2$SnCl$_2$ and 2-aminopyrimidine in the presence of diethyl ether, followed by recrystallization from a MeCN/MeOH mixture is the first example of a five-coordinated anionic distannoxane\(^{299}\). Its X-ray crystal structure resembles the dimeric anions 64 and consists of tin units with di-$\mu$-oxo bridging. The coordination geometry of the tin unit is a distorted TBP with two phenyl groups and one $\mu$-oxo, at a Sn-O distance of 2.032 Å, in equatorial positions, and the other two $\mu$-oxo and chlorine atoms, at a O $\rightarrow$ Sn distance of 2.187 Å and Sn-Cl = 2.467 Å, in axial positions. The ranges of Sn-O bond lengths, and of the OSnO and SnOSn bond angles, are close for all the distannoxanes\(^{299}\).

Anionic sulfur as well as chloride bridged ditin complexes 66a–c were most recently prepared by the reaction of diorganotin sulfides, cyclo-(R$_2$SnS)$_n$ ($n = 2, 3$) with the appropriate amounts of R$_2$SnCl$_2$ in the presence of [(Ph$_3$P)$_2$N]Cl\(^{300}\). Single-crystal diffraction studies of 66a,c revealed the first crystallographic examples of structures containing a Sn($\mu$-S)($\mu$-Cl)Sn core. The geometry about each tin atom is best described as TBP with the equatorial and axial positions being occupied by two C and one S, and by two Cl, respectively, in each case. The respective ClSnCl axial angles are 175.1° and 173.6° for 66a but 166.6° and 165.6° for 66c. As expected, the Sn-Cl(bridging) distances (2.74–2.83 Å) are significantly longer than the Sn-Cl(terminal) distance (2.47–2.51 Å). Both tin atoms are displaced out of the C$_2$Sn equatorial plane in the direction of the Cl(terminal) atoms, by 0.12 and 0.16 Å for 66a.

The $^{119}$Sn, $^{13}$C and $^1$H NMR spectra in CDCl$_3$ are in agreement with the exclusive formation of 66a,b in solution, while the equilibrium \{[Sn(t-Bu)$_2$SnCl]$_2$·Cl$^-\} \rightleftharpoons 1/2[[t-(Bu)$_2$SnS]$_2$ + (t-Bu)$_2$SnCl$_3$\(^-\) takes place for the anion in 66c\(^{300}\).

A number of hypervalent tin species including the monoanions [Ph$_2$SnCl$_2$F]$^-$, [Ph$_2$SnClF$_2$]$^-\) and [Ph$_3$SnF$_3$]$^-$, as well as the dinegatively charged anions [Ph$_2$SnF$_4$]$^{2-}$ and [Ph$_2$SnCl$_4$]$^{2-}$, have been identified in CH$_2$Cl$_2$ solutions of Ph$_2$SnCl$_2$ and Bu$_4$NF·3H$_2$O mixtures by $^{119}$Sn and $^{19}$F NMR spectroscopy\(^{237}\). The NMR data are consistent with static TBP geometries at $-100$ °C for both [Ph$_2$SnCl$_2$F]$^-$ and [Ph$_2$SnClF$_2$]$^-$, while at $-60$ °C the latter become fluxional, probable via a Berry pseudorotation mechanism. Variable-temperature $^{119}$Sn and $^{19}$F NMR spectra of the Ph$_2$SnF$_3$\(^-\) anion are indicative of intramolecular exchange of axial and equatorial fluorine atoms followed by an intermolecular fluoride exchange at a higher temperature. It was also found that the addition of fluoride ion to Ph$_2$SnCl$_2$ causes appreciable migration of the Ph group to give the [Ph$_3$SnClF]$^-$ and [Ph$_3$SnCl$_2$]$^-\) anions as minor species. In chloride or bromide
ion addition to diorganotin dihalides, only the 1:1 adducts R₂SnX₃⁻ (R = Me, Bu, Ph; X = Cl, Br) have been detected.

High level ab initio SCF MO calculations of monoanions Me₂SnX₃⁻, their precursors Me₂SnX₂, the dinegatively charged anions trans-Me₂SnX₄²⁻ (X = F, Cl, Br, I) as well as the related derivatives cis-R₂SnCl₄²⁻ (R = Me, Et), Et₂SnCl₂, Et₂SnCl₃⁻ and trans-Et₂SnCl₄²⁻ have been recently reported. The gas-phase formation of pentacoordinate R₂SnX₃⁻ anions from R₂SnX₂ and X⁻ is an exothermic process, while the following addition of X⁻ to monoanions R₂SnX₃⁻ is an endothermic one. The pentacoordinate R₂SnX₃⁻ anions show a TBP geometry with the R groups in equatorial positions and longer Sn−X distances for the axial bonds than for the equatorial ones. Thus, these calculations are in good agreement with experimental data.

5. Organotetrahalostannates and related species

As compared to anions of the R₃SnHal₂⁻ or R₂SnHal₃⁻ types, much less is known about the nature of halide adducts of monoorganylhalostannanes. In particular, the tin atom in the salt [MeSnCl₄][Ph₄As] has approximately a TBP coordination, with the carbon atom occupying an equatorial position. The equatorial Sn−Cl distances are ca. 2.34 Å while the axial distances are longer at ca. 2.45 Å (Table 13, entry 15).

A number of hypervalent tin species, including MeSnCl₄⁻, BuSnCl₄⁻, PhSnCl₄⁻ and PhSnCl₂F²⁻, are identified in the reactions of chloride ion or fluoride ion with monoorganyltin halides RSnCl₃ (R = Me, Bu, Ph) in CH₂Cl₂ solution using variable-temperature ¹⁹F and ¹¹⁹Sn NMR spectroscopies. The Ph group migration with formation of the five-coordinated anion, PhSnCl₄⁻, has been observed to be reversible (equation 12).

\[
\text{Ph}_2\text{SnCl}_2 + [\text{SnCl}_6]^{2-} \rightleftharpoons 2[\text{PhSnCl}_4]^- \tag{12}
\]

Unlike the interaction of bis(halodiphenylstannyl)alkanes with halide ions which lead to anionic 1:1 adducts with bridged halogen, ¹¹⁹Sn NMR spectroscopy indicates the formation of five-coordinate dinuclear 1:2 chloride and bromide complexes 67a−d, and 68a,b, respectively, from the reactions between X₃Sn(CH₂)ₙSnX₃ (X = Cl, Br; n = 1, 3, 4, 8) and halide ions in CHCl₃ solution (equation 13).

\[
\text{Cl}_3\text{Sn(CH}_2)_n\text{SnCl}_3 + 2\text{MX} \rightarrow \text{[MX]}^{2-} \tag{13}
\]

MX = [BnPPh₃]Cl, R₄NBr
The crystal structure of 67c reveals a distorted TBP geometry about each tin atom with the two axial Sn−Cl bond distances being significantly longer than the equatorial Sn−Cl bonds (Table 13, entry 16). Moreover, a significant disparity is noted between the axial Sn−Cl distances (0.08 Å) that is explained in terms of Cl···H interactions. As a result, the tin atom lies 0.08 Å out of the equatorial CCl₂ plane in the direction of the chlorine atom having the shorter bond length.

The allylation reaction of CH₂O by the pentacoordinate adducts F₄M(CH₂CH=CH₂)⁻ (M = Ge, Sn) was studied by the ab initio Hartree–Fock method. Their adduct formation from F₃M(CH₂CH=CH₂) and F⁻ is exothermic. These adducts display enhanced nucleophilicity of the allylic γ-carbon and a significant Lewis acidity and form hexacoordinate adducts F₄M(OCH₂)(CH₂CH=CH₂)⁻ by the addition of CH₂O. The reactivity of the Ge and Sn complexes is expected to be greater than that of their Si analogues because of the lowering of the potential energy barriers.

Anionic complexes [PhPbX₄][Ph₄E] (X = Cl, Br; E = P, As) have been prepared by the reaction of PhPb(O)OH with HCl or HBr and Ph₄EX₃. Anionic complexes of the simplest pentacoordinate germanane species, GeCl₅⁻, as the (1,2-bis(t-butylamido)ethene)-phosphenium and -arsenium salts has been described in both cases, the GeCl₅⁻ anion, like the SnCl₅⁻ anion (entries 19 and 20 in Table 13), has a near-regular TBP with the axial ClGeCl angles at ca 178° and the axial Ge−Cl distances at 2.25–2.32 Å while the equatorial bonds are shorter, being 2.12–2.17 Å, as expected.

6. Zwitterionic stannates

A number of zwitterionic stannates, namely 69a, 69b, 69c, 69d and Bu₃Sn(Cl)OCOCH₂CH₂PPh₃ (69e) were described, in which the tin is formally negative, with a cationic nitrogen or phosphorus as a part of the ligand. The carboxylato compounds were prepared in good yields by mixing ethanolic solutions containing stoichiometric quantities of Ph₃SnCl, Ph₃SnNCS or (PhCH₂)₃SnCl and 2-pyridinecarboxylic acid or 3-triphenylphosphonopropiobetaine, respectively. The geometry at tin is TBP, like in anionic and neutral pentacoordinate tin complexes. The Sn−O, Sn−Cl and Sn−N distances in these zwitterionic stannates are comparable to those for anionic stannates (Table 10).

The fluorostannyl-substituted phosphonium salts, (t-Bu)₂Sn(CH₂PPh₃)F₂ · BF₃ (69f) and (t-Bu)₂Sn[C(=CH₂)PPh₃]F₂ · BF₃ (69g), have an intermolecular contact between one fluorine atom of the BF₄ tetrahedron and the tin atom that leads to distorted TBP configurations of the tin atoms. Thus, these complexes can be considered as zwitterionic stannates with the formally negatively charged tin atoms including one normal Sn−F distance while the other Sn···F contact is elongated by 0.755 Å in 69f and 0.88 Å in 69g (Table 10). The tin atom is displaced out of the plane formed by the three carbon atoms at 0.35 Å in 69f and 0.32 Å in 69g, respectively. The relative shortening of the averaged Sn−F bonds (ca 2.41 Å) is ca 23% as compared to those of the corresponding tetrahedral derivatives. This shortening is larger than that in the corresponding dichloro- and dibromo-triorganylstannates (see above).

B. Intramolecular Complexes

Various monocyclic and bicyclic pentacoordinate anionic germanium and tin complexes are known which possess bidentate dianionic oxo and related ligands, such as aliphatic or aromatic 1,2-diols, α-hydroxycarboxylic acids and their thio analogues (for early references see References 191, 307–309). Anionic mono- and bis-chelated germanium and
tin compounds containing four-membered ring were discussed in a review\textsuperscript{310} and are not reviewed here.

1. Monocyclic derivatives

   a. Tin. The monocyclic organostannates 69h and 69i with four Sn–C bonds were recently prepared by the reaction of their corresponding tetracoordinate precursors 69j and 69k with \( p \)-TolLi (equation 14)\textsuperscript{311}. The complexes obtained were found to be thermally stable but were unstable to moisture, giving quantitatively the initial compounds upon aqueous workup.
119Sn NMR spectra of the solution of 69j and 69k with p-TolLi show a remarkable upfield shift relative to those for 69j and 69k, $\Delta \delta = 182$ and 212 ppm, respectively, indicating an increase in the coordination number of tin. It is noteworthy that the organostannates 69h and 69i react with 1,3-bis(methoxycarbonyl)pyridinium chloride to give the corresponding alkylated(arylated) dihydropyridines.311

The triphenyltin derivatives of oxalic acid 70a, 70b, mercaptoacetic acid 71 and 2-mercaptobenzoic acid 72 were prepared by the reaction of triphenyltin hydroxide with the corresponding amine and acid in a 1 : 1 : 1 molar ratio.

X-ray crystallography of stannates 70–72 revealed rare examples of a cis-TBP geometry at tin with oxygen and one of phenyl groups in the apical positions. The axial Sn–O bonds are longer than those in tetrahedral derivatives and, of the three Sn–C bonds, the axial bond is statistically longer than the two equatorial bonds (Table 14).

Organotin 1,2-dithiolate complexes were featured in many studies; the ligands used include aliphatic derivatives, e.g. ethane-1,2-dithiolate $-SCH_2CH_2S^-$ (EDT), $-SCH_2CHMeS^-$, alkenyl derivatives, e.g. $-SCH=CHS^-$, maleonitriledithiolate (MNT), aryl derivatives, 1,2–$-SC_6H_4S^-$ (BDT) and toluene-3,4-dithiolate (TDT), as well as heterocyclic derivatives, 1,3-dithiane-2-one-4,5-dithiolate (DMIO) and 1,3-dithiane-2-thione-4,5-dithiolate (DMIT)191.

The general synthetic route to monocyclic complexes $[R_3M(MNT)] [Alk_4N]$ (M = Ge, Sn, Pb; R = Me, Ph) involves the reaction between Na2(MNT) and RMCl3 in the presence of tetraalkylammonium halides. In the case of Ph3SnCl and NH4Br, this reaction proceeds without tin–carbon bond cleavage giving the stannate [Ph3Sn(MNT)]$^-$ as its Me4N$^+$ salt 73316.
TABLE 14. X-ray data for pentacoordinate anions in chelate triphenyltin complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sn-X&lt;sub&gt;ax&lt;/sub&gt; (Å)</th>
<th>Sn-Y&lt;sub&gt;eq&lt;/sub&gt; (Å)</th>
<th>Sn-C&lt;sub&gt;ax&lt;/sub&gt; (Å)</th>
<th>Sn-C&lt;sub&gt;eq&lt;/sub&gt; (Å)</th>
<th>XSnY deg</th>
<th>XSnC&lt;sub&gt;ax&lt;/sub&gt; deg</th>
<th>C&lt;sub&gt;eq&lt;/sub&gt;SnC&lt;sub&gt;eq&lt;/sub&gt; deg</th>
<th>TBP → RP (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>70a</td>
<td>2.260</td>
<td>2.115</td>
<td>2.159</td>
<td>2.140</td>
<td>73.3</td>
<td>158.7</td>
<td>134.7</td>
<td>55</td>
<td>312</td>
</tr>
<tr>
<td>70b&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.276&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.112&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.157&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.144</td>
<td>72.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>157.0&lt;sup&gt;a&lt;/sup&gt;</td>
<td>124.0</td>
<td>30&lt;sup&gt;a&lt;/sup&gt;</td>
<td>313</td>
</tr>
<tr>
<td>71</td>
<td>2.608</td>
<td>2.432</td>
<td>2.177</td>
<td>2.145</td>
<td>74.2</td>
<td>166.8</td>
<td>120.8</td>
<td>—</td>
<td>314</td>
</tr>
<tr>
<td>72</td>
<td>2.704</td>
<td>2.426</td>
<td>2.179</td>
<td>2.137</td>
<td>74.3</td>
<td>168.7</td>
<td>120.7</td>
<td>—</td>
<td>315</td>
</tr>
<tr>
<td>73</td>
<td>2.864</td>
<td>2.496</td>
<td>1.183</td>
<td>2.156</td>
<td>76.5</td>
<td>161.6</td>
<td>127.7</td>
<td>35.1</td>
<td>316</td>
</tr>
</tbody>
</table>

<sup>a</sup>Average value.
<sup>b</sup>C<sub>eq</sub>SnO<sub>eq</sub>.
<sup>c</sup>Two independent ion pairs.

An X-ray study shows that the anion in 73 can be referred to a TBP. However, the remarkable difference between the Sn–S<sub>eq</sub> bond length of 2.496 Å and the Sn–S<sub>ax</sub> bond length of 2.864 Å (Table 14), which significantly exceeds the typical range for Sn–S<sub>ax</sub> bond lengths (2.49–2.54 Å), is evident for a residual tetrahedral character at the tin atom. The latter is displaced 0.28 Å out of the equatorial plane in a direction away from S<sub>ax</sub>. Retention of the solid state structure of the anion 73 in solution is supported by the high negative value of −173.8 ppm (1:1, CDCl<sub>3</sub>/CH<sub>3</sub>CN) observed in the <sup>119</sup>Sn NMR spectrum.

Other examples of monocyclic dithiolato stannates are two series of diorganohalo– and diorganopseudohalo–tin complexes, containing DMIO and DMIT ligands, which were recently obtained from organotin halides and the dithiolato Zn derivatives (Scheme 4)<sup>191</sup>,<sup>309</sup>,<sup>318</sup>. When these reagents were used in a 2:1 ratio, the DMIO or DMIT stannates, 74<sup>191</sup>,<sup>319</sup> and 75<sup>309</sup>,<sup>318</sup>, respectively, were generally obtained in acetone or methanol solution (stage a). Neutral diorganotin DMIO and DMIT compounds, 76<sup>191</sup> and 77<sup>197</sup>, were isolated by the following treatment of the reaction mixture with water (stage b). The stannates 74 and 75 could also be formed from the neutral compounds 76 and 77, respectively, on reaction with onium halides MX (stage c). Hence, in the preparation of 74 and 75, the presence of water required to remove the inorganic salts was kept to a minimum.

Another route to 74 and 75 is halide (pseudohalide) exchange reaction between the chlorides 74 or 75 (X = halogen) and NaX′ or KX′ (X′ = Br, I, NCS, NCS<sub>e</sub>)<sup>191</sup>,<sup>309</sup> (stage d). Analogously, exchanges of [R<sub>2</sub>Sn(DMIT)Cl][M] with I<sup>−</sup><sup>318</sup> or NCS<sup>−</sup><sup>320</sup> took place while attempts to replace Cl<sup>−</sup> by [Et<sub>2</sub>NCS]<sup>−</sup> had failed<sup>318</sup>.
Scheme 4. Formation of monocyclic DMIT and DMIO derivatives

(74) E = O; M = Et₄N, FeCH₂NMe₃; R = Ph, Alk; X, X' = Cl, Br, I, NCS
(75) E = S; M = Alk₄N, 4-MeC₆H₄NMe (DMP; R = Ph, Alk; X, X' = Cl, Br, I, NCS, NCSe, N₃
(76) E = O; R = Me, Et, Bu, Ph
(77) E = S; R = Me, Et, Bu, octyl, Ph, o-MeOC₆H₄
The interactions between the neutral DMIT derivatives 77 and MX (e.g. Et₄NB₃, Bu₄NB₃, stage c) were studied directly in solution by ¹¹⁹Sn NMR spectroscopy. The δ¹¹⁹Sn values recorded for the MX-R₂Sn(DMIT) systems reflect the average values for rapidly equilibrating R₂Sn(DMIT) and [R₂Sn(DMIT)]⁻ species.

X-ray diffraction shows that the DMIO and DMIT complexes, 74a-c (74a, M = Et₄N, R = Ph, X = Cl); 74b, M = Et₄N, R = Et, X = Br; 74c, M = Et₄N, R = Ph, X = NCS) and 75a-d (75a, M = Bu₄N, R = Me, X = Cl; 75b, M = DMP, R = Ph, X = Br; 75c, M = Et₄N, R = Ph, X = I; 75d, M = DMP, R = Ph, X = NCS), exist as ionic species, with the geometries at tin in the anions being TBP with some distortions toward RP structures (Table 15). Chelating DMIT and DMIO ligands are bonded to Sn via dithiolate S atoms in axial and equatorial sites, with an SSnS angle of 95°, while the second axial position is occupied by halogen or NCS group, with the XₐₓSₐₚ bond lengths (2.55–2.66 Å), a larger variation is found for the Sn-Sₐₚ bond lengths (2.55–2.66 Å). There is a particularly narrow range of values for the equatorial Sn-Sₑq bond lengths (2.43–2.46 Å), while a larger variation is found for the Sn-Sₐₚ bond lengths (2.55–2.66 Å). The latter, as well as the axial Sn-Hal or Sn-N bond lengths, are longer than those for their values in tetrahedral derivatives. For example, in the case of the DMIT derivatives 75a-c the Sn–N(CS), Sn–Cl, Sn–Br and Sn–I distances are ca 5, 7, 7 and 9% longer, respectively, than the appropriate sum of the covalent bond radii of 2.15, 2.39, 2.54 and 2.73 Å.

The neutral species MePhSn(DMIT) (77a) is linked into zigzag chains via Sn–S–S interactions. The δ¹ⁱ⁹Sn values recorded for the MX-R₂Sn(DMIT) complexes reflect the average values for rapidly equilibrating R₂Sn(DMIT) and [R₂Sn(DMIT)]⁻ species.

A series of monocyclic halo stannates with mixed oxygen–sulfur ligands, 78a-d, 79, 80, 82, as well as the homo-ligand TDT derivative 81, all containing aromatic ortho-ligand chelated to tin, were obtained by reacting the halide salt with the tetracoordinated stannate precursor in acetonitrile solution. A similar method was used for the preparation of salt [Me₂Sn(S₂N₂)Cl][Ph₄As]. X-ray diffraction of the fluoro 78a, chloro 80 and iodo 79 derivatives revealed TBP structures with the more electronegative oxygen and halogen atoms in the apical positions, with increased distortion as the halogen size increases (Table 15). Thus, the Sn atom in fluoro 78a is only 0.006 Å out of the equatorial plane toward the halogen atom. In chloride 80, the Sn atom is slightly displaced (at 0.076 Å) from the equatorial plane in the direction of the halogen while in the iodo derivative 79 the large Sn atom displacement of 0.178 Å takes place away from the axial iodine atom. The latter forms a weakly coupled dimeric unit formed by intermolecular Sn–S coordination at 2.646 Å.

The most pronounced angular change for this series of halostannates occurs in the CSnC equatorial angle. It increases from 117.6° for fluoro 78a to 130.3° for the chloro derivative 80 and to 140.1° for iodo compound 79.

Unlike chloride 80, the Sn atom in the mono(dithiolato) tin complex 81 is displaced from the equatorial plane toward the axial S atom (but not the axial chlorine). The anion in salt 82 adopts distorted TBP structure with equatorial methyl groups and a long axial Sn–Cl bond (2.652 Å).

The anionic binuclear monocyclic tin derivatives, 83a and 83b, containing ring saturation, were isolated from the reaction of MeSnCl₃ or n-BuSnCl₃, respectively, with Na₂(EDT) in the presence of Et₄NCI (see below).
X-ray investigation shows that the geometry about the tin atom in the dianion of 83a closely approaches the TBP with one of the S atoms and a Cl in axial positions. The $^{119}$Sn NMR data on 83a show a single resonance at $-52.3$ ppm (CH$_3$CN) that is consistent with its five-coordinate tin structures in solution.

It should be noted that the geometries about the Sn atom in the monocyclic stannates can alternatively be viewed as being somewhat displaced from a TBP toward a RP having C$_{eq}$ (compounds 70–73, 75a, 83a, see Tables 14 and 15) or S$_{eq}$ (compounds 78a, 79–81, see Table 15) in the apical (Z) position (Scheme 5).

**b. Lead.** Earlier data concerning organolead dithiolate complexes, namely R$_2$PbL$_2$ (R = Me, Ph; L = EDT, o-S$_2$C$_6$H$_4$, TDT or MNT), [Ph$_3$Pb(MNT)][Ph$_4$As], [Ph$_2$Pb(MNT) Cl][Ph$_4$E] (E = P, As), [(Ph$_3$Pb)$_2$(TDT)], [Ph$_2$Pb(MNT)$_2$][Me$_4$N]$_2$ and [Ph$_3$Pb(MNT)]
TABLE 15. Selected structural parameters and $^{119}$Sn chemical shifts for monocyclic tin anions with DMIO, DMIT and related ligands

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sn–X$_{ax}$ (Å)</th>
<th>Sn–S$_{ax}$ (Å)</th>
<th>Sn–S$_{eq}$ (Å)</th>
<th>Sn–C (Å)$^b$</th>
<th>XSn$_{ax}$ (deg)</th>
<th>C$<em>{eq}$SnS$</em>{eq}$ (deg)</th>
<th>TBP → RP (%)$^c$</th>
<th>δ$^{119}$Sn (ppm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ph$_2$Sn(DMIO)Cl][Et$_4$N] (74a)</td>
<td>2.524</td>
<td>2.626</td>
<td>2.463</td>
<td>2.246</td>
<td>165.4</td>
<td>127.9</td>
<td>—</td>
<td>$-178.5^d$</td>
<td>191</td>
</tr>
<tr>
<td>[Et$_3$Sn(DMIO)Br][Et$_4$N] (74b)</td>
<td>2.878</td>
<td>2.562</td>
<td>2.458</td>
<td>2.093</td>
<td>167.1</td>
<td>110.3$^e$</td>
<td>—</td>
<td>$-172.2^f,g$</td>
<td>322</td>
</tr>
<tr>
<td>[Ph$_2$Sn(DMIO)NCS][Et$_4$N] (74c)</td>
<td>2.240</td>
<td>2.583</td>
<td>2.433</td>
<td>2.147</td>
<td>166.4</td>
<td>123.5</td>
<td>—</td>
<td>$-182.4^e$</td>
<td>191, 319</td>
</tr>
<tr>
<td>[Me$_2$Sn(DMIT)Cl][Et$_4$N] (75a)</td>
<td>2.556</td>
<td>2.662</td>
<td>2.451</td>
<td>2.131</td>
<td>167.3</td>
<td>120.8$^h$</td>
<td>5.9$^i$</td>
<td>$-24.7^j,k$</td>
<td>309, 318</td>
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<tr>
<td>[Ph$_2$Sn(DMIT)Br][DMP] (75b)</td>
<td>2.714</td>
<td>2.596</td>
<td>2.453</td>
<td>2.160</td>
<td>165.8</td>
<td>123.8</td>
<td>—</td>
<td>$-149.8^l$</td>
<td>309</td>
</tr>
<tr>
<td>[Ph$_2$Sn(DMIT)I][Et$_4$N] (75c)</td>
<td>2.985</td>
<td>2.551</td>
<td>2.454</td>
<td>2.147</td>
<td>166.4</td>
<td>123.5</td>
<td>—</td>
<td>$-158.2^m$</td>
<td>309</td>
</tr>
<tr>
<td>[Ph$_2$Sn(DMIT)NCS][DMP] (75d)</td>
<td>2.261</td>
<td>2.592</td>
<td>2.440</td>
<td>2.138</td>
<td>164.6</td>
<td>121.9</td>
<td>—</td>
<td>$-163.3^o$</td>
<td>309, 320</td>
</tr>
<tr>
<td>[Me$_2$Sn(OC$_6$H$_4$S)(F)][Et$_4$N] (78a)</td>
<td>2.041</td>
<td>2.145$^j$</td>
<td>2.432</td>
<td>2.140</td>
<td>166.7</td>
<td>122.4</td>
<td>11</td>
<td>—</td>
<td>323</td>
</tr>
<tr>
<td>[Me$_2$Sn(OC$_6$H$_4$S)I][Ph$_4$P] (79)$^m$</td>
<td>3.225</td>
<td>2.117</td>
<td>2.452</td>
<td>2.120</td>
<td>165.4</td>
<td>108.2$^p$</td>
<td>22</td>
<td>—</td>
<td>323</td>
</tr>
<tr>
<td>[Me$_2$Sn(O$_2$CC$_6$H$_4$S)Cl][Et$_4$N] (80)</td>
<td>2.558</td>
<td>2.191$^f$</td>
<td>2.422</td>
<td>2.136</td>
<td>170.7</td>
<td>116.5$^o$</td>
<td>19</td>
<td>—</td>
<td>323</td>
</tr>
<tr>
<td>[Ph$_2$Sn(TDT)Cl][Et$_4$N] (81)</td>
<td>2.588</td>
<td>2.544</td>
<td>2.436</td>
<td>2.149</td>
<td>165.9</td>
<td>121.2</td>
<td>14.1</td>
<td>—</td>
<td>324</td>
</tr>
<tr>
<td>[Me$_2$Sn(S$_2$N$_2$)Cl][Ph$_4$As] (82)</td>
<td>2.652</td>
<td>2.176$^p$</td>
<td>2.469</td>
<td>2.120</td>
<td>163.7$^q$</td>
<td>120.6</td>
<td>—</td>
<td>26$^r$</td>
<td>326</td>
</tr>
<tr>
<td>[MeSnCl(EDT)SCH$_2$][Et$_4$N]$_2$ (83a)</td>
<td>2.629</td>
<td>2.506</td>
<td>2.420</td>
<td>2.137</td>
<td>167.3</td>
<td>124.0</td>
<td>23.5$^f$</td>
<td>$-52.3^s$</td>
<td>325</td>
</tr>
<tr>
<td>[Ph$_2$Sn(TBT)Cl][Et$_4$N] (86b)</td>
<td>2.736</td>
<td>2.632</td>
<td>2.515</td>
<td>2.218</td>
<td>165.8</td>
<td>127.6</td>
<td>—</td>
<td>—</td>
<td>327</td>
</tr>
<tr>
<td>[Ph$_2$Sn(TBT)Br][Et$_4$N] (86c)</td>
<td>2.898</td>
<td>2.627</td>
<td>2.514</td>
<td>2.21</td>
<td>166.2</td>
<td>129.9</td>
<td>—</td>
<td>—</td>
<td>327</td>
</tr>
</tbody>
</table>

$^a$See list of abbreviations.

$^b$Average value.

$^c$The percent displacement from the ideal TBP toward the RP is calculated from unit bond distances on the basis of the dihedral angle method$^{328}$ using sulfur as the pivotal ligand.

$^d$In Me$_2$CO-d$_6$.

$^e$The CSnC angle is 138.0°.

$^f$For [Ph$_2$Sn(DMIO)Br][Et$_4$N]$^{191}$.

$^g$In Me$_2$SO-d$_6$.

$^h$The CSnC angle is equal 120.9°.

$^i$Me is the pivotal ligand.

$^j$In CDCl$_3$.

$^k$−33.2 (solid state).

$^l$Sn–O$_{ax}$.

$^m$A dimer with the six-coordinated tin atom due to the intermolecular Sn–O′ contact (2.646 Å).

$^n$The CSnC angle is 140.1°.

$^o$The CSnC angle is 130.3°.

$^p$Sn–N.

$^q$ClSnN.

$^r$In MeCN.
TABLE 16. Comparison of $\delta^{119}\text{Sn}$ values ($\text{Me}_2\text{SO-}d_6$) of the stannates $\text{Ph}_2\text{SnX}([\text{C}_3\text{S}_4\text{E}][\text{Et}_4\text{N}])$\textsuperscript{191}

<table>
<thead>
<tr>
<th>X</th>
<th>E = O (74)</th>
<th>E = S (75)</th>
<th>$\Delta\delta^{119}\text{Sn}$\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>$-178.5$</td>
<td>$-143.2$</td>
<td>$35.3$</td>
</tr>
<tr>
<td>Br</td>
<td>$-172.2$</td>
<td>$-149.6$</td>
<td>$22.6$</td>
</tr>
<tr>
<td>I</td>
<td>$-179.4$</td>
<td>$-158.2$</td>
<td>$21.2$</td>
</tr>
<tr>
<td>NCS</td>
<td>$-182.4$</td>
<td>$-162.9$</td>
<td>$19.5$</td>
</tr>
</tbody>
</table>

\textsuperscript{a}$\Delta\delta^{119}\text{Sn} = \delta^{119}\text{Sn}(E = S) - \delta^{119}\text{Sn}(E = O)$.

SCHEME 5. Relationship between trigonal bipyramid and rectangular pyramid for anionic pentacoordinate monocyclic tin complexes with (a) $\text{Ph}_3\text{Sn}$ and (b) $\text{R}_2\text{Sn}$ frameworks

[Me\textsubscript{4}N], were cited elsewhere\textsuperscript{308}. Compound $\text{Ph}_2\text{Pb(DMIT)}$ (84), which is light-sensitive in solution, was recently prepared from $\text{Ph}_2\text{Pb(OAc)}_2$ and $[\text{Zn(DMIT)}_2][\text{Et}_4\text{N}]_2$\textsuperscript{308}. The $^{207}\text{Pb}$ NMR spectrum (248 ppm, solid state) indicates a coordination number of lead higher than four. The ionic species, $[\text{Ph}_2\text{Pb(DMIT)}\text{I}]\text{[M]}$ (M = Et\textsubscript{4}N, 4-MeC\textsubscript{6}H\textsubscript{4}NMe), were obtained from reaction of $\text{Ph}_2\text{PbI}_2$ with $[\text{Zn(DMIT)}_2][\text{Et}_4\text{N}]_2$ or by addition of $\text{M}\text{I}$ to 84, respectively. An attempt to prepare the anionic triorganolead complex by the reaction of $\text{Ph}_3\text{PbOAc}$ with either Na\textsubscript{2}(DMIT) or $[\text{Zn(DMIT)}_2][\text{Et}_4\text{N}]_2$ yields the neutral compound ($\text{Ph}_3\text{Pb}$)$\textsubscript{2}$ (DMIT) (85). X-ray investigation revealed 85 to be a monomeric compound with each Pb atom having a distorted tetrahedral geometry\textsuperscript{308}.

The monocyclic dithiolato halo plumbates, 86a–c, were synthesized by the condensation of diphenyllead dichloride with toluene-3,4-dithiol in the presence of Et\textsubscript{3}N, followed by the addition of tetraethylammonium halide as shown in equation 15\textsuperscript{327}.

Compounds 86b and 86c are the only representatives of five-coordinated plumbates, whose structures were proved so far by X-ray diffraction. The Pb atoms in the anions of these compounds have a distorted TBP geometry, which is close to the related dithiolato monocyclic tin structures (Table 15). In particular, the $\text{S}_{ax}\text{Mc}_{ax}$ and $\text{C}_{eq}\text{Mc}_{eq}$ angles (M = Pb, Sn) in the chloro derivative 86b and its Sn analogue, 81, are 165.8 and 165.9°, 127.6 and 121.2°, respectively. Thus, in the former the extent of the TBP → RP distortion is greater than for the stannate 81. The arrangement at the central atom in bromide 86c is presumably close to RP when compared with compounds 86b and 81, as evidenced by the values of the $\text{S}_{ax}\text{PbBr}_{ax}$ and $\text{C}_{eq}\text{PbC}_{eq}$ angles (166.2 and 129.9°, respectively)\textsuperscript{327}.

2. Spiro cyclic derivatives

a. Germanium. Two bidentate oxo or related ligands at the central atom form a complex with a spiro arrangement around this atom. The earlier example of such compounds is the hexafluorocumyl alcohol derivatives 87 (R = Me, n-Bu, All, Ph), which were synthesized.
from nucleophilic addition of RLi to the corresponding tetracoordinated precursor, followed by an exchange with Et₄NX. The anion in 87a M = Ge according to X-ray diffraction is primarily TBP as the OGeO angle widens to 173.8° and the internal OGeC angles narrow to an average of 83.4° (see Table 17 below). The Ge–O and Ge–C bond lengths are increased relative to those of the tetracoordinated precursors, with the axial Ge–O bond being lengthened much more than the equatorial Ge–C bonds (average increases ca. 0.2 and ca. 0.05 Å). Two spirocyclic germanium complexes, 88 and 89, both containing HOGeO₄ moiety, were recently described. The former was prepared from germanium dioxide, pinacol and methanol in the presence of sodium hydroxide. X-ray diffraction of 88·3H₂O reveals that the Ge atom in the anion of the sodium derivative has the TBP geometry with one O atom of each bidentate ligand and the hydroxo group in equatorial positions. The other two O atoms of the bidentate ligands are in axial sites (angle 173.5°). The Ge–O(H) bond length (1.769 Å) is slightly shorter than the other two equatorial Ge–O bonds (1.796 and 1.806 Å), which in turn are significantly shorter than the axial Ge–O bonds (1.866 and 1.870 Å), as expected. In contrast, the lithium derivative 89 contains a pentacoordinate germanium in a spirocyclic arrangement as part of a polymer chain due to the O⋯Li contacts, with the Ge atom array having an almost RP structure (the trans-basal angles are 150.7 and 150.2°).

Holmes and his coworkers described a number of pentacoordinated anionic germanium complexes containing a spirocyclic framework with methyl, phenyl, halogen or hydroxyl ligand at the acyclic site. Reaction of an organogermainium trichloride with a catechol or thiocatechol derivative in the presence of triethylamine, followed by a metathetical exchange, led to desired products as illustrated by the formation of the phenyl-substituted derivatives 90 and 91 (equation 16).

Analogously, the tetrachlorocatechol derivative [(o-OC₆Cl₄O)₂GePh][Et₄N] (92), as well as methyl-substituted germanates, namely [(o-OC₆H₄O)₂GeMe][Et₄N] (93) and [(o-OC₆Cl₄O)₂GeMe][Et₄N] (94), were prepared.
(87) (a) R = n-Bu, R¹ = Et

(88)

(89)

(90)

\[ \text{2 OH} \xrightarrow{\text{PhGeCl₃, 4Et₃N}} [\text{C}_6\text{H}_4\text{O}_2]_2\text{GePh}[\text{Et}_3\text{NH}] \]

(16)

(91)
A number of spirocyclic tetra-, penta- and hexacoordinated germanium complexes have been described in the course of studying interaction between GeCl₄ and catechol, 3,5-di-tert-butylcatechol and toluene-3,4-dithiol in the presence of triethylamine. Among them, the spirocyclic systems, bis(o-phenylenedioxy)germane as a water adduct (o-OC₆H₄O)₂Ge·2H₂O (95) and (TDT)₂Ge (96), are precursors of the neutral and anionic hypervalent germanium compounds. In particular, halogermanates 97a–c were obtained by the reaction of 95 with the corresponding tetraethylammonium halide. Their hydrolytic stability decreases in the order F > Cl > Br.

Unlike catechol, 3,5-di-tert-butylcatechol reacts with GeCl₄ and Et₃N to yield the penta-coordinated 3,5-di-tert-butylcatecholato (DTBC) germanate [(DTBC)₂GeCl][Et₃NH]. The latter gives the corresponding hydroxyl derivative [(DTBC)₂Ge(HO)][Et₃NH] (98) by the action of water.

As for dithiagermanate derivatives, the methyl-substituted compound containing the TDT ligand, 99, was prepared analogously by the reaction given in equation 16 using toluene-3,4-dithiol, triethylamine and MeGeCl. In turn, the air-unstable fluoro-thio germanate [(TDT)₂GeF][Et₄N] was obtained by the reaction of 96 with tetraethylammonium fluoride while the more stable germanate 100 was synthesized by the reaction of 96 with [MePPh₃][Br] and KF.
The synthetic route to the oxo-thio mixed-ligand halo germanates 101a–d\textsuperscript{335} is similar to the synthesis for related oxo derivatives 97a–c\textsuperscript{307,334}. In the first stage the tetracoordinated spirocyclic system is formed. In a following reaction with an appropriate halide reagent the desired product is easily obtained for all of the halides (equation 17)\textsuperscript{335}.

\[
\begin{align*}
\text{GeCl}_4 + 4\text{HCl} & \rightarrow \text{Ge} \underbrace{\text{S}}_{\text{SH}} \underbrace{\text{O}}_{\text{OH}} \\
\text{Et}_4\text{NX} & \rightarrow \text{Ge} \underbrace{\text{S}}_{\text{X}} \underbrace{\text{O}}_{\text{X}}
\end{align*}
\]

(101) (a) X = F  
(b) X = Cl  
(c) X = Br  
(d) X = I

Systematic studies of the distortion coordinate for anionic five-coordinated germanium and tin chelates as a model for nucleophilic substitution have been carried out by Holmes and his coworkers\textsuperscript{316,332,333,335,336}. The Ge atom in spirocyclic germanates varying in the ring composition and the nature of a monodentate ligand lies on the coordinate connecting a trigonal bipyramid (TBP) to a square or rectangular pyramid (RP) having four basal chalcogen atoms (X, Y = O, S) and an apical group Z (Z = Me, Ph, Hal, OH), where Z is pivotal in the Berry pseudorotation process (Scheme 6).

\[
\begin{align*}
\text{Trigonal bipyramid} & \rightarrow \text{Rectangular pyramid} \\
X_{\text{ax}} - M - X'_{\text{ax}} & \rightarrow X_{\text{ax}} - M - X'_{\text{ax}} \\
Y_{\text{eq}} - M - Y'_{\text{eq}} & \rightarrow Y_{\text{eq}} - M - Y'_{\text{eq}}
\end{align*}
\]

M = Ge, Sn; X,X', Y,Y' = O, S; Z = Me, Ph, Hal, OH

SCHEME 6. Relationship between trigonal bipyramid and rectangular pyramid for pentacoordinated spirocyclic germanium and tin complexes

Some geometrical parameters for spirocyclic germanates, including the extents of distortions away from TBP toward RP structure calculated using the dihedral method, initially outlined by Mütterties and Guggenberge\textsuperscript{337} and further developed by Holmes
and his coworkers\textsuperscript{316,328}, have been compiled in Table 17. Large structural variations were reported, between 22.6\% deviation in \textcolor{red}{93} from a near-ideal TBP to an almost perfect RP, with a calculated 95.7\% deviation from TBP in \textcolor{red}{98}. A convenient view of the extents of the structural distortions for pentacoordinated species can be obtained from the changes in the axial and equatorial angles of the TBP, which become the \textit{trans}-basal angles of the corresponding RP. These structural variations are parallel to the progress along the Berry pseudorotation reaction coordinate, in which RP is the assumed transition state.

The unique apical bond becomes shorter, in general, as the pentacoordinated structure more closely approaches the RP in accordance with the VSEPR theory\textsuperscript{334,345}. For example, the Ge–F bond length in \textcolor{red}{97a} (1.727 Å, for TBP $\rightarrow$ RP 80.6\%) is significantly shorter than that in \textcolor{red}{100} (1.780 Å, for TBP $\rightarrow$ RP 40.3\%). Highly electronegative monodentate ligands drive the structure toward the RP geometry. Thus, the extent of approaching to RP increases in the order $\text{Br} < \text{Cl} < \text{F}$ for the most halo germanates, with one exception of the chloro derivative \textcolor{red}{97b}. More electronegative substituents in the bidentate ligand such as tetrachlorocatechol (\textcolor{red}{92} and \textcolor{red}{94}) give an analogous result.

It is noteworthy that the Et\textsubscript{3}NH\textsuperscript{+} salt \textcolor{red}{90} is closer to RP in comparison with the Et\textsubscript{4}N\textsuperscript{+} salt \textcolor{red}{91} due to hydrogen bonding to the cation which lengthens the Ge–O bonds\textsuperscript{333}. Analogously, compound \textcolor{red}{98} with geometry closer to RP contains an apical hydroxyl group that is also hydrogen bonded to the triethylammonium cation\textsuperscript{335}.

When the ring atoms in a spirocyclic system are different as in the mixed-ligand-containing germanates \textcolor{red}{101b} and \textcolor{red}{101c}, the structure tends to be close to the TBP. This is a consequence of the disparity in electronegativity between the ring atoms and the preference for the positioning of the more electronegative ring atom in the axial site of the TBP\textsuperscript{335}. For the most part, however, the structural variations are understandable in terms of substituent effects, and more complete discussions are available elsewhere\textsuperscript{332,333}.

The degree of TBP $\rightarrow$ RP distortions in the spirocyclic anionic and zwitterionic germanates (Section IV.B.3) is rather similar to that observed for the corresponding silicon analogues\textsuperscript{42} for a comparable set of ligands, although as a rule the structures of Si analogues are close to the TBP.

\textit{b. Tin.} A series of the stable anionic tin complexes \textcolor{red}{87}, $M = \text{Sn} (R = \text{Me, Bu, Ph, } p$-$\text{MeC}_6\text{H}_4; R^1 = \text{Me, Et, } n$-$\text{Bu}$), the Sn analogues of germanium hexafluorocumyl alcohol derivatives \textcolor{red}{87}, $M = \text{Ge}$, was prepared by the reaction of their tetracoordinated precursor with RLi followed by an exchange with a tetraalkylammonium halide\textsuperscript{346}. Reaction of \textcolor{red}{87}, $M = \text{Sn} (R = \text{Ph, } p$-$\text{MeC}_6\text{H}_4)$ with SO\textsubscript{2}Cl\textsubscript{2} gave the corresponding chlorostannates \textcolor{red}{87}, $M = \text{Sn} (R = \text{Cl})$, which were converted to fluorostannate \textcolor{red}{87}, $M = \text{Sn} (R = F, R^1 = n$-$\text{Bu})$ by reaction with Bu\textsubscript{4}NF. Its anion has a distorted TBP structure as shown by X-ray crystallography.

Attempts to obtain stable pentacoordinated derivatives bearing only ring Sn–O coordination failed\textsuperscript{316}, in contrast with the predominant formation of ring Ge–O bonding in anionic spirogermanates (see above). In particular, the hexacoordinated dianionic tris(catecholate), [($\text{o}$-$\text{OC}_6\text{H}_4\text{O}$)$_3$$\text{Sn}$][Et\textsubscript{3}NH\textsubscript{2}] (\textcolor{red}{102}), was formed from unstable [$($\text{o}$-$\text{OC}_6\text{H}_4\text{O}$)$_2$$\text{SnPh}$][Et\textsubscript{3}NH] (\textcolor{red}{103}) by hydrolytic scission of the Sn–C(phenyl) bond. Intermediate \textcolor{red}{103} was obtained from phenylstannonic acid and catechol in the presence of Et\textsubscript{3}N\textsuperscript{336}.

More stable mixed-ligand five-coordinated species \textcolor{red}{104a, b} were synthesized by reaction of Sn(OAc)$_4$, with $\text{o}$-mercaptophenol followed by halide salt addition (equation 18)\textsuperscript{336}.

The fluoro stannate \textcolor{red}{104a} like the phenyl derivative \textcolor{red}{103} is not sufficiently stable and gives the hexacoordinated salt [($\text{C}_6\text{H}_4\text{OS}$)$_3$Sn]$_2$[H$_3$][Et\textsubscript{4}N] (\textcolor{red}{105}) upon recrystallization as a result of hydrolysis. Hexacoordination of the tin atoms in \textcolor{red}{102} and \textcolor{red}{105} was proved by X-ray studies\textsuperscript{336}.
TABLE 17. Some geometrical parameters and percent (TBP → RP) deviation for anionic and zwitterionic pentacoordinated spirocyclic germanium complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ge−Z</th>
<th>Ge−X(X′)</th>
<th>Ge−Y(Y′)</th>
<th>XGeX′</th>
<th>YgeY′</th>
<th>XGeY</th>
<th>TBP → RP (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(o-OC₆H₄C(CF₃)₃)₂2GeBu][Et₄N] (87a, M = Ge)</td>
<td>1.947</td>
<td>1.989</td>
<td>1.951</td>
<td>173.8</td>
<td>119.2</td>
<td>83.4</td>
<td>—</td>
<td>329</td>
</tr>
<tr>
<td>[(HO)Ge(L)₂][Na]·3H₂O (88)</td>
<td>1.769</td>
<td>1.868</td>
<td>1.801</td>
<td>173.5</td>
<td>123.8</td>
<td>87.5</td>
<td>—</td>
<td>330</td>
</tr>
<tr>
<td>(89)·H₂O</td>
<td>1.772</td>
<td>1.826</td>
<td>1.824</td>
<td>150.7</td>
<td>150.2</td>
<td>87.4</td>
<td>—</td>
<td>331</td>
</tr>
<tr>
<td>[(o-OC₆H₄O)₂2GePh][Et₃NH]·MeCN (90)</td>
<td>1.937</td>
<td>1.883</td>
<td>1.832</td>
<td>150.5</td>
<td>141.8</td>
<td>86.2</td>
<td>82.2 (59.4)</td>
<td>333</td>
</tr>
<tr>
<td>[(o-OC₆H₄O)₂2GePh][Et₄N] (91)</td>
<td>1.936</td>
<td>1.890</td>
<td>1.846</td>
<td>160.1</td>
<td>134.0</td>
<td>86.3</td>
<td>51.8 (29.5)</td>
<td>333</td>
</tr>
<tr>
<td>[(o-OC₆H₄O)₂2GeMe][Et₄N] (92)</td>
<td>1.930</td>
<td>1.874</td>
<td>1.871</td>
<td>150.7</td>
<td>143.3</td>
<td>85.6</td>
<td>85.2 (89.8)</td>
<td>333</td>
</tr>
<tr>
<td>[(o-OC₆H₄O)₂2GeMe][Et₄N] (93)</td>
<td>1.946</td>
<td>1.920</td>
<td>1.834</td>
<td>166.3</td>
<td>123.1</td>
<td>86.3</td>
<td>22.6</td>
<td>332</td>
</tr>
<tr>
<td>[(o-OC₆H₄O)₂2GeMe][Et₄N] (94)</td>
<td>1.901</td>
<td>1.887</td>
<td>1.873</td>
<td>149.4</td>
<td>142.5</td>
<td>85.2</td>
<td>85.5</td>
<td>332</td>
</tr>
<tr>
<td>[(o-OC₆H₄O)₂2GeF][Et₄N] (97a)</td>
<td>1.727</td>
<td>1.837</td>
<td>1.828</td>
<td>160.8</td>
<td>149.0</td>
<td>87.2</td>
<td>80.6 (68.7, 52.8)</td>
<td>338</td>
</tr>
<tr>
<td>[(o-OC₆H₄O)₂2GeCl][Et₄N] (97b)</td>
<td>2.185</td>
<td>1.847</td>
<td>1.819</td>
<td>157.5</td>
<td>151.6</td>
<td>87.7</td>
<td>90.7</td>
<td>334</td>
</tr>
<tr>
<td>[(o-OC₆H₄O)₂2GeBr][Et₄N] (97c)</td>
<td>2.321</td>
<td>1.842</td>
<td>1.822</td>
<td>160.8</td>
<td>143.9</td>
<td>87.2</td>
<td>70.4</td>
<td>335</td>
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<tr>
<td>[(HO)Ge(DTBC)₂][Et₃NH] (98)</td>
<td>1.766</td>
<td>1.852</td>
<td>1.839</td>
<td>152.0</td>
<td>151.3</td>
<td>87.5</td>
<td>95.7</td>
<td>335</td>
</tr>
<tr>
<td>[(TDT)₂GeMe][Et₄N] (99)</td>
<td>1.97</td>
<td>2.398</td>
<td>2.273</td>
<td>165.2</td>
<td>130.4</td>
<td>87.5</td>
<td>37.1</td>
<td>332</td>
</tr>
<tr>
<td>[(TDT)₂GeF][MePPh₃]·MeCN (100)</td>
<td>1.780</td>
<td>2.336</td>
<td>2.250</td>
<td>171.1</td>
<td>136.2</td>
<td>90.0</td>
<td>40.3</td>
<td>338</td>
</tr>
<tr>
<td>[(o-OC₆H₄O)₂2GeCl][Et₄N] (101b)</td>
<td>2.194</td>
<td>1.898</td>
<td>2.229</td>
<td>171.9</td>
<td>133.5</td>
<td>89.3</td>
<td>34.2</td>
<td>335</td>
</tr>
<tr>
<td>[(o-OC₆H₄O)₂2GeBr][Et₄N]·MeCN (101c)</td>
<td>2.350</td>
<td>2.070</td>
<td>2.226</td>
<td>174.5</td>
<td>129.7</td>
<td>89.3</td>
<td>23.6</td>
<td>335</td>
</tr>
<tr>
<td>(114)·1/4MeCN</td>
<td>2.348</td>
<td>2.070</td>
<td>2.226</td>
<td>174.5</td>
<td>131.1</td>
<td>89.7</td>
<td>26.2</td>
<td>116a</td>
</tr>
<tr>
<td>116a</td>
<td>1.96</td>
<td>1.889</td>
<td>1.832</td>
<td>167.2</td>
<td>128.0</td>
<td>86.7</td>
<td>38.9 (21.0)</td>
<td>340</td>
</tr>
<tr>
<td>(116b)·H₂O</td>
<td>1.954</td>
<td>1.935</td>
<td>1.779</td>
<td>171.5</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>341</td>
</tr>
<tr>
<td>(116d)·H₂O</td>
<td>1.947</td>
<td>1.921</td>
<td>1.786</td>
<td>170.8</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>341</td>
</tr>
<tr>
<td>(116f)·H₂O</td>
<td>1.955</td>
<td>1.924</td>
<td>1.792</td>
<td>171.2</td>
<td>121.3</td>
<td>87.2</td>
<td>14.0 (13.4)</td>
<td>343</td>
</tr>
<tr>
<td>(117)·H₂O</td>
<td>1.935</td>
<td>1.907</td>
<td>1.777</td>
<td>172.2</td>
<td>122.7</td>
<td>86.9</td>
<td>13.9 (11.5)</td>
<td>344</td>
</tr>
</tbody>
</table>

* A description of ligands is given in scheme 6; L = 2,3-dimethylbutane-2,3-diolato-O,O′.

* Z is the pivotal ligand in the Berry pseudorotation process.

* Average value.

* The XGeX′ and YGeY′ angles are the axial and equatorial angles of the TBP, which correspond to trans-basal angles of the corresponding RP.

* The percent displacement from the ideal TBP toward the RP is calculated from unit bond distances on the basis of the dihedral angle method. 316, 328.

* 1.897 for H-bonded.

* 1.870 for H-bonded.

* For the Si analogue.

* Two crystallographically independent species.
16. Hypervalent compounds of organic germanium, tin and lead derivatives

In contrast to homo-ligand oxo spirostannates, pentacoordinated anionic stannates exhibiting only Sn–S bonding with cyclic compounds are well known. This was attributed to the special stability of Sn–S bonding in these compounds provided by a proper balance of low tin atom electronegativity vs. the tendency of Sn to increase its coordination number toward hexacoordinate when Sn–O bonds are present, by virtue of the resultant greater tin acidity. The synthetic procedure used for the preparation of the bicyclic derivatives 106 and 107 containing saturated EDT rings is given in equations 19.

\[
\text{RSnCl}_3 + \text{Et}_4\text{NCl} \xrightarrow{\text{Me}_2\text{CO}} [\text{RSnCl}_4][\text{Et}_4\text{N}] \\
\text{not isolated}
\]

\[
[\text{RSnCl}_4][\text{Et}_4\text{N}] + 2\text{Na}_2(\text{SCH}_2\text{CH}_2\text{S}) \xrightarrow{\text{MeOH}, \text{Me}_2\text{CO}} 4\text{NaCl} + \left[\begin{array}{c}
\text{S} \\
\text{S} \\
\text{Sn} \\
\text{S} \\
\text{S}
\end{array}\right] [\text{Et}_4\text{N}] \\
(106) \text{R} = \text{n-Bu} \\
(107) \text{R} = \text{Ph}
\]

When the same procedure was used with MeSnCl₃, only the binuclear tin species 83a was formed (see above). Moreover, in addition to the mononuclear stannate 106 (equation 19), n-BuSnCl₃ reacts with Na₂(EDT) yielding the binuclear derivative 83b under other conditions (a shorter reaction time, 1 : 1.5 molar ratio). Thus, the formation of the binuclear species 83a,b as intermediates was suggested for reactions leading to the bicyclic stannates 106 and 107.

The bicyclic distannates 108a and 108b were formed presumably as partial hydrolysis products by the reaction of Sn(EDT)₂ with the corresponding amine. The \(^{119}\text{Sn}\) NMR spectra of 107 and 108a in MeCN show single resonances in the range \(-15\) to \(-82\) ppm that are consistent with their five-coordinated tin structures in solution.

The syntheses of bicyclic analogues of the monocyclic 73 containing ring unsaturation, namely stannates 109a and 109b, are similar to those for their saturated EDT derivatives and involve the reaction of organotin trichloride, tetraalkylammonium halide and Na₂(MNT)₃. In the reaction of PhSnCl₃ with Na₂(MNT) and Et₄NCl, Sn–C bond cleavage occurs with formation of the tricyclic stannate [Sn(MNT)₃][Et₄N][Na] (110), most likely as a result of the presence of adventitious water. Unlike in monocyclic 73 which has a near-TBP arrangement about the tin atom, the geometries of the bicyclic stannates 109a and 109b are square pyramidal, while in stannate 110 the geometry is distorted octahedral with an average Sn–S bond length at ca 2.54 Å, which is ca 0.03 Å longer than that for the pentacoordinated 109a and 109b.
The general synthetic route to the other types of pentacoordinated unsaturated spirostan-

ates, namely DMIO 111347 and DMIT 112348,349 derivatives, involves the reaction of an organotin trichloride with the appropriate zinc salt (equation 20).

\[
\text{RSnCl}_3 + [\text{Zn(L)}_2][\text{M}]_2 \rightarrow \text{M}^+ \text{Sn}[\text{E=S, } R=n-\text{Bu, } M=\text{Bu}_4\text{N}]
\]

(20)

= DMIO, DMIT

\[
(111\text{a}) \text{ E} = \text{O, } R = \text{CH}_2\text{CH}_2\text{COOMe}, M = \text{Et}_4\text{N}
(111\text{b}) \text{ E} = \text{O, } R = \text{CH}_2\text{CH}_2\text{COOMe}, M = \text{DMP}
(111\text{c}) \text{ E} = \text{O, } R = \text{CH}_2\text{CH}_2\text{COOMe}, M = \text{Ph}_4\text{P}
(112\text{a}) \text{ E} = \text{S, } R = n-\text{Bu}, M = \text{Bu}_4\text{N}
(112\text{b}) \text{ E} = \text{S, } R = \text{Ph}, M = \text{Bu}_4\text{N}
(112\text{c}) \text{ E} = \text{S, } R = \text{CH}_2\text{CH}_2\text{COOMe}, M = \text{Et}_4\text{N}
(112\text{d}) \text{ E} = \text{S, } R = \text{CH}_2\text{CH}_2\text{COOMe}, M = \text{DMP}
\]
Among L = DMIO, (L = O), DMIT (L = S) compounds 111 and 112, those containing the ROOCCH₂CH₂Sn moiety, so-called ‘estertin’ compounds, are of particular interest due to the ability of the ROOCCH₂CH₂ unit to act as a chelating ligand utilizing the carbonyl oxygen as an additional donor center. Indeed, as shown by X-ray crystallography, the tin atoms in the anions of 111a and 112d from five strong bonds to carbon and the four thiolato S atoms (Sn−S 2.46 to 2.56 Å). The arrangement of these five bonds about tin is between TBP and RP, but close to the former for 111a and to the latter for 112d (Table 18). There is an additional intramolecular, but weaker, interaction with the carbonyl oxygen atom (Sn−O = 3.11, 3.37 Å, respectively), and tin becomes six-coordinate with a much distorted octahedral geometry. Correspondingly, the ν(C=O) value in the solid state of ca 1714 cm⁻¹ for 111a and 112d is between that for a coordinated and noncoordinated ester group (1670–1680 and 1730–1740 cm⁻¹, respectively). However, the situation for 112c is different from that found for 111a and 112d. In the anion of 112c the ‘estertin’ group acts as a monodentate ligand, with the carbonyl oxygen being directed away from the tin atom (Sn⋅⋅⋅O 4.84 Å), which is more than the sum of the van der Waals radii of Sn and O. This difference can be related to crystal packing effects.

Whereas the DMIO and DMIT ligands in 111a and 112a–d are individually planar, the compounds are not coplanar and the tin atoms are displaced from the basal planes in a direction toward the apical R groups. For example, the angles between the DMIT mean planes in 112a and 112b are 19.2 and 10.8° while the corresponding displacements from the basal plane for these compounds are 0.731 Å and 0.733 Å, respectively. The δ¹¹⁹Sn values of 112a and 112b in CDCl₃ solution are only slightly different than those in the solid state (Table 18). Hence, there are no major changes in the molecular structures on passing from the solid state to solution. Comparison of δ¹¹⁹Sn values for 112b in CDCl₃ and 107 in MeCN (−21.9 and −82.4 ppm, respectively) indicates that the DMIT ligand causes a larger shift to a lower field than that caused by the EDT ligand. In turn, the tin atoms in the spirocyclic DMIO complexes are more upfield shielded than in the DMIT analogues as indicated by comparison of the δ¹¹⁹Sn values for 111a–c and 112c and 112d (ca −50 ppm in CDCl₃, and ca 6.0 ppm in CD₃COCD₃, respectively).

Anionic spirocyclic pentacoordinate tin species having aromatic rings, namely bis(TDT) complexes 113a and 113b, were prepared in high yields by addition of halide ion to bis(toluene-3,4-dithiolato)tin, Sn(TDT)₂, (equation 21).

As in the spirocyclic five-coordinated germanium complexes discussed above, the geometry about the tin atom in some of the mono- and bi-cyclic stannates, listed in
<table>
<thead>
<tr>
<th>Compound</th>
<th>Sn–Z (Å)(^b)</th>
<th>Sn–X(Z') (Å)(^c)</th>
<th>Sn–Y(Y') (Å)(^c)</th>
<th>XSnX' (deg)(^d)</th>
<th>YSnY' (deg)(^d)</th>
<th>XSnY (deg)</th>
<th>TBP → RP (%)(^e)</th>
<th>(\delta^{119}\text{Sn}) (ppm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{o-OC}_6\text{H}_4\text{C}(\text{CF}_3)_2)_2\text{SnF})[\text{Et}_4\text{N}] (87a, M = Sn)</td>
<td>1.992</td>
<td>2.105</td>
<td>2.085</td>
<td>178.7</td>
<td>135.4</td>
<td>81.4</td>
<td>—</td>
<td>—</td>
<td>346</td>
</tr>
<tr>
<td>((\text{o-OC}_6\text{H}_4\text{S})_2\text{SnCl})[\text{Et}_4\text{N}] (104b)</td>
<td>2.362</td>
<td>2.054</td>
<td>2.397</td>
<td>169.7</td>
<td>134.0</td>
<td>85.4</td>
<td>38.0</td>
<td>—</td>
<td>336</td>
</tr>
<tr>
<td>((\text{EDT})_2\text{SnBu})[\text{Et}_4\text{N}] (106)</td>
<td>2.17</td>
<td>2.522</td>
<td>2.473</td>
<td>153.5</td>
<td>142.3</td>
<td>85.6</td>
<td>78.7</td>
<td>—</td>
<td>325</td>
</tr>
<tr>
<td>((\text{EDT})_2\text{SnPh})[\text{Et}_4\text{N}] (107)</td>
<td>2.17</td>
<td>2.530</td>
<td>2.472</td>
<td>159.2</td>
<td>137.6</td>
<td>86.3</td>
<td>60.2</td>
<td>—</td>
<td>325</td>
</tr>
<tr>
<td>((\text{EDT})_2\text{SnSCH}_2)[\text{Et}_3\text{NH}]_2 (108a)</td>
<td>2.444</td>
<td>2.515</td>
<td>2.438</td>
<td>169.0</td>
<td>130.9</td>
<td>86.9</td>
<td>33.6</td>
<td>—</td>
<td>325</td>
</tr>
<tr>
<td>((\text{EDT})_2\text{SnMe})[\text{Et}_4\text{N}] (109a)</td>
<td>2.130</td>
<td>2.519</td>
<td>2.480</td>
<td>150.2</td>
<td>140.7</td>
<td>85.1</td>
<td>80.4</td>
<td>—</td>
<td>316</td>
</tr>
<tr>
<td>((\text{DMIT})_2\text{SnBu})[\text{Et}_4\text{N}] (109b)</td>
<td>2.142</td>
<td>2.521</td>
<td>2.516</td>
<td>144.8</td>
<td>144.8</td>
<td>85.2</td>
<td>96.7</td>
<td>—</td>
<td>316</td>
</tr>
<tr>
<td>((\text{DMIT})_2\text{SnBu}[\text{CH}_2\text{CH}_2\text{COOMe}])[\text{Et}_4\text{N}] (111a)</td>
<td>2.136(^g)</td>
<td>2.571</td>
<td>2.480</td>
<td>164.3</td>
<td>117.1</td>
<td>85.3</td>
<td>—</td>
<td>-51.3(^{h,i})</td>
<td>347</td>
</tr>
<tr>
<td>((\text{DMIT})_2\text{SnBu})[\text{Bu}_4\text{N}] (112a)</td>
<td>2.29</td>
<td>2.549</td>
<td>2.461</td>
<td>157.5</td>
<td>127.7</td>
<td>85.0</td>
<td>47.8</td>
<td>27.0(^h,i) (37.6)(^k)</td>
<td>348</td>
</tr>
<tr>
<td>((\text{DMIT})_2\text{SnPh})[\text{Bu}_4\text{N}] (112b)</td>
<td>2.17</td>
<td>2.523</td>
<td>2.483</td>
<td>152.3</td>
<td>136.8</td>
<td>84.9</td>
<td>69.5</td>
<td>-21.9(^h) (−9.4)(^k)</td>
<td>348</td>
</tr>
<tr>
<td>((\text{DMIT})_2\text{Sn}[\text{CH}_2\text{CH}_2\text{COOMe}])[\text{Et}_4\text{N}] (112c)</td>
<td>2.147</td>
<td>2.546</td>
<td>2.476</td>
<td>155.4</td>
<td>133.6</td>
<td>85.6</td>
<td>63</td>
<td>5.7(^l,m) (32.5)(^k)</td>
<td>349</td>
</tr>
<tr>
<td>((\text{DMIT})_2\text{Sn}[\text{CH}_2\text{CH}_2\text{COOMe}])[\text{DMP}] (112d)</td>
<td>2.151(^n)</td>
<td>2.525</td>
<td>2.496</td>
<td>149.9</td>
<td>133.4</td>
<td>85.3</td>
<td>70</td>
<td>6.2(^l) (57.3)(^k)</td>
<td>349</td>
</tr>
<tr>
<td>((\text{TDT})_2\text{SnCl})[\text{Me}_4\text{N}] (113a)</td>
<td>2.413</td>
<td>2.460</td>
<td>2.442</td>
<td>161.3</td>
<td>147.6</td>
<td>86.3</td>
<td>76.9</td>
<td>—</td>
<td>324</td>
</tr>
<tr>
<td>((\text{TDT})_2\text{SnBr}[\text{Me}_3\text{PPh}_4] (113b)-2\text{C}_6\text{H}_6)</td>
<td>2.529</td>
<td>2.458</td>
<td>2.455</td>
<td>155.7</td>
<td>152.0</td>
<td>85.9</td>
<td>94.2</td>
<td>—</td>
<td>336</td>
</tr>
</tbody>
</table>

\(^a\) For a description of ligands, see Scheme 6.

\(^b\) Z is the pivotal ligand in the Berry pseudorotation process.

\(^c\) Average value.

\(^d\) The XSnX' and YSnY' angles are the axial and equatorial angles of the trigonal bipyramids, which correspond to trans-basal angles of the corresponding rectangular pyramids.

\(^e\) The percent displacement from the ideal TBP toward the RP is calculated from unit bond distances on the basis of the dihedral angle method.\(^316,328\)

\(^f\) In CH\(_3\)CN.

\(^g\) An additional intramolecular Sn–O interaction at 3.111 Å.

\(^h\) In CDCl\(_3\).

\(^i\) \(^1\)J\(^{119}\text{Sn}–^{13}\text{C}\) 622 Hz.

\(^j\) \(^1\)J\(^{119}\text{Sn}–^{13}\text{C}\) 510 Hz.

\(^k\) In the solid state.

\(^l\) In CD\(_3\)COCD\(_3\).

\(^m\) \(^1\)J\(^{119}\text{Sn}–^{13}\text{C}\) 636.4 Hz.

\(^n\) An additional intramolecular Sn–O interaction at 3.371 Å.
Tables 14, 15 and 18, was analyzed as being on the coordinate connecting an ideal TBP with an ideal SP or RP\textsuperscript{316}. The extents of the TBP $\rightarrow$ RP distortions have been quantified using the dihedral method\textsuperscript{316,325,336,348} and from the changes in the axial and equatorial angles of TBP, which become the trans-basal angles of the corresponding RP, as discussed above for the spirocyclic germanates.

Generally, the monocyclic stannates have geometries approaching the TBP (TBP $\rightarrow$ RP, 6–50%), while the geometrical arrangement for the most bicyclic bis(dithiolato) stannates is based on the square or rectangular pyramid (48–97%)\textsuperscript{316}. Comparison of the TBP $\rightarrow$ RP distortions for the monocyclic stannates with Ph$_3$Sn and R$_2$(Hal)Sn frameworks (Tables 14 and 15) indicates that the structures of diphenylhalo tin complexes are less close to a RP (6–24%) than their triphenyltin analogues (30–50%). The extents of the distortion of TBP geometry for the mono- and bicyclic EDT, MNT and DMIT derivatives are close. In the case of spirocyclic stannates, introduction of dissimilar bonding ring atoms, in particular O and S, as in \textsuperscript{104b}\textsuperscript{336}, allows the apicophilicity rule\textsuperscript{350} to take preference over the ring-strain effect and causes structural displacement back to the inherently more stable TBP (TBP $\rightarrow$ RP, 38% for \textsuperscript{104a} as compared 76.9% for \textsuperscript{113a})\textsuperscript{336}.

The axial Sn–S$_{ax}$ bond lengths for the monocyclic stannates (Table 15) are longer than the equatorial Sn–S$_{eq}$ distances (at ca 0.15 Å), of the order expected for trigonal bipyramids\textsuperscript{324}. The differences in the Sn–S bond lengths, $\Delta$(Sn–S), for bis(dithiolato) stannates can be also used as a reflection of the distortions from regular rectangular pyramidal arrays: generally, the smaller the $\Delta$(Sn–S), the closer is the structure to that of a RP. In particular, a residual TBP character is apparent in compounds \textsuperscript{106, 107} and \textsuperscript{108a} in that the Sn–S$_{ax}$ bonds (2.49–2.54 Å) are longer than the Sn–S$_{eq}$ bonds (2.42–2.48 Å)\textsuperscript{325}. The Sn–S$_{ax}$ bond lengths at 2.540 Å found in \textsuperscript{108a} are longer in comparison with those for other stannanes given in Table 18. This is evidently due to S···H hydrogen bonding to the cation which lengthens the corresponding Sn–S bond.

For the spirocyclic tin complexes \textsuperscript{113a} and \textsuperscript{109b}, the Sn–S bond lengths are much closer. They are two shorter ones, averaging 2.458 and 2.521 Å, and two longer ones, averaging 2.455 and 2.516 Å, respectively\textsuperscript{324}. This small difference is indicative of a residual TBP character that was expressed by the ca 94 and 97% displacement toward RP.

For the monocyclic stannates \textsuperscript{106} and \textsuperscript{107}, the Sn–S bond lengths are much closer. They are two shorter ones, averaging 2.458 and 2.521 Å, and two longer ones, averaging 2.455 and 2.516 Å, respectively\textsuperscript{324}. This small difference is indicative of a residual TBP character that was expressed by the ca 94 and 97% displacement toward RP.

In general, solid-state five-coordinated tin structures lie along the Berry pseudorotational coordinate as an expression of their structural nonrigidity. Comparison with other elements of group 14 shows that the nonrigid character increases along the series Si < Ge < Sn as determined by the ease of TBP $\rightarrow$ RP structural distortion\textsuperscript{316,335}. For example, the TBP $\rightarrow$ RP distortions are 80.6 and average ca 61% for the germanium derivative \textsuperscript{97a} and its Si analogue, 40.3, 76.9 and 94.2% for the chloro germanate \textsuperscript{100a} and the halo stannates \textsuperscript{113a} and \textsuperscript{113b}, as well as 34.2 and 38.0% for the mixed-ligand complexes \textsuperscript{101b} and \textsuperscript{104b} (Tables 17 and 18)\textsuperscript{335}.

3. Zwitterionic spirogermanates

Tacke and his coworkers have recently reported the synthesis and structural characterization of a series of pentacoordinated anionic germanium complexes based on the GeO$_4$C ligand framework\textsuperscript{340–344}. The route to these compounds involves the reaction of (chloromethyl)trimethoxygermane with a secondary amine in the presence of triethylamine, followed by an exchange with two equivalents of bidentate ligands, such as aromatic 1,2-diols or $\alpha$-hydroxycarboxylic acids, as shown for the synthesis of \textsuperscript{114} (equations 22 and 23).
The catechol or glycolic acid derivatives, 115a–c and 116a–f, including the dinuclear germanate 117, were prepared similarly.

(115a) NR₃ = NMe₂H  
(115b) R = Me  
(115c) NR₃ = c-HN(CH₂)₂O

(116a) R = Me, R¹ = H  
(116b) R = R¹ = Me  
(116c) R = Me, R¹ = Ph  
(116d) NR₂ = c-N(CH₂)₂O, R¹ = H  
(116e) NR₂ = c-N(CH₂)₂O, R¹ = Me  
(116f) NR₂ = c-N(CH₂)₂O, R¹ = CH₂COOH

(117)
As shown by X-ray crystallography, the coordination polyhedra surrounding the Ge atoms of zwitterionic germanates can be described as more or less distorted TBP with the carboxylate oxygen atoms in axial positions while the carbon atom and two other oxygen atoms occupy equatorial positions. The axial Ge−O distances (1.89–1.92 Å) are significantly longer than the equatorial ones (1.78–1.83 Å). These values as well as the Ge−C distances (1.89–1.92 Å) are similar to the Ge−O and Ge−C distances of related anionic spirogermanates with GeO<sub>4</sub>C frameworks (Table 17). The two chiral TBP germanate units in dinuclear germanate exhibit opposite absolute configurations due to the center of inversion. Consequently, its molecular structure represents the meso configuration.

Like the anionic spirogermanates (Table 17), the geometries at germanium in the zwitterionic germanates can be inspected as being in a region between TBP and SP. In terms of the Berry pseudorotation coordinate, the dihedral angle method shows that the geometries of these coordination polyhedra are displaced by 38.9, 11.4, 14.0 and 13.9% for compounds 114, 116a, 116f and 117, respectively, from the ideal TBP to the ideal SP (pivot atom C). These distortions are rather similar to those observed for the corresponding silicon analogues (TBP → SP: 21, -, 13.4 and 11.5%, respectively).

**V. PENTACOORDINATE INTERMOLECULAR NEUTRAL COMPOUNDS**

**A. Germanium**

While SiCl<sub>4</sub> gives structurally investigated hexacoordinate 1 : 2 adducts with donor atoms from only the III period, for example Cl<sub>4</sub>Si·2PMe<sub>3</sub> (P → Si = 2.26 Å), GeCl<sub>4</sub> produces pentacoordinate 1 : 1 adducts, in particular Cl<sub>4</sub>Ge·NMe<sub>3</sub> (N → Ge = 2.19 Å). The smaller coordination number of the former adducts is most likely due to the smaller size of N compared with the P atom (r<sub>cov</sub> = 0.734 and 1.107 Å, respectively) and, consequently, to a larger steric interaction of the ligands in the germanium coordination sphere.

<sup>73</sup>Ge and <sup>14</sup>N NMR spectra were used to study the reaction products and chemical exchange processes in the system GeCl<sub>4</sub> + KSCN + acetone-d<sub>6</sub>. At a GeCl<sub>4</sub> to KSCN ratio from 2 : 1 to 1 : 4, germanium(IV) derivatives of the type Ge(NCS)<sub>n</sub>Cl<sub>n</sub>−4 were formed. Rapid exchange with Cl and NCS groups due to intermolecular interactions was observed between Ge(NCS)<sub>n</sub>Cl<sub>n</sub>−4 (n = 0–4) molecules with varying n.

**B. Tin**

Hypervalent compounds of organic derivatives of tin with nitrogen- and oxygen-containing ligands have been studied extensively by means of various methods, including X-ray diffraction and <sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn NMR spectroscopy. The conclusions concerning the nature of the D → Sn coordination bonds on going from one complex to another have been deduced as a rule on the basis of direct structural parameters (D → Sn bond lengths) and from the changes of indirect spectral parameters such as δ<sup>119</sup>Sn chemical shifts and <sup>1</sup>J(<sup>13</sup>C−<sup>119</sup>Sn) and <sup>2</sup>J(<sup>1</sup>H−<sup>119</sup>Sn) coupling constants.

1. N → Sn coordination

In Table 19, selected bond distances and angles are reported for intermolecular N → Sn<sub>3</sub>X complexes. All adducts have a distorted TBP configuration with the organic groups in the equatorial position and the more electronegative nitrogen and halide or pseudohalide in the axial positions. The smallest N → Sn distance, and hence the strongest donor...
### TABLE 19. Selected structural parameters for tin adducts with N → SnC₃X ligand framework

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>X</th>
<th>N → Sn (Å)</th>
<th>Sn−X (Å)</th>
<th>N → Sn−X (deg)</th>
<th>ΔSn¹</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(C₅H₅N)Me₃SnCl</td>
<td>Cl</td>
<td>2.262</td>
<td>2.426</td>
<td>179.2</td>
<td>−0.01</td>
<td>354</td>
</tr>
<tr>
<td>2</td>
<td>[Me₂ClSnCH₂Sn(NC₃H₅)Cl₂</td>
<td>Cl</td>
<td>2.439</td>
<td>2.638</td>
<td>175.4</td>
<td>0.01</td>
<td>355a</td>
</tr>
<tr>
<td>3</td>
<td>(NMI)Ph₃SnCl²</td>
<td>Cl</td>
<td>2.372</td>
<td>2.546</td>
<td>175.3</td>
<td>0.11</td>
<td>356</td>
</tr>
<tr>
<td>4</td>
<td>[Me₂Cl(N₂C₃H₃)Sn]₂CH₂</td>
<td>Cl</td>
<td>2.459</td>
<td>2.578</td>
<td>174.6</td>
<td>0.11</td>
<td>355a</td>
</tr>
<tr>
<td>5</td>
<td>[(p-Tol)₃SnCl]₂ · 4,4’-bipy</td>
<td>Cl</td>
<td>2.668</td>
<td>2.452</td>
<td>176.0</td>
<td>0.16</td>
<td>357</td>
</tr>
<tr>
<td>6</td>
<td>[Me₂ClSnCH₂SnClMe₂]₂</td>
<td>Cl</td>
<td>2.622</td>
<td>2.524</td>
<td>176.2</td>
<td>0.20</td>
<td>355a</td>
</tr>
<tr>
<td>7</td>
<td>[Me₂ClSnCH₂SnClMe₂]</td>
<td>Cl</td>
<td>2.651</td>
<td>2.473</td>
<td>177.6</td>
<td>0.26</td>
<td>355a</td>
</tr>
<tr>
<td>8</td>
<td>[BrPh₂SnCH₂-1,2,4-triazole]₂</td>
<td>Br</td>
<td>2.463</td>
<td>2.641</td>
<td>170.5</td>
<td>0.12</td>
<td>358</td>
</tr>
<tr>
<td>9</td>
<td>[(p-Tol)₃SnBr]₂ · 4,4’-bipy</td>
<td>Br</td>
<td>2.653</td>
<td>2.619</td>
<td>176.6</td>
<td>0.27</td>
<td>357</td>
</tr>
<tr>
<td>10</td>
<td>[(p-Tol)₃SnI]₂ · 4,4’-bipy</td>
<td>I</td>
<td>2.655</td>
<td>2.830</td>
<td>176.8</td>
<td>0.23</td>
<td>357</td>
</tr>
</tbody>
</table>

¹Toward the halide atom.
²Two independent molecules.
³N₂C₃H₃ = pyrazole.
⁴N₂C₄H₄ = pyridaziné.
⁵For another example of a pentacoordinate ditin complex, 2,6-(i-Pr)₂C₆H₃N(SnMe₂Cl)₂ · Pyr, which contains one bridged chlorine atom, see Reference 355b.

interaction, is found in the derivatives showing the lowest ΔSn. There is also a correlation related to the hypervalent N → Sn−Hal axis in the two independent molecules of entries 2, 3, 7 and 8 in Table 19: as the N → Sn distance becomes shorter, the Sn−X bond tends to become longer.

For compounds [(p-Tol)₃SnHal]₂ · 4, 4’-Bipy, where Hal = Cl (entry 5), Br (9) and I (10), the deviation (Δ) of the tin atom from the equatorial plane decreases on increasing the electron-withdrawing effect of the substituent X: ΔSn(Cl) < ΔSn(I and Br) (Table 19). However, for the pair Br and I this is not true. The same anomaly for I and Br atoms was observed in the coordinate bond length in the range N → Sn(Cl) > N → Sn(I) > and N → Sn(Br).

In two independent molecules of ClPh₃Sn · 1-methylimidazole (NMI, entry 3), one tin atom is displaced by 0.307 Å out of the imidazole plane, whereas the other tin is almost coplanar with the plane of the imidazole donor. Differences in coordination geometries of ligands as well as nonsystematic variations in N → Sn−X angles can be ascribed to crystal packing effects.

The ¹¹⁹Sn NMR spectra of triorganotin(IV) adducts exhibit a single absorption typical of four- to five-coordinate central tin atom. For example, the signals for (1-BzIm)Me₃SnCl (δ¹¹⁹Sn = −14.5 ppm, CDCl₃) and (1-BzIm)Ph₃SnCl (δ¹¹⁹Sn = −125.9 ppm) are shifted upfield with respect to those reported for the starting acceptor (δ¹¹⁹Sn = 154.3 ppm and −48 ppm, respectively).

In diorganotin adducts D → SnR₂X₂ the Sn−X bond length differences between axial and equatorial positions in the pentacoordinate species 118 are of particular interest since they conform quite well to expectations of hypervalent D → Sn−X bonding (Section V.B.3). The longer Sn−Clax bond length by ca. 0.06 Å due to N → Sn donor interaction is consistent with the expected lower s character of the axial bond compared to...
TABLE 20. Selected structural parameters for tin adducts with $N \rightarrow \text{SnR}_2\text{Cl}_2$ ligand framework

<table>
<thead>
<tr>
<th>R</th>
<th>D$a$</th>
<th>$N \rightarrow \text{Sn}$ (Å)</th>
<th>$\text{Sn} - \text{X}_{\text{ax}}$ (Å)</th>
<th>$\text{Sn} - \text{X}_{\text{eq}}$ (Å)</th>
<th>$\Delta \text{Sn}$ (Å)</th>
<th>$N \rightarrow \text{Sn} - \text{X}$ (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>Pyz</td>
<td>2.746</td>
<td>2.424</td>
<td>2.366</td>
<td>0.058</td>
<td>173.2</td>
<td>360</td>
</tr>
<tr>
<td>Ph</td>
<td>Pyz</td>
<td>2.683</td>
<td>2.404</td>
<td>2.340</td>
<td>0.064</td>
<td>178.5</td>
<td>82</td>
</tr>
<tr>
<td>Ph</td>
<td>BzTh$^b$</td>
<td>2.548</td>
<td>2.445</td>
<td>2.335</td>
<td>—</td>
<td>176.2</td>
<td>361</td>
</tr>
</tbody>
</table>

$a$Donor.

$^b$BzTh = benzothiazole.

those of the equatorial bond (Table 20). The tin atom in all adducts is displaced from the least-squares plane defined by the equatorial chloride and carbon atoms in the direction of the axial chloride by an almost identical distance $\Delta \text{Sn} = 0.32$ Å.

An adduct having a composition most closely represented as $\text{SnPh}_2\text{Cl}_2 \cdot \text{Pyz}/(\text{SnPh}_2\text{Cl}_2)_2 \cdot \text{Pyz}$ has a structure composed of layers in which polymeric chains with six-coordinate tin alternate with layers containing noninteracting $\text{SnPh}_2\text{Cl}_2 \cdot \text{Pyz}$ molecules with five-coordinate tin$^82$ (Table 20). The interaction of imidazoles with $R\text{SnX}_3$ proceeded similarly to that with $R_2\text{SnX}_2$. The major difference is the ligand since not only 1 : 1 and 2 : 1 but also 3 : 1 and 3 : 2 adducts can be obtained, depending on the reaction conditions$^{362}$.

2. $O \rightarrow \text{Sn}$ coordination

Tables 21 and 22 provide structural parameters for neutral aqua-triorganotin adducts. The longest tin-water distance of 2.500 Å is found for the 3-pyridylacrylato derivative (Table 21, entry 9). The coordinate bond of 2.253 Å in $\text{SnPh}_3(\text{SCN})$ (entry 10) is the shortest. The strengthening of the $O \rightarrow \text{Sn}$ bond in compounds with the same $\text{SnR}_3$ groups is accompanied by an increase in the tin pyramidalization. This is reflected in the corresponding decrease in the deviation of the tin atom from the equatorial plane ($\Delta \text{Sn}$) of the neighboring carbon atoms.

X-ray diffraction studies on hydrated triorganotin compounds $\text{H}_2\text{O} \rightarrow \text{SnR}_3\text{X}$ have provided several examples of water engaged in inner-sphere coordination to tin in five-coordinate molecules. For inner-sphere coordination, the complexes tend to pack in arrangements in which the number of hydrogen bonding interactions involving the coordinated water molecule is maximized. For example, $o$-phenanthroline monohydrate, which chelates to a plethora of transition metals, forms with triphenyltin chloride an outer-sphere coordination complex in which the coordinated water molecule [O $\rightarrow$ Sn = 2.42 Å]
TABLE 21. Selected structural parameters for H$_2$O $\rightarrow$ Sn$_3$X adducts

<table>
<thead>
<tr>
<th>Entry</th>
<th>$X^a$</th>
<th>R</th>
<th>O $\rightarrow$ Sn (Å)</th>
<th>Sn$-X$ (Å)</th>
<th>O $\rightarrow$ Sn$-X$ (deg)</th>
<th>$\Delta$Sn$^b$ (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>X$^1$</td>
<td>Et</td>
<td>2.342</td>
<td>2.333</td>
<td>177.0</td>
<td>0.01</td>
<td>363</td>
</tr>
<tr>
<td>2</td>
<td>X$^2$</td>
<td>n-Bu</td>
<td>2.339</td>
<td>2.360</td>
<td>176.8</td>
<td>0.03</td>
<td>363</td>
</tr>
<tr>
<td>3</td>
<td>OSO$_3$Ph</td>
<td>Me</td>
<td>2.300</td>
<td>2.370</td>
<td>176.3</td>
<td>0.04</td>
<td>364</td>
</tr>
<tr>
<td>4</td>
<td>OSO$_2$SnMe$_3$ (H$_2$O)</td>
<td>Me</td>
<td>2.362</td>
<td>2.235</td>
<td>174.0</td>
<td>0.04</td>
<td>365</td>
</tr>
<tr>
<td>5</td>
<td>OSO$_2$SnMe$_3$ (H$_2$O)</td>
<td>Me</td>
<td>2.335</td>
<td>2.239</td>
<td>174.3</td>
<td>0.05</td>
<td>366</td>
</tr>
<tr>
<td>6</td>
<td>X$^3$</td>
<td>Me</td>
<td>2.355</td>
<td>2.261</td>
<td>175.9</td>
<td>0.12</td>
<td>367</td>
</tr>
<tr>
<td>7</td>
<td>c-$\omega$-C$_6$H$_4$SO$_2$CON$^c$</td>
<td>Me</td>
<td>2.468</td>
<td>2.294</td>
<td>178.2</td>
<td>0.16</td>
<td>368</td>
</tr>
<tr>
<td>8</td>
<td>X$^4$</td>
<td>Me</td>
<td>2.417</td>
<td>2.101</td>
<td>174.8</td>
<td>0.18</td>
<td>369</td>
</tr>
<tr>
<td>9</td>
<td>X$^5$</td>
<td>c-Hex</td>
<td>2.500</td>
<td>2.180</td>
<td>173.9</td>
<td>0.20</td>
<td>370</td>
</tr>
<tr>
<td>10</td>
<td>SCN</td>
<td>Ph</td>
<td>2.253</td>
<td>2.226</td>
<td>176.8</td>
<td>0.05</td>
<td>371</td>
</tr>
<tr>
<td>11</td>
<td>ClF$_2$CC(O)O</td>
<td>Ph</td>
<td>2.298</td>
<td>2.186</td>
<td>177.0</td>
<td>0.07</td>
<td>372</td>
</tr>
<tr>
<td>12</td>
<td>X$^6$</td>
<td>Ph</td>
<td>2.386</td>
<td>2.174</td>
<td>176.6</td>
<td>0.10</td>
<td>373</td>
</tr>
<tr>
<td>13</td>
<td>Cl</td>
<td>Ph</td>
<td>2.310</td>
<td>2.549</td>
<td>177.0</td>
<td>0.11</td>
<td>374</td>
</tr>
<tr>
<td>14</td>
<td>X$^7$</td>
<td>Ph</td>
<td>2.388</td>
<td>2.160</td>
<td>168.4</td>
<td>0.14</td>
<td>375</td>
</tr>
<tr>
<td>15</td>
<td>X$^8$</td>
<td>Ph</td>
<td>2.422</td>
<td>2.149</td>
<td>172.4</td>
<td>0.14</td>
<td>376</td>
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<tr>
<td>16</td>
<td>Cl</td>
<td>Ph</td>
<td>2.354</td>
<td>2.476</td>
<td>175.3</td>
<td>0.15</td>
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</tr>
<tr>
<td>17</td>
<td>Cl</td>
<td>Ph</td>
<td>2.358</td>
<td>2.503</td>
<td>178.2</td>
<td>0.15</td>
<td>378</td>
</tr>
<tr>
<td>18$^d$</td>
<td>Cl</td>
<td>4-CIC$_6$H$_4$</td>
<td>2.352</td>
<td>2.482</td>
<td>176.2</td>
<td>0.15</td>
<td>379</td>
</tr>
<tr>
<td>19</td>
<td>X$^9$</td>
<td>Ph$^c$</td>
<td>2.413</td>
<td>2.142</td>
<td>172.8</td>
<td>0.17</td>
<td>380</td>
</tr>
<tr>
<td>20$^f$</td>
<td>Cl</td>
<td>Ph</td>
<td>2.348</td>
<td>2.491</td>
<td>177.5</td>
<td>0.19</td>
<td>381</td>
</tr>
<tr>
<td>21</td>
<td>ArCOO</td>
<td>Ph</td>
<td>2.471</td>
<td>2.120</td>
<td>177.4</td>
<td>0.26</td>
<td>382</td>
</tr>
<tr>
<td>22</td>
<td>Br</td>
<td>4-MeC$_6$H$_4$</td>
<td>2.440</td>
<td>2.622</td>
<td>175.0</td>
<td>—</td>
<td>383</td>
</tr>
</tbody>
</table>

$^a$Substituent X:
X$^1$ = 3-[2-(Aqua-triethylstannyl)tetrazol-5-yl]pyridine;
X$^2$ = 4-[2-(Aqua-triethylstannyl)tetrazol-5-yl]pyridine monohydrate;
X$^3$ = N-(4-Methylphenylsulphonyl)carbodiimide;
X$^4$ = 3-Methoxybenzoyl-1-phenyl-3-methylpyrazolon-5-ato;
X$^5$ = Aqua-tricyclohexyl-3-pyridilacrylato;
X$^6$ = 8-Quinolinoxyacetato;
X$^7$ = Bis(N,N-dimethylthio carbamoyl)acetate hydrate;
X$^8$ = N,N-3-Oxapentamethylene thiocarbamoylethioacetato;
X$^9$ = 1,3-Dioxisoindoline-2-acetato-O.

$^b$In the direction opposite to H$_2$O.

$^c$XH = Saccharin.
$^d$The coordinated water forms hydrogen bonds to the nitrogen atoms of two 1,10-phenanthrolines.
$^e$R$_3$ = (4-CIC$_6$H$_4$)Ph$_2$.
$^f$The coordinated water forms hydrogen bonds to the two nitrogen atoms of 3,4,7,8-tetramethyl-1,10-phenanthroline.

is linked by hydrogen bonds (O···N = 2.96 and 3.02 Å) to two 1,10-phenanthroline bases$^384$. The molecule crystallizes as a centrosymmetric dimer in which the heterocycles are positioned midway between the two aqua-chlorotriphenyltin entities$^384$. The heterocycle also yields isostructural dimeric complexes with tri-p-chlorophenylnitride$^384$ and triphenyltin trifluoroacetate$^385$.

Addition of four methyl substituents to the 1,10-phenanthroline ligand increases the basicity of its N atoms, enhancing the propensity for hydrogen bonding with the water
of the aqua-chlorotriphenyltin molecule. Thus, the outer-sphere coordination complex of aqua-chlorotriphenyltin with 3,4,7,8-tetramethyl-1,10-phenanthroline (Table 21, entry 20)\textsuperscript{381} has much shorter hydrogen bonds (O···N = 2.661 and 2.767 Å) with aqua-chlorotriphenyltin than does 1,10-phenanthroline. This suggests that electronic factors can influence the formation of these outer-sphere complexes. Both electronic effects and packing forces probably account for the monomeric nature of aqua-bromotriphenyltin o-phenanthroline.

In the crystal structure of pyrazolone derivatives (Table 21, entry 8), the bond length between H\textsubscript{2}O and Sn is longer (2.42 Å) and the distortion from the ideal TBP geometry (the O−Sn−O axis is bent to 174.8°) is probably due to steric hindrance of the 4-acyl-5-pyrazolonate ligand. In chloroform solution, the adduct loses the molecule of water and adopts a tetrahedral arrangement\textsuperscript{369}.

Triorganyltin halides and pseudohalides form stable five-coordinate adducts with the donor oxygen atom of a strong ligand, such as C=O (Table 23), P=O (Table 24), S=O (Table 25), N=O (Table 26) and As=O (Table 27), which have almost TBP geometry at tin.

That the chlorotriorganotin(IV) adducts with carbonyl (Table 23) are invariably five-coordinate rather than six-coordinate has been attributed to steric crowding by the organic groups attached to the tin atom\textsuperscript{253,422a}. Structural study on the R\textsubscript{3}SnCl·L adducts, L = 1-[(4-methylphenylimino)methyl]-2-naphthol and R = Me\textsuperscript{422b} and Ph\textsuperscript{422c}, has revealed that the electronic effect outweighs the steric effect in the formation of the five-coordinate trimethyltin adduct.

The five-coordinate triphenylphosphine oxide and HMPA complexes of triorganotins (Table 24) adopt the common trans-TBP geometry at the Sn atom. The presence of HMPA in the axial position and aryl groups in the equatorial positions promotes a decrease in the ΔSn value, and consequently, approach to ideal TBP configuration. The elongation of the Sn−X distance is due to the hypervalent bond character in the O → Sn−X axial fragment. For example, the Sn−Br bonds of 2.57–2.75 Å are lengthened relative to the bond of 2.295 Å in the parent triphenyltin bromide\textsuperscript{189}.  

### TABLE 22. Selected structural parameters for ROH → SnR\textsubscript{3}X adducts

<table>
<thead>
<tr>
<th>Entry</th>
<th>ROH</th>
<th>X\textsuperscript{a}</th>
<th>R\textsubscript{3}</th>
<th>O → Sn (Å)</th>
<th>Sn−X (Å)</th>
<th>O → Sn−X (deg)</th>
<th>Σ\textsuperscript{b}</th>
<th>ΔSn (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EtOH</td>
<td>OMe</td>
<td>Ph\textsubscript{2}R\textsubscript{1}e</td>
<td>2.374</td>
<td>2.144</td>
<td>177.0</td>
<td>—</td>
<td>—</td>
<td>386</td>
</tr>
<tr>
<td>2\textsuperscript{d}</td>
<td>MeOH</td>
<td>X\textsuperscript{1}</td>
<td>Bu\textsubscript{3}</td>
<td>2.394</td>
<td>2.273</td>
<td>177.5</td>
<td>359.5</td>
<td>0.09</td>
<td>387</td>
</tr>
<tr>
<td>3</td>
<td>MeOH</td>
<td>X\textsuperscript{2}</td>
<td>Ph\textsubscript{3}</td>
<td>2.339</td>
<td>2.282</td>
<td>176.6</td>
<td>359.1</td>
<td>0.11</td>
<td>388</td>
</tr>
<tr>
<td>4</td>
<td>EtOH</td>
<td>X\textsuperscript{3}</td>
<td>Ph\textsubscript{3}</td>
<td>2.401</td>
<td>2.147</td>
<td>166.8</td>
<td>—</td>
<td>0.20</td>
<td>388</td>
</tr>
<tr>
<td>5</td>
<td>i-PrCH\textsubscript{2}OH</td>
<td>i-PrCH\textsubscript{2}O</td>
<td>X\textsuperscript{4}</td>
<td>2.549</td>
<td>2.066</td>
<td>173.5</td>
<td>357.1</td>
<td>0.21</td>
<td>102</td>
</tr>
<tr>
<td>6</td>
<td>EtOH</td>
<td>X\textsuperscript{4}</td>
<td>Ph\textsubscript{3}</td>
<td>2.394</td>
<td>2.240</td>
<td>176.7</td>
<td>356.8</td>
<td>0.22</td>
<td>389</td>
</tr>
<tr>
<td>7</td>
<td>MeOH</td>
<td>X\textsuperscript{5}</td>
<td>Me\textsubscript{3}</td>
<td>2.463</td>
<td>2.607</td>
<td>174.7</td>
<td>356.4</td>
<td>0.24</td>
<td>390</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Substituents X:
- X\textsubscript{1}H = 5,5′-m-Phenylenebis(tetrazole);
- X\textsubscript{2} = OCOC\textsubscript{13};
- X\textsubscript{3} = Coumarin-3-carboxylato;
- X\textsubscript{4} = c-o-C\textsubscript{6}H\textsubscript{4}SO\textsubscript{2}CON(X\textsubscript{4}H = saccharin);
- X\textsubscript{5}H = 5,5′-p-phenylenebis(tetrazolylthio).

\textsuperscript{b}The sum of the CSnC equatorial angles.

\textsuperscript{c}In the direction opposite to ROH or to the more shorter Sn−O bond in the case of O → Sn−O.

\textsuperscript{d}Two independent molecules.

\textsuperscript{e}R\textsubscript{1} = CH\textsubscript{2}SnPh\textsubscript{2}OMe.
TABLE 23. Selected structural parameters for C=O → SnR3X framework with carbonyl ligands D

<table>
<thead>
<tr>
<th>Entry</th>
<th>D^a</th>
<th>X</th>
<th>R</th>
<th>O → Sn (Å)</th>
<th>Sn–X (Å)</th>
<th>O → Sn–X (deg)</th>
<th>Σ^b</th>
<th>ΔSn (Å)^c</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>D^1</td>
<td>Cl</td>
<td>Ph</td>
<td>2.384</td>
<td>2.485</td>
<td>179.1</td>
<td>358.2</td>
<td>0.16</td>
<td>391</td>
</tr>
<tr>
<td>2</td>
<td>D^2</td>
<td>Cl</td>
<td>Ph</td>
<td>2.399</td>
<td>2.485</td>
<td>175.9</td>
<td>357.4</td>
<td>0.20</td>
<td>392</td>
</tr>
<tr>
<td>3</td>
<td>D^3</td>
<td>X^1</td>
<td>Ph</td>
<td>2.424</td>
<td>2.107</td>
<td>168.8</td>
<td>357.6</td>
<td>0.20</td>
<td>388</td>
</tr>
<tr>
<td>4</td>
<td>D^4</td>
<td>X^2</td>
<td>Ph</td>
<td>2.403</td>
<td>2.242</td>
<td>176.0</td>
<td>357.2</td>
<td>0.21</td>
<td>393</td>
</tr>
<tr>
<td>5</td>
<td>D^5</td>
<td>Cl</td>
<td>Ph</td>
<td>2.499</td>
<td>2.451</td>
<td>179.2</td>
<td>355.7</td>
<td>0.26</td>
<td>394</td>
</tr>
<tr>
<td>6</td>
<td>D^3</td>
<td>Cl</td>
<td>Ph</td>
<td>2.510</td>
<td>2.439</td>
<td>175.9</td>
<td>355.3</td>
<td>0.27</td>
<td>395</td>
</tr>
<tr>
<td>7</td>
<td>D^6</td>
<td>NCO</td>
<td>Ph</td>
<td>2.807</td>
<td>2.122</td>
<td>173.2</td>
<td>353.9</td>
<td>0.30</td>
<td>396</td>
</tr>
</tbody>
</table>

^aD^1 = (Me_2N)_2CO
D^2 = ε-caprolactam-O
D^3 = diphenylcyclopropenone.
D^4 = Me_2NCHO
D^5 = 2,3-diphenylthiazolidin-4-one
D^6 = (Ph_3SnNCO)_n
X^1 = coumarin-3-carboxylate.
X^2 = c-c-C_6H_4SO_2CON(X^2H = saccharin).
^bThe sum of the CSnC equatorial angles.
^cIn the direction opposite to C=O.

TABLE 24. Selected structural parameters for P=O → SnR3X framework

<table>
<thead>
<tr>
<th>Entry</th>
<th>R_3SnX or compd^d</th>
<th>D</th>
<th>O → Sn (Å)</th>
<th>Sn–X (Å)</th>
<th>O → Sn–X (deg)</th>
<th>Σ^b</th>
<th>ΔSn (Å)^e</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>I HMPA</td>
<td>2.211</td>
<td>2.608, 2.432^d</td>
<td>175.5</td>
<td>360.0</td>
<td>0.01</td>
<td>397</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>II^e HMPA</td>
<td>2.236</td>
<td>2.611,</td>
<td>176.9</td>
<td>360.0</td>
<td>0.02</td>
<td>398</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.258</td>
<td></td>
<td>176.1</td>
<td>359.8</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>III HMPA</td>
<td>2.256</td>
<td>2.599, 2.432^d</td>
<td>176.8</td>
<td>359.6</td>
<td>0.08</td>
<td>269</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Ph_3SnCl Ph_3PO</td>
<td>2.375</td>
<td>2.509</td>
<td>177.8</td>
<td>358.8</td>
<td>0.14</td>
<td>399</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Me_3SnCl Ph_3PO</td>
<td>2.404</td>
<td>2.501</td>
<td>177.4</td>
<td>358.4</td>
<td>0.15</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Ph_3SnCl D^1</td>
<td>2.523</td>
<td>2.423</td>
<td>172.7</td>
<td>357.4</td>
<td>0.20</td>
<td>401</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Ph_3SnCl Ph_3PO</td>
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<td>2.470</td>
<td>178.6</td>
<td>357.3</td>
<td>0.20</td>
<td>402</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Me_3SnCl HMPA</td>
<td>2.277</td>
<td>2.525</td>
<td>179.0</td>
<td>357.1</td>
<td>0.21</td>
<td>227^f</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>IV HMPA</td>
<td>2.220</td>
<td>2.752, 2.586^d</td>
<td>173.7</td>
<td>359.8</td>
<td>0.06</td>
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<tr>
<td>10</td>
<td>Ph_3SnBr Ph_3PO</td>
<td>2.336</td>
<td>2.619</td>
<td>178.7</td>
<td>357.9</td>
<td>0.18</td>
<td>404</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>V Ph_3PO</td>
<td>2.335</td>
<td>2.651</td>
<td>179.4</td>
<td>357.8</td>
<td>0.18</td>
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<td>12</td>
<td>Ph_3SnN_3 HMPA</td>
<td>2.304</td>
<td>2.217</td>
<td>176.4</td>
<td>359.7</td>
<td>0.06</td>
<td>73</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>VI Ph_3PO</td>
<td>2.341</td>
<td>2.236</td>
<td>171.8</td>
<td>358.8</td>
<td>0.14</td>
<td>406</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Ph_3SnNO_3 Ph_3PO</td>
<td>2.289</td>
<td>2.220</td>
<td>174.2</td>
<td>359.4</td>
<td>0.10</td>
<td>407</td>
<td></td>
</tr>
</tbody>
</table>

^aCompounds and donors: I, (ClPh_2Sn)_2CH_2; II, o-C_6H_4(SnClMe_2)_2; III, (ClPh_2Sn)_2(CH_2)_2; IV, (BrPh_2Sn)_2 CH_2; V, tris(3-thienyl)bromotin; VI, (1,2-benzothiazol-3(2H)-one-1,1-dioxide)triphenyl tin; D^1 = OP(c-C_6H_11)_2 CONHMe.
^bThe sum of the CSnC equatorial angles.
^cIn the direction opposite to P=O.
^dSn(2)–Hal(2).
^eTwo independent molecules.
^fFor NMR investigation, see Reference 403.
TABLE 25. Selected structural parameters for O → SnR₃X ligand framework of adducts with S=O compounds

<table>
<thead>
<tr>
<th>Entry</th>
<th>O → Sn (Å)</th>
<th>Sn–X (Å)</th>
<th>O → Sn–X (deg)</th>
<th>Σᵇ</th>
<th>ΔSn (Å)ᶜ</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.264</td>
<td>2.252</td>
<td>176.9</td>
<td>360.0</td>
<td>0.01</td>
<td>118</td>
</tr>
<tr>
<td>2</td>
<td>2.307</td>
<td>2.348</td>
<td>170.2</td>
<td>360.0</td>
<td>0.01</td>
<td>409</td>
</tr>
<tr>
<td>3</td>
<td>2.37 3</td>
<td>2.259</td>
<td>172.4</td>
<td>359.6</td>
<td>0.08</td>
<td>409</td>
</tr>
<tr>
<td>4</td>
<td>2.412</td>
<td>2.237</td>
<td>175.7</td>
<td>359.2</td>
<td>0.10</td>
<td>410</td>
</tr>
<tr>
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<td>0.19</td>
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<tr>
<td>7</td>
<td>3.046</td>
<td>2.378</td>
<td>170.9</td>
<td>347.9</td>
<td>—</td>
<td>421</td>
</tr>
</tbody>
</table>

ᵃCompounds according to entries: 1, [(Ph₃Sn)₂O₃S]n; 2, catena-(µ₂-dimesylamido-O, O’)-tricyclohexyltin; 3, catena-(µ₂-dimesylamide-O, O’)-triphenyltin; 4, (1,2-benzothiazol-3(2H)-one-1,1-dioxide-N-(dibenzylsulfoxide-O)triphenyltin; 5, µ₂-1,2-bis(n-propylsulfinyl)-ethylen-O, O’-bis(chlorotriphenyltin); 6, catena-(µ₂-dimesylamide-O, O’)-(µ₂-hydroxo-bis(triphenyltin)) [Me₃Sn(SO₂Me)₂·Me₃SnOH]n; 7, catena-(chloro-tris(p-methylsulfonylphenyl)tin).

ᵇThe sum of the CSnC equatorial angles.

ᶜIn the direction opposite to S=O.

TABLE 26. Selected structural parameters for O → SnR₃X ligand framework of adducts with N=O compounds

<table>
<thead>
<tr>
<th>Entry</th>
<th>O → Sn (Å)</th>
<th>Sn–X (Å)</th>
<th>O → Sn–X (deg)</th>
<th>Σᵇ</th>
<th>ΔSn (Å)ᶜ</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.227</td>
<td>2.245</td>
<td>171.4</td>
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<td>0.06</td>
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</tr>
<tr>
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<td>2.319</td>
<td>2.265</td>
<td>174.5</td>
<td>359.3</td>
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<td>414</td>
</tr>
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<td>2.400</td>
<td>2.533</td>
<td>177.4</td>
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<td>415</td>
</tr>
<tr>
<td>4</td>
<td>2.296</td>
<td>2.472, 2.365</td>
<td>172.8</td>
<td>359.0</td>
<td>0.13</td>
<td>415</td>
</tr>
<tr>
<td>5</td>
<td>2.407</td>
<td>2.163</td>
<td>174.8</td>
<td>358.3</td>
<td>0.16</td>
<td>388</td>
</tr>
<tr>
<td>6</td>
<td>2.355</td>
<td>2.169</td>
<td>176.2</td>
<td>358.2</td>
<td>0.17</td>
<td>416</td>
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<tr>
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<td>2.147</td>
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<td>357.5</td>
<td>0.20</td>
<td>417</td>
</tr>
<tr>
<td>8</td>
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<td>2.544</td>
<td>167.4</td>
<td>—</td>
<td>—</td>
<td>418</td>
</tr>
</tbody>
</table>


ᵇThe sum of the CSnC equatorial angles.

ᶜIn the direction opposite to S=O.

TABLE 27. Selected structural parameters for O → SnR₃X ligand framework of adducts with As=O compounds

<table>
<thead>
<tr>
<th>Entry</th>
<th>O → Sn (Å)</th>
<th>Sn–X (Å)</th>
<th>O → Sn–X (deg)</th>
<th>Σᵇ</th>
<th>ΔSn (Å)ᶜ</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.181</td>
<td>2.274</td>
<td>175.6</td>
<td>360.0</td>
<td>0.00</td>
<td>419</td>
</tr>
<tr>
<td>2</td>
<td>2.162</td>
<td>2.325</td>
<td>176.7</td>
<td>359.9</td>
<td>0.03</td>
<td>420</td>
</tr>
<tr>
<td>3</td>
<td>2.260</td>
<td>2.170</td>
<td>175.1</td>
<td>359.9</td>
<td>0.03</td>
<td>388</td>
</tr>
<tr>
<td>4</td>
<td>2.479</td>
<td>2.123</td>
<td>168.6</td>
<td>356.8</td>
<td>0.22</td>
<td>421</td>
</tr>
</tbody>
</table>

ᵃCompounds according to entries: 1, nitrato-(triphenylarsineoxide)triphenyltin; 2, isothiocyanato-(triphenylarsineoxide)tribenzyltin; 3, (µ₂-coumarin-3-carboxylato)-(coumarin-3-carboxylato)hexaphenyltriphenylarsineoxide-ditin; 4, (µ₂-1,2-bis(diphenylarsoryl)-ethane-O, O’)-bis(chlorotriphenyltin).

ᵇThe sum of the CSnC equatorial angles.

ᶜIn the direction opposite to As=O.
The crystal structure of the complex \( \text{o-C}_6\text{H}_4(\text{SnClMe}_2)_2 \cdot (\text{Me}_2\text{N})_3\text{PO} \) (entry 2) confirms the conclusion drawn from the low-temperature \( ^{119}\text{Sn} \) NMR measurement. The HMPA molecule acts as a monodentate donor toward one Sn atom, which is displaced from the plane by 0.023 Å in the direction of Cl\( ^{398} \). The O \( \rightarrow \) Sn distance of 2.236 Å is comparable with the O \( \rightarrow \) Sn distances of 2.211 and 2.256 found for related complexes (Ph\( _2\)ClSn\( _2\)CH\( _2 \cdot (\text{Me}_2\text{N})_3\text{PO} \) (entry 1)\(^{397} \) and (Ph\( _2\)ClSnCH\( _2 \cdot (\text{Me}_2\text{N})_3\text{PO} \) (entry 3)\(^{269} \), respectively.

Adduct formation of triethylphosphine oxide (TEPO) with Ph\( _2\)BrSn(CH\( _2 \)\( _n\)SnBrPh\( _2 \), where \( n = 6, 10 \) and 12, and \( (\text{n-C}_4\text{H}_9)\text{SnO}_2\text{C(CH}_2\text{)}\text{pCO}_2\text{Sn(}-\text{n-C}_4\text{H}_9)\text{)} \), where \( n = 2, 6, 10, 12 \) and 14, was monitored by \( ^{31}\text{P} \) NMR. Equilibrium constants for the former were approximately independent of the chain length from \( n = 6 \) to 12, while for the carboxylates the constants for \( n = 2 \) and \( n = 14 \) were small. Equilibrium constants for the intermediate chains were approximately the same. Solid state NMR shows that the adduct is probably not symmetrically chelated\(^{408} \).

The P=O \( \rightarrow \) Sn bonds in phosphine oxide complexes (Table 24) are somewhat shorter than those found in the same carbonyl (Table 23), sulfoxide (Table 25) and N-oxide (Table 26) complexes, reflecting the greater Lewis basicity of the former.

Organotin compounds with intermolecular S=O \( \rightarrow \) Sn interaction are relatively rare and only a few single-crystal X-ray crystal structure analyses have been reported (Table 25). A structure for bis(triphenylstannyl)sulfite, \([\text{Ph}_3\text{Sn}]_2\text{SO}_3\text{TBP}\) (entry 1)\(^{118} \), contains pentacoordinated tin atoms.

The Sn atom in the quinoline-N-oxide derivative (Table 26, entry 7) shows trans-C\( _5\text{SnO}_2\) TBP coordination [\( \Sigma\text{C}=\text{Sn}=\Sigma\text{C}=357.5^\circ \), O \( \rightarrow \) Sn \( =\)0 171.4°]\(^{417} \), but the O \( \rightarrow \) Sn bond of 2.446 Å is much longer than that (2.319 Å) found in the quinoline N-oxide complex of the benzothiazolone derivative (entry 2)\(^{414} \).

Among triorganotin compounds, coordination higher than four at tin is not often realized when a sulfur atom is linked covalently to the metal atom. The structure of triphenyltin isopropylxanthatoquinoline N-oxide (Table 26, entry 8) represents an unusual example of a Lewis-acidic organotin sulfido compound. The geometry of the tin atom is a distorted trans-C\( _5\text{SnOS} \) TBP (O \( \rightarrow \) Sn = 2.448, Sn–S = 2.544 Å; O \( \rightarrow \) Sn–S = 167.4°)\(^{418} \). The oxygen \( \rightarrow \) tin bond distance compares well with those found in the quinoline N-oxide adducts of the triphenyltin derivatives of benzothiazol-3(2\( H \))-one 1,1-dioxide (entry 2) (O \( \rightarrow \) Sn = 2.319 Å)\(^{414} \) and with that (2.459 Å) found in tri-\( p\)-tolyltin bromide quinoline N-oxide\(^{423a} \). The Sn–S distance of 2.544 Å in the xanthate complex is longer than that (2.445 Å) in the parent Lewis acid\(^{423b} \) molecule. Triphenyltin isopropylxanthate itself shows a distorted tetrahedral geometry as a result of an intramolecular contact of 2.950 Å; the Sn–O interaction is apparently preferred to an Sn–S interaction.

In general, the halides Sn\( _n\)X tend to form pentacoordinate adducts with oxygen-containing ligands, but the Sn\( _n\)X\( _2 \) and SnRX\( _3 \) tend to form hexacoordinate adducts (Section X.A). Only a few crystallographic data are available for the former case (Table 28) that confirms the Sn–X bond length difference between axial and equatorial positions in the pentacoordinate species\(^{118} \). The complexes SnPh\( _2\)Cl\( _2 \cdot \text{OPPh}_3 \) and SnPh\( _2\)Br\( _2 \cdot \text{OPPh}_3 \) (entries 1 and 2) are isostructural and replacement of chloride by bromide has remarkably little effect on the angles about tin; the biggest change was recorded in the O \( \rightarrow \) Sn–X (X = Cl or Br) bond angle, which increases by 1.6°. The bond parameters of the phosphine oxide to SnPh\( _2\)Cl\( _2 \) and SnPh\( _2\)Br\( _2 \) are remarkably constant despite the difference in Lewis acidity of the organotin species\(^{424} \).

In a hydrogen-bonded adduct of aqua-dichlorodiphenyltin(IV) (entry 3), the Ph\( _2\)Sn(H\( _2\)O)Cl\( _2 \) unit exhibits a distorted TBP coordination geometry around tin\(^{425} \). The distortion is illustrated by the deviation of the axial O \( \rightarrow \) Sn–Cl bond angle (172.3°) from linearity.
TABLE 28. Selected structural parameters for pentacoordinate adducts SnPh$_2$X$_2$·D

<table>
<thead>
<tr>
<th>Entry</th>
<th>X</th>
<th>D</th>
<th>O → Sn (Å)</th>
<th>Sn–X$_{ax}$ (Å)</th>
<th>Sn–X$_{eq}$ (Å)</th>
<th>O → Sn–X (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cl</td>
<td>OPPh$_3$</td>
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<td>2.354</td>
<td>2.470</td>
<td>176.3</td>
<td>424</td>
</tr>
<tr>
<td>2</td>
<td>Br</td>
<td>OPPh$_3$</td>
<td>2.287</td>
<td>2.500</td>
<td>2.632</td>
<td>177.9</td>
<td>424</td>
</tr>
<tr>
<td>3</td>
<td>Cl</td>
<td>H$_2$O</td>
<td>2.304</td>
<td>2.469</td>
<td>2.338</td>
<td>172.3</td>
<td>425</td>
</tr>
<tr>
<td>4</td>
<td>Cl</td>
<td>H$_2$O</td>
<td>2.372</td>
<td>2.477</td>
<td>2.367</td>
<td>176.8</td>
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<td>D$_1$</td>
<td>2.307</td>
<td>2.477</td>
<td>2.333</td>
<td>176.6</td>
<td>427</td>
</tr>
</tbody>
</table>

$^a$D$_1$ = Ph$_2$Sn(2-OC$_{10}$H$_6$CH=NCH$_2$COO).

The axial Sn–Cl bond length (2.469 Å) is considerably longer than the equatorial Sn–Cl bond length (2.338 Å).

Mono-aqua adducts of dimethyltin dichloride with [Ni$^{II}$L]·H$_2$O [H$_2$L = N,N’-bis(3-methoxysalicylidene)ethylenediamine] and N,N’-bis(3-methoxysalicylidene)propane-1,2-diamine] have different structures. In the former the tin is in a TBP environment, whereas in the latter it is in an octahedral environment as a result of an intermolecular Cl···Sn contact of 3.615 Å$^{426}$.

A new dinuclear tin complex, [Ph$_2$Sn(2-OC$_{10}$H$_6$CH=NCH$_2$COO)]SnPh$_2$Cl$_2$ (entry 5), was characterized as a 1 : 1 adduct between the diorganotin dichloride and bicycloazastannoxide with the O → Sn bond distance being 2.307 Å. The TBP geometry of the Sn is distorted as indicated by the O → Sn–Cl bonding angle of 176.6°$^{427}$.

Structure 119 is doubly bridged by the methylene carbon and the oxygen of DMSO, with each Sn atom displaying distorted trigonal-bipyramidal geometry. The bridging methylene group is in the equatorial position in both the Sn$^1$ and Sn$^2$ coordination while the bridging oxygen atom occupies an axial position in both cases. The second apical position is occupied by the Cl$_1$ and Cl$_2$ atoms for Sn$^1$ and Sn$^2$, respectively. The equatorial Sn$^1$–Cl$_3$ distance of 2.372 Å is significantly shorter than the axial distance Sn$^1$–Cl$_1$ of 2.410 Å, trans (174.2°) to the O → Sn bond, 2.572 Å$^{428}$.

Adducts of SnR$_2$X$_2$ appear to be structurally more complex than their triorganotin analogues. Compounds O{(t-Bu)$_2$SnO)$_2$E·(t-Bu)$_2$Sn(OH)$_2$ (E = SiMe$_2$$^{429}$, SiPh$_2$$^{94}$, BMes$^{430}$ and CO$^{94}$) display a unique tricyclic structure 120 consisting of fused six-membered Sn$_2$EO$_3$ and four-membered Sn$_2$O$_2$ rings to form a planar ESn$_3$O$_4$ skeleton, with distorted trigonal-bipyramidal coordination at tin. In the former the distortion of the
axial hypervalent $O \rightarrow Sn^{1,2}$—O bonds is not so great, $O \rightarrow Sn = 2.274$ and 2.279 Å, $Sn-O = 2.006$ and 2.000 Å, $O \rightarrow Sn-O = 163.5$ and 163.6°, respectively.\(^{429}\)

$N$-Methylpyrrolidinone (NMP) is able to react as a bidentate ligand, but a 1 : 2 complexation by dimethyltin dichloride leads to two different pentacoordinated adducts with monodentate NMP ligand.\(^{2183}\) Atom $Sn^1$ has apical ligands with an angle of 177.35° ($O \rightarrow Sn^{1-Clax}$) close to the ideal angle of 180°.\(^{183}\) The $O \rightarrow Sn^1$ bond length (2.278 Å) is shorter and the axial $Sn^1-Clax$ bond (2.570 Å) is longer than in other pentacoordinated diorganotin complexes. The long axial $Sn^1-Clax$ bond in this compound may be caused by its bridging character due to its participation in the second hypervalent bonding $O \rightarrow Sn^{1-Clax} \rightarrow Sn^2-Cl$. Also, the axial $Sn^1-Clax$ bond is long compared with that in other complexes containing bridging $Cl$ ligands such as $Me_3SnCl$\(^{162}\) and $Me_2SnCl_2$\(^{171}\).

The interactions between diethyltin dichloride and pyrimidine nucleotides (5'-CMP, 5'-dCMP and 5'-UMP) in aqueous solution were investigated by multinuclear 1D and 2D NMR techniques including $^{119}Sn$, $^{15}N$ and $^{31}P$ nuclei. At pH values higher than 2.0–3.0, the $Et_2Sn$ moiety of the $Et_2SnCl_2$ is involved in bonding with the phosphate group of the three nucleotides studied. Around neutral pH (5.5–9.0), there is no evidence for interaction of the $Et_2Sn$ moiety with the nucleotide. In a 1 : 1 nucleotide/$Et_2SnCl_2$ mixture at pH > 9.0, $Et_2SnCl_2$ reacts with the two oxygen atoms of the sugar unit of the nucleotide.\(^{431}\)

In general, the halides $RSnX_3$ tend to form hexacoordinate complexes (Section X.A) and pentacoordinate ones are rare. In adduct $MeSnBr_3 \cdot DMF$, the axial $Sn-Br$ bond (2.576 Å) is considerably longer than the equatorial bond (2.475 Å) due to the coordinate $O \rightarrow Sn$ bond (2.28 Å) with the near to ideal linear $O \rightarrow Sn-Brax$ bond angle of 179.2°.\(^{432}\)

The $^{119}Sn$ chemical shift of trichlorobutyltin mixed with 1 equiv of methanol in CDCl$_3$, was at $-181$ ppm with respect to the uncoordinated molecule ($-141.2$ ppm), which confirmed the pentacoordination. In esters, intermediate values may suggest an equilibrium between tetra- and pentacoordinated species, or a weak coordination. Besides, the $^1J(SnC)$ for butyltin trichloride in CDCl$_3$, where the metal is tetracoordinated, is 648 Hz in comparison with 939 Hz in the presence of 1 equivalent of methanol.\(^{433}\)

The coordination geometry of each tin atom in [($H_2O$)Cl$_3Sn(CH_2)_4SnCl_3(OH_2)$] is distorted TBP, with the Sn atom lying 0.270 Å out of the equatorial plane in the direction of the Cl atom in an axial hypervalent fragment $O \rightarrow Sn-Clax$ (bond angle 172.7°).\(^{434}\) The bonds between tin and the chlorine in the equatorial plane (2.330, 2.319 Å) are shorter than the axial bond (2.438 Å). The structure is similar to that found in $[MeOCH_2CH_2O(CH_2)_3SnCl_3( OH_2)]^+$, except that in the latter there is a close intramolecular $Sn \cdots O$ contact of 2.442 Å leading to a distorted octahedral geometry.

3. P → Sn coordination

Much attention has been focused on the nature of P → Sn coordination bonds in phosphines as ligands. The shift of the $^{119}Sn$ resonance to higher field upon adduct formation, the multiplicity of the resonance, the variation of $^{31}P-^{119}Sn$ coupling with the nature of the substituent and the change in the shape of the signals with concentration and temperature were used to determine the stoichiometry and the structure of the phosphine adducts of $Ph_3SnCl$, $R_2SnCl_2$ ($R = Et, Pr, Bu, t-Bu$ and $Ph$) and $RSnCl_3$ ($R = Bu$ and $Ph$)\(^{436}\).

The triorganotin chloride adducts readily exchange with base or with other adducts. The diorganotin dichlorides form only 1 : 1 adducts with tributylphosphine, even at high base to acid ratios. The lower dialkyltin dichlorides prefer to form 1 : 1 adducts (at 1 : 1 mole ratios) with tributylphosphine rather than tributylphosphine oxide (TBPO), whereas
diphenyltin dichloride and di(t-butyl)tin dichloride prefer TBPO adduct formation. The reactions of the trihalides with tributylphosphine and TBPO are complicated by aryl transfer or displacement of chloride by base and a consequent ion formation\(^{356}\).

Interaction of \(RSnHal_3\) and \(SnHal_4\) (Hal = Cl, Br) with monodentate tertiary phosphines (D = Pr\(_3\)P, Bu\(_3\)P, Ph\(_3\)P, Ph\(_2\)MeP and PhMe\(_2\)P) has been studied by \(^{119}\)Sn and \(^{31}\)P NMR spectroscopy in CH\(_2\)Cl\(_2\) at various ratios and temperatures of \(-90^\circ C\) and \(+30^\circ C\).\(^{26,27}\). Multiplicities of \(^{119}\)Sn NMR spectra are in good accord with formation of mainly hexacoordinate complexes\(^{26}\). It was found that equilibria take place in solutions of SnHal\(_4\) and 1 : 1 complexes are formed preferably at excess of the acceptor (A). NMR spectral parameters for the pentacoordinate complexes in CH\(_2\)Cl\(_2\) are given in Table 29.

Detailed analysis of the \(\delta^{119}\)Sn and \(\delta^{31}\)P values for SnCl\(_4\)–Bu\(_3\)P system shows an alternative mechanism for the complexation. An ionic \((SnCl_3 \cdot 2Bu_3P)^+SnCl_5^-\) complex with formal 1 : 1 stoichiometry is formed in excess of SnCl\(_4\) (D/A = 0.5) and at \(-90^\circ C\). On increasing the temperature to \(+30^\circ C\), an irreversible transformation of \((SnCl_3 \cdot 2Bu_3P)^+SnCl_5^-\) into SnCl\(_4\)·Bu\(_3\)P was observed. The complex SnCl\(_4\)·Bu\(_3\)P was transformed into Bu\(_3\)PCI\(^+\)·SnCl\(_5\)\(^-\) and SnCl\(_2\) at room temperature in several hours due to an oxidation–reduction process. Formation of either ionic or molecular complexes has been shown to be characteristic for other phosphines (Me\(_2\)PhP, MePh\(_2\)P)\(^{26}\).

Concentration and temperature dependencies of the NMR spectra of the SnBr\(_4\)–Bu\(_3\)P system shows that only AD\(_2\) complexes exist in solutions at \(-90^\circ C\) regardless of the D/A ratio. In this case there are no ionic structures due to the lower Lewis acidity of SnBr\(_4\). A temperature increase at D/A < 2 leads to dissociation of SnBr\(_4\)·2Bu\(_3\)P into SnBr\(_4\)·Bu\(_3\)P, which transforms immediately and much faster than the analogous SnCl\(_4\) complex into Bu\(_3\)PBr\(^+\)·SnBr\(_5\)\(^-\) due to an oxidation–reduction process\(^{26}\).

**TABLE 29.** \(^{31}\)P and \(^{119}\)Sn NMR parameters for the 1 : 1 SnHal\(_4\) complexes with tertiary phosphines in CH\(_2\)Cl\(_2\) at \(-90^\circ C\).\(^{26}\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\delta^{31})P (ppm)</th>
<th>(\Delta\delta^{31})P(^a) (ppm)</th>
<th>(\delta^{119})Sn (ppm)</th>
<th>(1J^{31})P–(^{119})Sn (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnCl(_4)·Bu(_3)P</td>
<td>36.0</td>
<td>68.5</td>
<td>-453</td>
<td>2200</td>
</tr>
<tr>
<td>SnCl(_4)·Me(_2)Bu(_3)P</td>
<td>14.4</td>
<td>54.4</td>
<td>-</td>
<td>2600</td>
</tr>
<tr>
<td>SnCl(_4)·MeBu(_2)P</td>
<td>8.4</td>
<td>36.4</td>
<td>-390</td>
<td>2060</td>
</tr>
<tr>
<td>SnCl(_4)·Ph(_3)P</td>
<td>19.0</td>
<td>27.4</td>
<td>-593</td>
<td>1960</td>
</tr>
<tr>
<td>SnBr(_4)·Bu(_3)P</td>
<td>19.3</td>
<td>51.8</td>
<td>-</td>
<td>1290</td>
</tr>
</tbody>
</table>

\(^a\)\(\Delta\delta = \delta(\text{complex}) - \delta(\text{phosphine})\).

\(^b\)No data due to poor solubility.

**TABLE 30.** Selected structural parameters for lead adducts with O→PbR\(_3\)X ligand framework

<table>
<thead>
<tr>
<th>Compound</th>
<th>X</th>
<th>R</th>
<th>O→Pb (Å)</th>
<th>Pb−X (Å)</th>
<th>O→Pb−X (deg)</th>
<th>(\Sigma^a)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph(_3)PbCl·HMPA</td>
<td>Cl</td>
<td>Ph</td>
<td>2.500</td>
<td>2.614</td>
<td>174.5</td>
<td>358.9</td>
<td>437</td>
</tr>
<tr>
<td>Ph(_3)PbBr·OPPPh(_3)</td>
<td>Br</td>
<td>Ph</td>
<td>2.556</td>
<td>2.754</td>
<td>176.9</td>
<td>358.0</td>
<td>399</td>
</tr>
<tr>
<td>Ph(_3)PbBr·L(^b)</td>
<td>Br</td>
<td>Ph</td>
<td>2.659</td>
<td>2.696</td>
<td>174.1</td>
<td>354.8</td>
<td>438</td>
</tr>
</tbody>
</table>

\(^a\)The sum of the CPbC equatorial angles.

\(^b\)L = diphenylcyclopropenone.
C. Lead

The organolead complexes contain few examples of monomeric neutral adducts (Table 30). The structure of \( \text{Ph}_3\text{PbBr}(\text{OPPh}_3) \) shows that the OPPh\(_3\) molecule (O \( \rightarrow \) Pb = 2.556 Å) and the bromine atom (Pb–Br = 2.754 Å) are both at the axial positions displaying hypervalent bonding for the lead atom. The other adducts have the same five-coordinate structure with the three equatorial phenyl groups.

VI. PENTACOORDINATE INTRAMOLECULAR NEUTRAL GERMANIUM COMPOUNDS

A. Monocyclic Complexes

1. Derivatives with bidentate C,O-chelating ligands

Among neutral pentacoordinate intramolecular germanium complexes, compounds containing a C,O-chelating ligand have been most extensively studied.

   a. Compounds with 8-(methoxynaphthyl) ligand. A series of 8-(methoxynaphthyl) germanium derivatives with intramolecular interaction between the germanium and the methoxy oxygen atom were described recently. The initial diorganodichloro- and organotrichlorogermanes were prepared from aryltrichlorogermanes and organolithium reagents or by an organomagnesium route. Their reduction by LiAlH\(_4\) gave the expected organogermanes \( \text{121} \) and \( \text{122} \) (Scheme 7\(^{439--441} \)).

   An X-ray crystallographic study of \( \text{121c} \) revealed a weak intramolecular O \( \rightarrow \) Ge interaction (2.75 Å) and the absence of intermolecular O \( \cdots \) Ge contacts\(^{441} \). The O–Ge distance observed is longer than that of the corresponding covalent bond but appreciably less than the sum of the van der Waals radii (Table 1). The Ge atom retains its tetrahedral geometry, though slightly deformed, with the two hydrogen atoms occupying equatorial positions and the OGeC(Mes) angle at 175.2°. It is noteworthy that in the case of diorganogermane \( \text{124} \) with two 2-methoxyphenyl ligands (equation 24), an intramolecular O \( \cdots \) Ge interaction is not observed\(^{439} \).

\[
\begin{align*}
\text{OMe} & \quad \text{MgBr} \quad \text{GeCl}_4 \quad \text{OMe} \\
\text{2} & \quad \text{GeCl}_2 \quad \text{LiAlH}_4 \quad \text{GeH}_2 \\
& \quad \text{(124)} \quad \text{(24)}
\end{align*}
\]

Reaction of the (8-methoxynaphthyl)germanes \( \text{121} \) and \( \text{122} \) with CF\(_3\)SO\(_3\)H in diethyl ether or with I\(_2\) in benzene yields the corresponding germanium triflates and iodides \( \text{123a–e} \) (Scheme 7). They are air-sensitive powders, insoluble in common hydrocarbon solvents but soluble in CH\(_2\)Cl\(_2\) and CHCl\(_3\)\(^{441} \). Treatment of the triflate \( \text{123c} \) with Lewis bases B(H\(_2\)O, DMSO, C\(_6\)H\(_5\)CH\(_2\)NH\(_2\)) leads to the formation of the corresponding 1 : 1 cationic complexes \( \text{123c} \cdot \text{B} \) (equation 25). According to X-ray data, the geometry at germanium in both the triflate \( \text{123c} \) and the complex \( \text{123c} \cdot \text{H}_2\text{O} \) is close to TBP; the structure of the latter is dimeric (Section VIII.A).

Hydrolysis of compounds \( \text{123a–e} \) by excess of water in the presence of Et\(_3\)N gives germoxanes \( \text{125} \) (R = H, Ph, (8-MeO)Np) instead of the expected germanols. Reaction
SCHEME 7. Synthesis of the 8-(methoxynaphthyl)germanium derivatives 121–123
of iodide $^{123e}$ with NaBPh$_4$ in CH$_3$CN leads to elimination of MeI and formation of germoxolene $^{126}$ instead of the expected anionic product.

$$\begin{align*}
\text{(123c)} & \quad \text{B (B = C}_6\text{H}_5\text{NH}_2, \text{H}_2\text{O, DMSO)} \\
\text{(123c-B)} & \quad \text{OTf}^-
\end{align*}$$

$^{123c}$

Formation of the mono- and dilithium derivatives from the diorganogermanes $^{121, 122}$ and $^{124}$ and $n$-BuLi or $t$-BuLi and their further reactions were discussed$^{442}$. In particular, for the monolithium derivatives $^{121b}$ and $^{121c}$ the authors suggest the structure $^{127}$ having a pentacoordinated Ge atom and intramolecular Li···OMe interaction$^{439}$.

As shown by X-ray crystallography, the geometry at Ge in triflate $^{123c}$ is very close to TBP, with the two 8-methoxynaphthyl ligands and the hydrogen atom forming the central plane. The axial positions are occupied by one methoxy group and the triflate group (the O(OMe)GeO(Tf) angle is 174.9°). The corresponding O—Ge distances, 2.357 and 1.988 Å, are longer than the standard O—Ge bond length (1.76 Å) in four-coordinate compounds$^9$ but are appreciably shorter than the sum of van der Waals radii (Table 1).
16. Hypervalent compounds of organic germanium, tin and lead derivatives

The deviation of the Ge atom from the equatorial plane defined (ΔGe) by the hydrogen and two carbon atoms is 0.166 Å in the direction of the oxygen atom of the triflate group. This contrasts drastically with the structural data for triflate L₆GeMe₂OTf (L₆ = 1-methyl-2-piperidinone) discussed below, for which the (C=O)O–Ge and Ge–O(Tf) distances are 1.90 and 2.58 Å, respectively, and ΔGe = −0.18 Å, which means a displacement toward the carbonyl oxygen.

The second methoxy group seems almost not linked to the germanium atom (the O···Ge contact is 2.799 Å). This is in agreement with the nonequivalence of the methoxy group signals in the ¹H NMR spectra of compounds 123c and 123e at low temperature. At higher temperatures an exchange process at the germanium center averages the NMR signals. The energies of activation of this process (10.5 and 10.8 kcal mol⁻¹, respectively) suggest a dissociative mechanism including rapid interconversion of the chelating groups.

The Ge–H bond (1.33 Å) in 123c is significantly shorter than that in usual four-coordinate compounds (1.52 Å)⁹. Taking into account a similar shortening of the Si–H bond observed in the case of silylum cation stabilized by amino group ⁴⁴³, as well as the high electroconductivity of triflate 123c in CH₂Cl₂ solution and the significantly high frequency shift of the ¹H NMR Ge–H resonances in compounds 123a–e as compared with their neutral precursors (Δδ = +1.45 to 2.06 ppm), a substantial positive charge is localized on the germanium atom ⁴⁴₁.

The unusual hydrated germyl cation structure of complex 123c·H₂O is discussed in Section VIII.A.

b. β-Germyl-substituted derivatives of carboxylic acids and ketones. These O–Ge chelate complexes containing a five-membered chelate ring GeCCCO have been studied extensively by Mironov and coworkers in 1980–1990 ⁴⁴⁴. Reaction of HGeCl₃ with α,β-unsaturated carboxylic acids⁴⁴⁵, esters⁴⁴⁶ or amides⁴⁴⁷ leads to the corresponding β-trichlorogermyl derivatives Cl₃GeCHR(X)R′COX (X = OH, OAlk, NH₂, NAlk₂; R,R′ = H, Me), e.g. compounds 128a–e (equation 26)⁴⁴⁶–⁴⁴⁹.

\[
\begin{align*}
H₂C\equiv C\equiv C\equiv O &\quad \xrightarrow{\text{HGeCl}_3} \quad O\equiv C\equiv C\equiv X \\
R &\quad \xrightarrow{\text{Cl}₃\text{Ge}R} \quad \xrightarrow{\text{Cl}} \quad \xrightarrow{\text{Cl}} \quad \xrightarrow{\text{Ge}} \quad \xrightarrow{X} \\
\text{(128a)} &\quad X = \text{OH}, R = \text{H} \\
\text{(128b)} &\quad X = \text{OH}, R = \text{Me} \\
\text{(128c)} &\quad X = \text{OMe}, R = \text{Me} \\
\text{(128d)} &\quad X = \text{NH₂}, R = \text{H} \\
\text{(128e)} &\quad X = \text{NMe₂}, R = \text{Me}
\end{align*}
\]

(26)

Germylated steroids 129a and 129b were recently prepared by the same method⁴⁵⁰. Imide 128f (R = H, X = NMeCOMe) was obtained by treatment of Cl₃GeCH₂CH₂COCl with MeCONMeSiMe₃⁴⁵¹.
Reduction of GeCl₄ by disiloxane (Me₂SiH)₂O in the presence of a target organic compound (e.g. esters of acrylic acid, etc.) as a solvent is a convenient one-pot alternative to the reaction in equation 26.⁴⁴⁶

Tribromogerme was also used in an analogous reaction to equation 26 for the preparation of β-tribromogermyl analogues of compounds 128 including acids Br₃GeCH₂CHMeCOOH (130a), (Br₃Ge)₂CHCH₂COOH (130b) and ester Br₃GeCH₂CHMeCOOMe (130c).⁴⁵² According to NQR ⁷⁹,⁸¹Br spectra, a weak O → Ge coordination is present in the latter but not in the former compounds.⁴⁵³ X-ray crystallography of 130b confirmed a tetrahedral environment of the Ge atom.⁴⁵⁴

Reaction of the acids 128a and 128b with excess of PhMgBr leads to the corresponding triphenylgermyl derivatives Ph₃GeCH₂CHRCOOH (131) (R = H, Me) where intramolecular O → Ge coordination is absent.⁴⁵⁵ However, the high reactivity of these compounds and the formation of tertiary alcohols in their reactions with Grignard reagents suggest an effective intramolecular assistance in such transformation due to significant Lewis acidity of the Ph₃Ge group (equation 27).

A similar mechanism was proposed for the Ni-assisted intramolecular dehydrogenation of 3-hydroxygermyl acids 132 (R, R’, R”’, R”” = H, Me, Ph), which yields germalactones 133 instead of the anticipated polymeric products (equation 28).⁴⁵⁶,⁴⁵⁷

Reaction of HGeCl₃ with enolizable ketones produces compounds of the type Cl₃GeC(Me)(R)CH₂COR’ 134a and 134b. Their structures were confirmed by X-ray crystallography.⁴⁵⁸

Trichlorogermyl derivative 135 was obtained by passing ketene and acetone vapors through HGeCl₃.⁴⁵⁹

Structures and details of the intramolecular interaction of compounds 128–135 were studied by IR⁴⁴⁷,⁴⁶⁰ and NQR ³⁵Cl⁴⁴⁷,⁴⁶¹–⁴⁶⁴ spectroscopy and by X-ray crystallography whose results are given in Table 31.
In \(\beta\)-trichlorogermyl derivatives of acids 128a–f and ketones 129a, 129b, 134a and 134b containing a hypervalent fragment \(O \rightarrow GeCl_2 \cdots Cl\), the \(O \rightarrow Ge\) bond lengths vary from nearly the sum of the covalent radii of these elements (1.88 Å) to the sum of their van der Waals radii (3.67 Å). Consequently, the environment of the Ge atom changes from distorted tetrahedron with a weak additional \(O \cdots Ge\) interaction (in acids 128a and 128b) to significantly distorted TBP with axial O and Cl atoms (in ester 128c and the four ketones) to slightly distorted TBP (in amides 128d, 128e and imide 128f). In acids 128a and 128b the \(O \cdots Ge\) interaction seems to be of a purely electrostatic nature and

### Table 31. Crystallographic data for \((O \rightarrow Ge)\) chelates with the Cl\(_3\)GeCCCO fragment

<table>
<thead>
<tr>
<th>Compound</th>
<th>(O \rightarrow Ge) (Å)</th>
<th>(Ge-Cl_{ax}) (Å)</th>
<th>(Ge-Cl_{eq}) (Å)</th>
<th>(O \rightarrow Ge-Cl_{ax}) (deg)</th>
<th>(\Delta Ge^a) (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>128e</td>
<td>2.123</td>
<td>2.264</td>
<td>2.144, 2.134</td>
<td>175.6</td>
<td>0.201</td>
<td>465</td>
</tr>
<tr>
<td>128d</td>
<td>2.166</td>
<td>2.253</td>
<td>2.156, 2.138</td>
<td>176.0</td>
<td>0.223</td>
<td>460</td>
</tr>
<tr>
<td>129a(^b)</td>
<td>2.292</td>
<td>2.202</td>
<td>2.149, 2.102</td>
<td>177.1</td>
<td>0.32</td>
<td>450</td>
</tr>
<tr>
<td>129b</td>
<td>2.393</td>
<td>2.172</td>
<td>2.138, 2.132</td>
<td>177.2</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>128f</td>
<td>2.376</td>
<td>2.195</td>
<td>2.161, 2.168</td>
<td>176.3</td>
<td>0.334</td>
<td>451</td>
</tr>
<tr>
<td>129b</td>
<td>2.381</td>
<td>2.197</td>
<td>2.138, 2.137</td>
<td>177.5</td>
<td>0.32</td>
<td>450</td>
</tr>
<tr>
<td>134a</td>
<td>2.507</td>
<td>2.181</td>
<td>2.144, 2.138</td>
<td>176.9</td>
<td>0.428</td>
<td>466</td>
</tr>
<tr>
<td>134b</td>
<td>2.770</td>
<td>2.169</td>
<td>2.148, 2.139</td>
<td>177.5</td>
<td>0.476</td>
<td>467</td>
</tr>
<tr>
<td>128c</td>
<td>2.790</td>
<td>2.160</td>
<td>2.128, 2.137</td>
<td>177.0</td>
<td>0.52</td>
<td>468</td>
</tr>
<tr>
<td>128b</td>
<td>3.075</td>
<td>2.141</td>
<td>2.122, 2.127</td>
<td>161.9</td>
<td>0.553</td>
<td>476</td>
</tr>
<tr>
<td>128b</td>
<td>3.086</td>
<td>2.146</td>
<td>2.001, 2.133</td>
<td>162.2</td>
<td>0.517</td>
<td>469</td>
</tr>
<tr>
<td>128a</td>
<td>3.228</td>
<td>2.134</td>
<td>2.121, 2.123</td>
<td>—</td>
<td>0.577</td>
<td>460</td>
</tr>
<tr>
<td>130b</td>
<td>3.233</td>
<td>2.141</td>
<td>2.125, 2.128</td>
<td>146.1</td>
<td>0.575</td>
<td>470</td>
</tr>
<tr>
<td>130b</td>
<td>3.687</td>
<td>2.271(^c)</td>
<td>2.267(^c), 2.272(^c)</td>
<td>154.6(^c)</td>
<td>—</td>
<td>454</td>
</tr>
</tbody>
</table>

\(^a\) Deviation of the Ge atom from the equatorial plane toward Cl.

\(^b\) Two independent molecules in the unit cell.

\(^c\) Data for the analogous Br\(_3\)GeCCCO fragment.
there is no coordination with the nearest O···Ge contacts being 4.60 Å (intramolecular) and 4.18 Å (intermolecular)\textsuperscript{471}.

In amides \textbf{128d} and \textbf{128e} the O → Ge distance is the shortest due to a high donor capacity of the amide group. Replacement of the Me group at nitrogen in \textbf{128e} by the acetyl group in imide \textbf{128f} leads to a weakening of the O → Ge interaction\textsuperscript{451}. At the same time the concurrent C=O···H interaction in acids \textbf{128a} and \textbf{128b} weakens the intramolecular O → Ge coordination.

There is a linear relationship between the endocyclic angles OGeC ($\alpha$) and COGe ($\beta$) and the coordination O → Ge bond length (equations 29)\textsuperscript{472}.

\[
\alpha = -20.8 \, d(\text{Ge-O}) + 126.8 \, (r = 0.991, \, n = 7) \quad (29a)
\]
\[
\beta = -18.2 \, d(\text{Ge-O}) + 150.8 \, (r = 0.979, \, n = 6) \quad (29b)
\]

On extrapolation of the equations 29 to a O–Ge distance equal to the covalent bond length (1.75 Å), the environment of pentacoordinate germanium atom corresponds to that of an ideal trigonal bipyramid ($\alpha = 90^\circ$), whereas the valent C–O → Ge angle acquires a value $\beta = 120^\circ$.

As the O → Ge interaction strengthens, a simultaneous weakening of the Ge–Cl\textsubscript{ax} bond and a reduced difference between axial and equatorial Ge–Cl bond lengths takes place (Table 31). The weakening of the O → Ge coordination is accompanied by an increase in the deviation of the germanium atom from the equatorial plane toward the halogen substituent (Scheme 8) and it nearly reaches a value of 0.67 Å for the tetrahedral molecule GeCl\textsubscript{4}\textsuperscript{473}.

\[
\text{SCHEME 8. The deviation } \Delta \text{Ge of the germanium atom from the equatorial plane}
\]

Evaluation of the changes in the O → Ge and Ge–Cl\textsubscript{ax} bond orders by using Pauling’s relation\textsuperscript{474} $\Delta d(n) = d(n) - d(l) = c \ln n$, where $d(l)$ is the ordinary bond length and $d(n)$ denotes the length of the bond of $n$ order, leads to equation 30 for 14 experimental points:

\[
\Delta d(\text{Ge-Cl, Ge-O}) = -0.89 \log(0.50 \pm 0.82\Delta \text{Ge}) \quad (30)
\]

By using a sum of the bond order of 4 in the hypervalent O → GeCCl\textsubscript{2}–Cl fragment and a value of 1 for the axial bonds, values of 0.92 and 0.87, respectively, are obtained for the coefficient $c$. These and the previously calculated value of 0.80 for penta- and hexacoordinate Ge compounds\textsuperscript{475} are lower than $c$ for tin (1.20\textsuperscript{475}). This demonstrates a decreased tendency toward expanding the coordination sphere of germanium atom compared to that of tin\textsuperscript{476}.
The O → Ge bond distances of 2.29–2.39 Å in the steroids 129a and 129b are in the range of 'average' coordination\textsuperscript{177}. The extent of the deviation of the geometry of a hypervalent fragment from the ideal TBP is characterized by the $\Delta \Omega$ value ($\Delta \Omega = 2\pi - \Omega$, where $\Omega$ is the solid angle formed by the directions of the three equatorial bonds around the Ge atom\textsuperscript{478}) of about $91 \pm 1$ deg for the solid angle for both compounds\textsuperscript{450}. This value is intermediate between those for an ideal TBP (0°) and for an ideal tetrahedral coordination (180°).

Quantum-chemical calculations of molecular and electronic structure of trichloroorganogermanes 128d, 128e, 134a and 134b were carried out using AMPAC and HyperChem software\textsuperscript{479}. In the case of amide 128d having one of the shortest O → Ge bond lengths (2.166 Å) in the solid state, only the PM3 method gives reasonable agreement between the theoretical and experimental data for this (ca 2.43 Å) and other distances as well as for valent and torsion angles. The O → Ge bond length increases significantly (up to 2.67 and 2.57 Å) on substitution of the chlorine atoms in 128d with hydrogens or methyl groups while more electronegative fluorine atoms decrease the distance to 2.31 Å.

c. Amide-type (O–Ge) compounds. Hetero-analogs of β-germyl-substituted carbonyl compounds, namely N-germylmethyl derivatives of amides, lactams and imides containing a five-membered GeCNCO chelate ring, were prepared originally by the reaction of trihalogenogermerane ethers with the corresponding N-halogenomethyl compounds (equations 31–34)\textsuperscript{452,480,481}.

$N$-Chloromethyl derivatives of $p$-halobenzyl amide are inactive toward HGeCl$_3$ · 2Et$_2$O. However, under severe conditions they react with HGeCl$_3$ · dioxane to yield the amides (136, $R = F, Cl$)\textsuperscript{480}.

The $\nu$(C=O) absorption band of the $N=\cdot C=\cdot O$ fragment in the IR spectra of compounds 136–140 is shifted significantly (by 60–100 cm$^{-1}$) to a low-frequency region compared with their NH and NCH$_2$Hal derivatives, indicating a rather strong O → Ge coordination\textsuperscript{480}.

\[
p-RC_6H_4CON(R')CH_2Cl \xrightarrow{\text{HGeCl}_3 \cdot 2\text{Et}_2\text{O}} p-RC_6H_4CON(R')CH_2GeCl_3 \quad (136a) \quad R = R' = Me
\]

\[
p-RC_6H_4CON(R')CH_2Cl \xrightarrow{\text{HGeCl}_3 \cdot 2\text{Et}_2\text{O}} p-RC_6H_4CON(R')CH_2GeCl_3 \quad (136a) \quad R = R' = Me
\]

The amide and lactam groups in 136 and 137 are inactive when boiled with concentrated HCl; on reaction with Grignard reagents they yield trialkylgermyl derivatives (equation 35). According to the IR spectra, there is no intramolecular O → Ge interaction in compounds of type 141\textsuperscript{480}.

Germatranes and germocanes were prepared by reaction of the trihalogenogermeranes 136–140 and triethanolamine or diethanolamines (Sections VI.B and VI.C.1.a). In these compounds the Ge atom participates in N → Ge transannular interaction and additional intra- or intermolecular interactions are absent. For example, the shortest O ··· Ge contacts for germatranes $N$(CH$_2$CH$_2$O)$_3$GeCH$_2$CH$_2$COOMe\textsuperscript{482} and
N(CH₂CH₂O)₃GeCH₂CH(Me)COOMe are 4.86 and 4.83 Å, respectively.

\[
\begin{align*}
\text{NCH}_2\text{Br} & \quad \text{HGeX}_3\cdot 2\text{Et}_2\text{O} \\
\text{NCH}_2\text{GeBr}_n\text{X}_{3-n} & \\
(139) & \\
X = \text{Cl}, n = 1-3 \\
X = \text{Br}, n = 3
\end{align*}
\]

\[
\begin{align*}
\text{PhCONHCH}_2\text{GeCl}_3 & \xrightarrow{\text{MeMgI}} \text{PhCONHCH}_2\text{GeMe}_3 \\
(136) R = R' = \text{H} & (141)
\end{align*}
\]

Reaction of ClCH₂GeMe₂Cl with N- or O-trimethylsilyl amides and lactams yields O → Ge pentacoordinate complexes 142–144.

The multistage mechanism of the reaction was studied by NMR monitoring (Scheme 9, equation 36). A trans-metallation leads to formation of the intermediate Me₂GeCH₂Cl derivative 145, which was identified shortly after the reagents were mixed.
in CDCl$_3$ at $-20^\circ$C. Under these conditions, the reaction is apparently reversible with the equilibrium shifted toward the initial compounds.

At higher temperatures (from $-10$ to $+10^\circ$C) the transmetallation products (145) undergo a gradual conversion to the O-alkylation products (146) by chlorine migration from carbon to germanium. Further increase in temperature (up to $60^\circ$C) results in isomerization to the N-alkylation products (142-144). The latter reaction is similar to Chapman rearrangement, although it occurs under remarkably mild conditions. The half-lives for conversion of imidates (146) ($R, R' = (CH_2)_n, n = 4, 5$) are 13 and 25 min, respectively.$^{488}$

Kinetically controlled imidates (146) may be isolated at $20^\circ$C on a preparative scale in 80% yields. The thermodynamically stable products (142-144) were obtained by heating of the initial reagents or the isolated imidates (146) at $60-100^\circ$C for several hours.

Conversions similar to (145) $\rightarrow$ (146) $\rightarrow$ (142-144) occur with the corresponding Si analogues under much milder conditions. In these cases, not only the trans-silylation products but also the corresponding Si imidates are formed as intermediates, which can only be observed by NMR monitoring.$^{492}$

Pentacoordination of the Ge atom in chlorides (142-144) may be detected from the IR spectra. Similar to the isostructural silicon compounds, the N–C=O fragment in (142-144) shows two characteristic absorption bands at 1500–1750 cm$^{-1}$, an intense band around $1600$ cm$^{-1}$ and a less intense band at ca $1510$ cm$^{-1}$.484

Among other compounds, the first optically active amide derivative (142b) containing an asymmetric carbon and a five-coordinated germanium was obtained by the same method$^{486}$ or by a one-pot synthesis from $N$-[(S)-1-phenylethyl]acetamide, hexamethyldisilazane and ClCH$_2$GeMe$_2$Cl. The latter method does not require the initial preparation of $N$-silylated amide and gives a higher overall yield of the final product.

The thermodynamically controlled reactions between ClCH$_2$GeMe$_2$Cl and O- or N-TMS derivatives of 5-ethyl-3-morpholinone$^{493}$ and 2,5-piperazinedione$^{489}$ yield the monochelate (147) and bis-chelate (148a), respectively.

The chlorine atom in (142b) and (144c) may be replaced with bromine or triflate group to give (149) or (150) by the reaction with the appropriate Me$_3$SiX ($X = Br^{486}, OTf^{489}$) reagent (equation 37). These substitutions proceed under mild conditions, which is a result of a
stronger O → Ge coordination in the reaction products than in initial chlorides. Dichloride 148a was converted into bis-chelate ditriflate product 148b by the same method\(^{489}\).

Treatment of the chloride 142a with 5\% solution of KOH in methanol followed by neutralization with citric acid gave germanol MeC(O)N(Me)CH\(_2\)GeMe\(_2\)OH. In the case of bis-germyl derivative 142d the product of heterocyclization 151 was obtained (equation 38)\(^{485}\).

Reduction of chlorides 142a,c,d with an excess of LiAlH\(_4\) affects two reaction centers and yields the corresponding hydrides EtN(R)CH\(_2\)GeHMe\(_2\) (R = Me, CH\(_2\)CH=CH\(_2\), CH\(_2\)GeHMe\(_2\)). The latter was also isolated by reduction of digermamorpholine 151\(^{485}\).
Reaction of chlorides 142b and 144d with Grignard reagents proceeds with high chemoselectivity at the Ge–Cl bond to give the Ge-alkylated products 152a–c (equation 39). According to the IR spectra, the Ge atom in 152a–c is four-coordinated.

Similarly, 142a reacts with BuLi to yield the alkylation product 152d.

\[
\text{RC(O)NR'CH}_2\text{GeMe}_2\text{Cl} \xrightarrow{R''\text{MgX} = \text{MeMgI, PhCH}_2\text{MgCl}} \text{RCONR'CH}_2\text{GeMe}_2\text{R''} \quad (39)
\]

(a) \( R = \text{Me}, R' = \text{CH(Me)Ph}, R'' = \text{Me} \\
(b) \( R = \text{R'Me}, R' = (\text{CH}_2)_5, R'' = \text{Me} \\
(c) \( R = \text{R'Me}, R' = (\text{CH}_2)_5, R'' = \text{CH}_2\text{Ph} \\
(d) \( R = \text{R'Me}, R'' = \text{Bu}
\]

(142b, 144d) (152)

The relative reactivities of 144d and Me3GeCl as well as of chlorides 142b, 144d and their Si analogues in the Grignard reaction have been determined by a competing reactions method and the results are given in Table 32.

The relative reactivity of 144d to Me3GeCl is significantly higher than in the other cases, probably due to Ge–Cl bond lengthening in the hypervalent O → Ge–Cl fragment of 144d compared with Me3GeCl. The difference in reactivity of the pentacoordinated chlorides of Ge and Si in their reaction with Grignard reagents is almost insignificant. This is a result of lesser relative lengthening of the Ge–Cl than Si–Cl bonds in pentacoordinate derivatives, in comparison with the tetracoordinate model compounds of these elements.

### i. Crystallographic data
Numerous X-ray structures for (O–Ge)-chelate complexes containing the GeCNCO fragment were reported in the literature and reviewed. The main geometrical characteristics of the central coordination sites are collected in Table 33. The major part of these compounds has the OGeC3X hypervalent fragment.

All of the compounds above have a near-TBP geometry, with the donor oxygen atom and an electronegative substituent X occupying the axial positions. The GeX angles are generally in the range of 169–171°. The axial O → Ge and Ge–X bonds are longer than the ‘standard’ values determined in tetrahedral derivatives. Correlations between structural parameters of the compounds with an OGeC3Cl unit and other five- and four-coordinated germanium derivatives were discussed. Some general features of the hypervalent bonding and the influence of the nature of central atom, axial substituent X and the C2O-chelated ligand on the character of intramolecular coordination in these complexes may be concluded from the data in Table 34.

### Table 32. Competing reactions of chlorogermanes and Me3GeCl or chlorosilanes with Grignard reagents in 1 : 1 ether–benzene

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initial chlorogermanes and chlorosilanes</th>
<th>Grignard reagent</th>
<th>Mole ratio of the products</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>144d</td>
<td>PhCH2MgCl</td>
<td>152c/Me3GeCH2Ph = 3.40/1</td>
</tr>
<tr>
<td>2</td>
<td>Si-144d$b$</td>
<td>PhCH2MgCl</td>
<td>Si-152c$b$/Me3SiCH2Ph = 1.55/1</td>
</tr>
<tr>
<td>3</td>
<td>144d</td>
<td>PhCH2MgCl</td>
<td>152c/Si-152c$b$ = 1.05/1</td>
</tr>
<tr>
<td>4</td>
<td>142b</td>
<td>MeMgI</td>
<td>152a/Si-152a$b$ = 1.13/1</td>
</tr>
<tr>
<td>5</td>
<td>Me3GeCl</td>
<td>PhCH2MgCl</td>
<td>Me3GeCH2Ph/Me3SiCH2Ph = 2.60/1</td>
</tr>
</tbody>
</table>

$a$Molar ratio of the reagents and the Grignard reagent is 5 : 5 : 1 (except in entry 2 where it is 1 : 1 : 1).

$b$The Si analogue of the compound given.
### TABLE 33. Crystallographic data for (O−Ge) chelates with the XMe$_2$GeCNCO and X$_3$GeCNCO fragment

<table>
<thead>
<tr>
<th>Compound</th>
<th>X</th>
<th>O−Ge (Å)</th>
<th>Ge−X (Å)</th>
<th>OGeX (deg)</th>
<th>ΔGe (Å)$^a$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chelates with the XMe$_2$GeCNCO fragment</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>142b</td>
<td>Cl</td>
<td>2.203</td>
<td>2.359</td>
<td>169.5</td>
<td>0.127 (0.05)$^b$</td>
<td>486</td>
</tr>
<tr>
<td>144a</td>
<td>Cl</td>
<td>2.311</td>
<td>2.324</td>
<td>171.3</td>
<td>0.192</td>
<td>477</td>
</tr>
<tr>
<td>144b</td>
<td>Cl</td>
<td>2.348</td>
<td>2.322</td>
<td>170.6</td>
<td>0.197 (0.096)$^b$</td>
<td>486</td>
</tr>
<tr>
<td>144c</td>
<td>Cl</td>
<td>2.181</td>
<td>2.363</td>
<td>170.6</td>
<td>0.147 (0.058)$^b$</td>
<td>489</td>
</tr>
<tr>
<td>144d</td>
<td>Cl</td>
<td>2.194</td>
<td>2.354</td>
<td>170.6</td>
<td>0.154 (0.055)$^b$</td>
<td>477</td>
</tr>
<tr>
<td>147</td>
<td>Cl</td>
<td>2.265</td>
<td>2.340</td>
<td>169.0</td>
<td>0.176 (0.082)$^{b,c}$</td>
<td>497</td>
</tr>
<tr>
<td>148a</td>
<td>Cl</td>
<td>2.310</td>
<td>2.322</td>
<td>170.6</td>
<td>0.20 (0.11)$^b$</td>
<td>489</td>
</tr>
<tr>
<td>148b</td>
<td>OTf</td>
<td>1.995</td>
<td>2.335</td>
<td>169.1</td>
<td>−0.09 (−0.12)$^b$</td>
<td>489</td>
</tr>
<tr>
<td>149</td>
<td>Br</td>
<td>2.138</td>
<td>2.558</td>
<td>169.4</td>
<td>0.066 (−0.218)$^{b,d}$</td>
<td>486</td>
</tr>
<tr>
<td>150</td>
<td>OTf</td>
<td>1.90</td>
<td>2.58</td>
<td>167.3</td>
<td>−0.18 (−0.30)$^b$</td>
<td>489</td>
</tr>
<tr>
<td><strong>Chelates with the Cl$_3$GeCNCO fragment</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>136a$^{e,f}$</td>
<td>Cl</td>
<td>2.080,</td>
<td>2.252,</td>
<td>174.5</td>
<td>0.175</td>
<td>498</td>
</tr>
<tr>
<td></td>
<td>2.092</td>
<td>2.239$^b$</td>
<td>176.5</td>
<td>0.200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>137a$^{e}$</td>
<td>Cl</td>
<td>2.140</td>
<td>2.253</td>
<td>178.3</td>
<td>0.19</td>
<td>465</td>
</tr>
<tr>
<td>137b$^{e}$</td>
<td>Cl</td>
<td>2.049</td>
<td>2.268$^b$</td>
<td>175.3</td>
<td>0.160 (0.087)$^{b,i}$</td>
<td>498</td>
</tr>
</tbody>
</table>

$^a$Deviation of the central atom (Ge) from the equatorial plane; positive Δ indicates deviation toward X.

$^b$For the corresponding Si analogue.

$^c$For 4-(dimethylchlorosilylmethyl)-2-ethyl-5-morpholinone.

$^d$For 1-(dimethylbromosilylmethyl)-2-piperidone.

$^e$The OGeCCl$_3$ central coordination site.

$^f$Two independent molecules in the unit cell.

$^{g}$Ge−Cl$_{eq}$ 2.132, 2.148 and 2.150, 2.141 Å.

$^{h}$Ge−Cl$_{eq}$ 2.125, 2.133 Å.

$^{i}$Reference 499.

In accordance with the rule of the constancy of the total order of the axial bonds in a hypervalent fragment$^{500}$, the shortening of the dative O → Ge distance is accompanied by a corresponding relative lengthening of the Ge−X distance. Thus, the O → Ge bond is longer in 144a (2.341 Å) than in 144c (2.181 Å). Consequently, in 144a the Ge−Cl distance is shorter (2.324 Å) than that in 144c (2.343 Å).

The smallest total relative lengthening of the bonds in a hypervalent fragment O → M−X (which may be calculated as the relative lengthening of the O → M and M−X bonds in comparison with ‘standard’ bond lengths in tetrahedral compounds; Δd, %) are observed for the compounds with minimal deviation of the central atom from the equatorial plane, i.e. for ΔM ≈ 0 (Tables 33 and 34). In the case of germanium, such a compound is the bromide 149 (ΔGe = 0.066 Å, Δd(O−Ge) = 22%, Δd(Ge−Br) = 10%). The higher ΔGe value in chlorides 144a,c,d (0.15−0.19 Å) leads to larger relative bond lengthening (25−32% for Δd(O−Ge) and 8−10% for Δd(Ge−Cl)). The behavior of the analogous silicon compounds is similar. The corresponding bond lengthenings are 30, 18, 9 and 6% for O−Si bonds and 5, 13, 41 and 53% for the Si−Hal bonds in fluoride MeC(O)N(CH(Ph)Me)CH$_2$SiMe$_2$F (153) and in 1-(dimethylhalosilylmethyl)-2-piperidones (Hal = Cl, Br, I, respectively).

According to the criteria proposed on the basis of X-ray structural data,$^{477,486,501}$ the O−Ge distances (2.18–2.35 Å) in monochlorides 142, 144, 147 and 148a fall within the region of ‘average’ coordination distances; the corresponding Ge−Cl bond lengths (2.32−2.36 Å) are larger than ‘standard’ (tetrahedral) distances by only 0.2−0.3 Å. The intramolecular O → Ge coordination in trichlorides 137 and 136d is ‘strong’ (for a
The nature of the axial ligand affects substantially the TBP geometry. In germanium derivatives the $\Delta \Omega$ values decrease by ca 20 and 78° upon substitution of the Cl atom (in 144a–d, 142b is stronger for the larger lactam derivatives or the acyclic compounds (the substituents, where $\Delta \Omega$ being 0.197, 0.192, 0.147, 0.154 and 0.127 Å, respectively). On the contrary, the $\Delta \Omega$ values increase from 0.147 to 0.176 and 0.20 Å, respectively). At the same time, most trichlorides except the amide and the steroid derivatives 128d, 128e, 129a and 129b (Table 31) have a ‘weak’ coordination (2.48–3.23 and 2.13–2.33 Å, respectively). The geometry of the hypervalent OMC$_3$X fragment (M = Ge, Si) may be also characterized by the $\Delta \Omega = 2\pi - \Omega$ parameter, where $\Omega$ is a solid angle formed by equatorial bonds of the central atom. $\Delta \Omega = 2\pi - \Omega$ (0° for ideal TBP and 180° for ideal tetrahedron).

The nature of the axial ligand affects substantially the TBP geometry. In germanium derivatives the $\Delta \Omega$ values decrease by ca 20 and 78° upon substitution of the Cl atom (in 144a–d, 142b is stronger for the larger lactam derivatives or the acyclic compounds (the substituents, where $\Delta \Omega$ being 0.197, 0.192, 0.147, 0.154 and 0.127 Å, respectively). On the contrary, the $\Delta \Omega$ values increase from 0.147 to 0.176 and 0.20 Å, respectively). At the same time, most trichlorides except the amide and the steroid derivatives 128d, 128e, 129a and 129b (Table 31) have a ‘weak’ coordination (2.48–3.23 and 2.13–2.33 Å, respectively). The geometry of the hypervalent OMC$_3$X fragment (M = Ge, Si) may be also characterized by the $\Delta \Omega = 2\pi - \Omega$ parameter, where $\Omega$ is a solid angle formed by equatorial bonds of the central atom. $\Delta \Omega = 2\pi - \Omega$ (0° for ideal TBP and 180° for ideal tetrahedron).
by Br (in 149) and Br by OTf (in 150), respectively. Thus, this parameter changes in the same order with the structural parameter $\Delta Ge$ (the deviation of the germanium from the plane defined by the three equatorial ligands) discussed above. The signs of both $\Delta Ge$ and $\Delta \Omega$ remain the same in the cases of Cl and Br and become negative while the inversion of the configuration of the central atom in the OTf derivative takes place ($\Delta Ge = -0.18$, $\Delta \Omega = -59^\circ$ for 150). In terms of the $S_N2$ reaction coordinate, the structures of 142b and other chlorogermanes with hypervalent OGeC$_3$X fragment (Table 34) represent an early stage of the reaction (Scheme 10, $M = Ge, X = Cl$). Bromide 149 ($X = Br$) is a model of a nearly TBP intermediate state, and triflate 150 ($X = OTf$) represents the final stage with inverted germanium center.

In the case of the silicon derivatives L$^n$SiMe$_2$X and R$^*$SiMe$_2$X ($R^* = MeC(O)N(CH(Ph)Me)CH_2, X = Hal or OTf$) a similar inversion of the TBP configuration takes place upon substitution of Cl by Br (Table 34, Scheme 10). The distortion of the TBP environment is increased in the series of Si, Ge, Sn, especially on replacement of the Si atom by Ge (the $\Delta \Omega$ values for chlorides L$^n$MMe$_2$Cl are 19, 45 and 55°).

Lactamomethyl and amidomethyl derivatives of five-coordinate germanium and silicon, in particular halides 142b, 144b, 149 and their Si analogues, Si-142b, Si-144b and 153, were compared with respect to the relative deviations of the central atoms from the plane of the three equatorial substituents. The relative deviations were defined as $\Delta M_s - \Delta M/\Delta M_s$ (where $\Delta M$ is the deviation of the five-coordinate M atom from the equatorial plane toward the Hal atom and $\Delta M_s$ is the deviation of the tetrahedral M atom from the plane through the three substituents in the model compound) on formally going from the four-coordinate state of the central atom to the five-coordinate state (Table 34). This parameter is suggested to characterize the ability of the four-coordinate Ge or Si atoms to deviate from the equatorial plane when subjected to the attack of the nucleophilic reagent (the O atom of the amide fragment) yielding a five-coordinated intermediate (i.e. geometric rigidity of the Ge or Si substrate) and the donor ability of the oxygen atom in the C,O-chelating ligand with respect to the corresponding electrophilic center. The deviation of the M atom from the plane of three carbon atoms in the Me$_3$MHal molecules calculated from the geometry of Me$_3$MHal optimized by the AM1 method was used as the standard value of $\Delta M_s$.

The values of the relative displacements of Ge and Si atoms in structural analogues (Table 34) indicate a higher geometric rigidity of the Ge atom environment and higher
donor ability of the O atoms in amides 142b and Si-142b compared to those in five-membered lactams 144b and Si-144b.

Electroconductivity of the pentacoordinated germanium compounds is lower than that of their Si analogues496. Nevertheless, the relatively high electroconductivity of triflate 150 indicates the possibility of a dissociative mechanism for reactions of pentacoordinated germanium compounds with relatively good leaving groups at the Ge atom which give cations with tetracoordinated germanium atom.

**ii. Dynamic 1H NMR spectroscopy.** In halides 142b, 144b and 149, the presence of a chiral carbon atom makes the methyl groups on Ge diastereotopic. The coalescence of their signals with a change in temperature was used to obtain ligand exchange barriers resulting from either pseudorotation, or O—Ge cleavage followed by rotation and reclosure, or intermolecular exchange (Table 35). Apparently, a process involving inversion of germanium (Berry-type pseudorotation) which take into account the low conductivity of chloride 144c (in CD2Cl2) can be suggested only for chlorides 142b and 144b in CDCl3 in the absence of added external nucleophiles. However, a noticeable decrease in the ΔG‡ value on going from chloride 142b to chloride 144b, as well as from Si-142b to Si-144b, i.e. on a change to compounds with a weaker O→M (M= Ge, Si) coordination bond, allows one to assume O—M cleavage as a most likely stage of the process. This stage can be also considered as probable when addition of a stoichiometric quantity of external nucleophiles resulted in lowering of the barrier.

The nature of the electronegative substituent at the central atom substantially affects the barrier for ligand exchange at both germanium and silicon. Thus, the replacement of Cl by Br on going from chloride 142b to bromide 149 decreases ΔG‡ (for example, to 17.8 kcal mol−1 in CDCl3). However, the effect of a change of the halogen atom in CD3OD (a solvent possessing higher solvating ability) is virtually absent. Thus, for bromide 149, ΔG‡ = 15.3 kcal mol−1, which is only 0.3 kcal mol−1 lower than that for chloride 142b.

A decrease in the barrier for ligand exchange on going from the germanium derivatives to the corresponding silicon ones when all other factors remain the same (Table 35) is indicative of the higher configurational stability of the five-coordinate Ge halides under

<table>
<thead>
<tr>
<th>Type of compound A</th>
<th>M Solvent, additive</th>
<th>Number</th>
<th>ΔG‡±0.1 (kcal mol−1)</th>
<th>M Number</th>
<th>ΔG‡±0.1 (kcal mol−1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R*MMe2Cl</td>
<td>Ge CDCl3</td>
<td>142b</td>
<td>&gt;23</td>
<td>Si Si-142b</td>
<td>14.9a 14.2</td>
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<tr>
<td></td>
<td>CD3CN</td>
<td></td>
<td>&gt;20</td>
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</tr>
<tr>
<td></td>
<td>CD3CN, DMAb</td>
<td></td>
<td>17.0</td>
<td></td>
<td>13.4c 11.9</td>
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<tr>
<td></td>
<td>CD3OD</td>
<td></td>
<td>15.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-Ph-L5MMe2Cl</td>
<td>Ge CDCl3</td>
<td>144b</td>
<td>17.8</td>
<td>Si Si-144b</td>
<td>11.0d</td>
</tr>
<tr>
<td></td>
<td>CD3CN</td>
<td></td>
<td>11.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R*MMe2Br</td>
<td>Ge CDCl3</td>
<td>149</td>
<td>—</td>
<td>Si Si-149</td>
<td>14.6a 14.2a</td>
</tr>
<tr>
<td></td>
<td>CD3CN</td>
<td></td>
<td>17.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CD3OD</td>
<td></td>
<td>15.3</td>
<td></td>
<td>11.9</td>
</tr>
<tr>
<td></td>
<td>CD3CN, LiBr</td>
<td></td>
<td>13.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

aReference 506.

bDMA =N, N-dimethylacetamide; for DMA, ΔG‡ = 21 kcal mol−1.

cIn CD3CN + LiBr.

d(10.8)507.
consideration compared to their Si analogues. This is in agreement with X-ray diffraction data on the higher rigidity of the central OGeC3Hal compared with the OSiC3Hal coordination unit discussed above.

The stereochemical flexibility of chloride 144d and its Sn analogue, Sn-144d, was studied by NMR spectroscopy. The protons of the NCH2M and MMe2 groups (M = Ge, Sn) were anisochronic at < −70°C. The values of activation free energy of the process resulting in chemical equivalence of the protons indicated were determined by the 1H DNMR method in 1 : 1 CDCl3 : C2D2Cl2 and were 9.4 kcal mol−1 (NCH2Ge) for chloride 144d, 9.6 (NCH2Sn) and 9.3 (SnMe2) kcal mol−1 for chloride Sn-144d. The signal anisochronicity was due to the restricted inversion of the seven-membered lactam ring.

2. Derivatives with other bidentate chelating ligands

Although the hypervalency of organogermanium compounds with monoanionic C,O-chelating ligands was the most extensively studied, complexes containing other monoanionic bidentate X,D-chelating ligands (X, D = C, N, O, S) have also been reported. Among them, the first representative triorganogermanium halides with C,N-chelating ligands is 154, whose solid state structure was unambiguously determined by an X-ray diffraction in 1981, as well as lactim ether 155 and the thiolactim ethers, 156a and 156b. The Ge atom in 154 is pentacoordinated due to intramolecular N → Ge coordination and it has a distorted TBP arrangement at the germanium center, with three equatorial carbon atoms and axial chlorine and nitrogen. The axial bond lengths (Table 36) are significantly longer than the sum of the covalent radii for these elements (Table 1).

The synthesis of 155 at the second stage of the reaction between ClCH2GeMe2Cl and the corresponding N-TMS lactam was described above (Scheme 9). The use of N-TMS thiolactam in this reaction leads to isolated 155, unlike 155, as the S-alkylated product. Thiolactim ether 156b was isolated as a by-product in the reaction of (ClCH2)2GeCl2 and N-TMS hexahydro-2-azepinthione (Section X.B).

X-ray determinations reveal for imidates 155 and 156a a TBP structure, with axial nitrogen and chlorine. The Ge–Cl bond is longer in the N–Ge chelate 155 than in the O–Ge chelate 144d (2.460 and 2.354 Å, respectively). In conformity with the constancy of the sum of the order of axial bonds at a TBP atom, it means that the N → Sn coordination is stronger than the O → Ge coordination. This is confirmed by comparison of the distortion degree of the TBP structure of the Ge atom in 155 and 144d.
TABLE 36. Selected structural parameters for pentacoordinated neutral (N → Ge) chelates

<table>
<thead>
<tr>
<th>Compound</th>
<th>( N \rightarrow Ge ) (Å)</th>
<th>Ge−Cl (Å)</th>
<th>( N \rightarrow Ge−Cl ) (deg)</th>
<th>( \Delta Ge ) (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MePhPhNGeCl (154)</td>
<td>2.479</td>
<td>2.327</td>
<td>174.0</td>
<td>—</td>
<td>509</td>
</tr>
<tr>
<td></td>
<td>2.508</td>
<td>2.301</td>
<td>173.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>155</td>
<td>2.15</td>
<td>2.458</td>
<td>164.9</td>
<td>0.00</td>
<td>491</td>
</tr>
<tr>
<td>156a</td>
<td>2.064</td>
<td>2.566</td>
<td>170.3</td>
<td>—0.05</td>
<td>477</td>
</tr>
<tr>
<td>Si-156a</td>
<td>1.945</td>
<td>2.423</td>
<td>172.5</td>
<td>—0.05</td>
<td>496</td>
</tr>
<tr>
<td>156b</td>
<td>2.07</td>
<td>2.41</td>
<td>174.2</td>
<td>—</td>
<td>487</td>
</tr>
</tbody>
</table>

\( a \)PhN = 2-[(dimethylamino)methyl]phenyl.

\( b \)Deviation of the central atom (Ge) from the equatorial plane; positive \( \Delta \) indicates deviation toward Cl.

\( c \)Two independent molecules.

\( d \)Data for the silicon analogue of 156a are given for comparison.

former, the Ge atom is essentially in the equatorial plane, whereas in the latter it is noticeably shifted from this plane toward the chlorine atom (\( \Delta Ge = 0.15 \) Å)\textsuperscript{491,487}.

The \( N \rightarrow Ge \) (2.054 Å) and Ge−Cl (2.566 Å) distances in thiolactim ether 156a are the shortest and the longest, respectively, among the values known for pentacoordinated germanium derivatives. Moreover, the Ge atom is displaced from the equatorial plane toward the N atom (\( \Delta Ge = −0.05 \) Å) i.e. the Ge−Cl bond represents an ‘additional’ bond.

Comparison of structural characteristics of the thiolactim ethers 156a and the Si analogue, Si-156a (Table 36), shows that the strength of the intramolecular \( N \rightarrow M \) (\( M = Si, Ge \)) interaction is approximately the same in the coordinative \( N \rightarrow MC_3 \)−Cl units. The relative lengthening of the N−M bond in these compounds relative to the normal bond length in the corresponding tetrahedral compounds, as well as \( \Delta Si, \Delta Ge \) and the N−M bond order is actually equal\textsuperscript{496}.

A numerous series of compounds containing a N,O-chelating ligand, namely the derivatives of anthranilic (157) and 3-amino-2-thiophenecarboxylic (158 and 159) acids, were prepared by the reactions of organohalogenermes with esters, amides or lithium derivatives of acids\textsuperscript{510−516}.

An intramolecular O → Ge coordination in the products is suggested on the basis of their IR spectra.

Reaction between 3-amino-2-thiophenecarboxylic acid and \( R_2GeCl_2 \) with a deficiency of the LiNH\(_2\) gives the monoamino compounds 158 while an excess of lithium amide leads to formation of the diamino derivatives 159\textsuperscript{513,515,516}. The authors suggest that intermolecular \( O \rightarrow Ge \) coordination increases the lability of chlorine substituent in the intermediate 158 and favors the formation of the diamino derivatives 159\textsuperscript{510,513,515}.

Reaction of halides 157a and 157c with \( t-\text{BuLi} \textsuperscript{511} \) or of chloride 158a with lithium\textsuperscript{515} leads respectively to germaimines 160a, 160b and 161 stabilized by \( O \rightarrow Ge \) coordination. The dimethylamino derivative 157b was prepared from the fluoride 157a and LiNMe\(_2\) at −40°C in THF while the formation of germaimine 160a requires more drastic conditions\textsuperscript{511}.

In the presence of reagents with labile hydrogen in the germaimines 160 and 161 undergo addition reactions and yield different known and new compounds of the types of 157 and 158, respectively\textsuperscript{512}.

Trifluoroacetoxygermane 162 obtained by the reaction of Ph\(_4\)Ge with CF\(_3\)COOH is a rare example of a pentacoordinated germanium compound where intramolecular coordination leads to formation of four-membered chelate ring\textsuperscript{517,518}. In solution, a O → Ge coordination in 162 was deduced on the basis of the IR spectrum. The \( \nu(C=O) \) absorption band (1745 cm\(^{-1}\)) is about 80 cm\(^{-1}\) lower than that in CF\(_3\)COOH. According to X-ray
The molecules of 162 are monomeric in the crystal. The environment of the Ge atom is a highly distorted tetrahedron with a weak (3.09 Å) additional O···Ge contact. The latter is only by 0.5 Å shorter than the sum of van der Waals radii of the O and Ge atoms (Table 1).

A series of new triphenylgermanium complexes of the type 163 (R = Me, Et, Ph and p-ClC₆H₄) was recently synthesized by the interaction of Ph₃GeCl with the sodium salt of sterically congested heterocyclic β-diketones. In view of their monomeric nature and the bidentate nature of the ligands, which are the conjugate bases of the corresponding
16. Hypervalent compounds of organic germanium, tin and lead derivatives

\[
\begin{align*}
\text{(162)} \quad & \quad \begin{array}{c}
\text{Ph}^- \quad \text{Ge} \quad \text{Ph} \\
\text{O} \quad \text{Ph} \quad \text{CF}_3 \quad \text{O}
\end{array} \\
\text{(163)} \quad & \quad \begin{array}{c}
\text{Ph} \quad \text{Ge} \quad \text{Ph} \\
\text{O} \quad \text{N} \quad \text{N} \quad \text{Me}
\end{array}
\end{align*}
\]

\[
\text{(164)} \quad (a) \ X = \text{Cl} \\
(b) \ X = \text{Br} \\
(c) \ X = \text{I}
\]

\(\beta\)-diketones, a pentacoordinate structure of these complexes was proposed in which the central germanium atom acquires the TBP geometry.

Halides \(\text{XMe}_2\text{Ge(DMTC)}\) 164a–c provide an example of distorted TBP germanium compounds with the anisobidentate dimethylidithiocarbamate (DMTC) ligand\(^{521,522}\). The latter is significantly asymmetric with a shorter Ge–S\(_{eq}\) bond and a longer Ge–S\(_{ax}\) distance (Table 37). The axial Ge–Hal bonds are considerably longer than those typically found for four-coordinate germanium halides. The Ge–S\(_{ax}\) bond lengths decrease along the series chloride, bromide, iodide, being 2.896, 2.828 (mean) and 2.685 Å, respectively, with a parallel increase in the SGeS bite angle.

The Ge(II) derivative \(165\) reacts with elemental S and Se to give the corresponding thione \(166a\) and selenone \(166b\) at room temperature but the dihydropyridinato compounds

\[
\begin{array}{|c|c|c|c|c|c|c|}
\hline
\text{Compound} & \text{D\(_{ax}\)} \quad \text{X\(_{eq}\)} & \text{Y\(_{ax}\)} & \text{D–Ge} \quad \text{Å} & \text{Y–Ge} \quad \text{Å} & \text{X–Ge} \quad \text{Å} & \text{DGeY} \quad \text{deg} & \text{DGeX} \quad \text{deg} & \Delta \text{Ge} \quad \text{Å} & \text{Reference} \\
\hline
162 & O & O & C & 3.084 & 1.981 & 1.866 & 143.6 & 44.8 & 0.65 & 519 \\
164a & S & S & Cl & 2.896 & 2.251 & 2.254 & 159.2 & 68.5 & 0.28 & 521 \\
164d & S & S & Br & 2.840 & 2.418 & 2.222 & 159.1 & 69.8 & 0.26 & 522 \\
164c & S & S & I & 2.817 & 2.430 & 2.252 & 161.1 & 69.6 & 0.28 & 522 \\
167a & N & C & N\(_a\) & 2.250 & 2.095 & 2.023 & 163.4 & 66.6 & — & 523 \\
\hline
\end{array}
\]

\(a\) Coordinating atom in ligand.
\(b\) Bite angle of chelate ligand.
\(c\) Deviation of the germanium atom from the quasi-equatorial plane toward the pseudo-axial carbon or halogen atom.
\(d\) Two independent molecules in the unit cell.
\(e\) Three molecules in the asymmetric unit; mean values.
167a and 167b at elevated temperatures (equation 40)\textsuperscript{523}. The latter are formed by a 1,3-TMS shift from one of the methyl bridges to the sulfur or selenium atoms in 166a and 166b, respectively.

\begin{align*}
\text{(165)} & \\
\text{Me}_3\text{Si} & \text{SiMe}_3 \\
\text{N} & \text{Ge} & \text{N} \\
\text{Me}_3\text{Si} & \text{SiMe}_3 \\
\begin{array}{c}
\text{X} \\
\text{(20°C)}
\end{array}
\end{align*}

\begin{align*}
\text{(166) (a) } X &= \text{S} \\
\text{(b) } X &= \text{Se}
\end{align*}

\begin{align*}
\text{N} & \text{Ge} & \text{SiMe}_3 \\
\text{Me}_3\text{Si} & \text{SiMe}_3 & \text{N} \\
\text{X} & \text{Me}_3\text{Si} & \text{SiMe}_3 \\
\text{(60–110°C)}
\end{align*}

\begin{align*}
\text{(167) (a) } X &= \text{S} \\
\text{(b) } X &= \text{Se}
\end{align*}

An X-ray determination reveals for 167a a distorted TBP structure, with the two N atoms at the axial positions and the two C and S atoms at the equatorial sites.

A novel type of pentacoordinate germanium compound 168 was recently obtained by the reaction of \textit{t}-BuGeCl\textsubscript{3} with mercaptaoacetic acid\textsuperscript{524}. It is likely that \textit{t}-BuGe(SCH\textsubscript{2}CO\textsubscript{2}H)\textsubscript{3} (169) is first formed. Subsequently, an intramolecular nucleophilic substitution takes place on germanium, where one of the \textendash\text{SCH\textsubscript{2}CO\textsubscript{2}H} moieties of 169 acts as nucleophile while the other is the leaving group to give 168.

As shown by X-ray crystallography, the germanium atom in 168 is pentacoordinate with a near-TBP structure. The two Ge\textendash S and Ge\textendash C bonds are equatorial while the two Ge\textendash O bonds are apical at an angle of 166.7° with equal length (\textit{ca} 2.04 Å), which is somewhat longer than the standard Ge\textendash O bond length (\textit{ca} 1.7\textendash 1.8 Å).

\begin{align*}
\text{t-Bu} & \text{Ge} \text{O} \text{S} \\
\text{S} & \text{O} \text{C} \text{OH} \\
\text{C} \text{O} & \text{OH} \text{C} \text{O}
\end{align*}

\begin{align*}
\text{(168)}
\end{align*}
16. Hypervalent compounds of organic germanium, tin and lead derivatives

Based on the $^1$H and $^{13}$C NMR spectra which exhibited only one signal each for the CH$_2$ protons and the carbonyl carbons in 168, a rapid equilibrium between two identical pentacoordinate species is proposed in solution (equation 41)$^{524}$.

**B. Bicyclic Complexes. Germocanes and their Analogues**

Bicyclic derivatives of germanium, tin and lead of the type XYM(ZCH$_2$CH$_2$)$_2$D 170 belong to the class of metallocanes. The presence of 1,5-transannular interaction between the D and M atoms in these compounds increases the coordination number of M. Depending on nature of the M atom and the ligands, the molecules of metallocanes may adopt one of the two basic configurations 170A and 170B both in the solid state and in solution. In addition to conformational and molecular dynamic studies, these compounds were also used by Dräger and coworkers for the development of a new concept of the hypervalent bonding for main group elements$^{525}$.

![Diagram of 170A and 170B]

The most common types of germocanes are 1-aza-4,6-dioxagermocanes 171$^{444,526}$ and 172$^{527}$, 1-oxa- and 1-thia-4,6-dithiagermocanes 173 and 174$^{528}$, and 1-aza-4,6-dicarbagermocanes 175–177$^{525}$.

![Structures of 171, 172, 173, 174, 175, 176, 177]

1-Azagermocanes 171 ($X = Y = Me$, Et, R = Me, n-Pr; $X = Y = 2$-Thi, R = Me (171a)) were prepared with good yields from dialkoxygermanes and dialkanolamines$^{444,526}$ (equation 42).

$\text{XYGe(OR')}_2 + (\text{HOCH}_2\text{CH}_2)_2\text{NR} \rightarrow \text{XYGe(OCH}_2\text{CH}_2)_2\text{NR} + 2\text{R'}\text{OH}$ (42) 

Synthesis of the dihydroxy derivatives 172a,b ($X = Y = OH$, R = H (a), Me (b)) was also reported$^{529}$. A new synthetic approach to 1-azagermocanes 171 ($X = Y = 2$-Thi,
R = t-Bu) and 171a, i.e. an exothermic dehydrocondensation of di(2-thienyl)germane and diethanolamines without a catalyst, was reported recently\(^{526}\) (equation 43).

\[
(2\text{-Thi})_2\text{GeH}_2 + (\text{HOCH}_2\text{CH}_2)_2\text{NR} \rightarrow (2\text{-Thi})_2\text{Ge(OCH}_2\text{CH}_2)_2\text{NR} + 2\text{H}_2
\]

\(R = \text{Me, t-Bu}\) (171), (171a) \(\quad (43)\)

1-Oxa- and 1-thiagermocanes 173 and 174 were prepared by refluxing the reagents in equation 44 in benzene until the complete removal of HCl\(^{528}\).

\[
\text{GeCl}_4 + (\text{HSCH}_2\text{CH}_2)_2\text{D} \rightarrow \text{Cl}_2\text{Ge(SCH}_2\text{CH}_2)_2\text{D} + 2\text{HCl}
\]

\(D = \text{O, S}\) (173), (174) \(\quad (44)\)

Reaction of the Grignard reagent \(\text{RN}[(\text{CH}_2)_3\text{MgCl}]_2\) with \(\text{GeCl}_4\)^\(^{530,531}\) or \(\text{PhGeCl}_3\)^\(^{525}\) gives carbagermocanes 175, 176 and 177, respectively, with low yields (3–15\%) (equation 45).

\[
\text{GeCl}_4 + \text{RN}[(\text{CH}_2)_3\text{MgCl}]_2 \rightarrow \text{Cl}_2\text{Ge(CH}_2\text{CH}_2\text{CH}_2)_2\text{NR}
\]

\(R = \text{Me, CH}_2\text{Ph, i-Bu}\) (175–177) \(\quad (45)\)

The yield of 1-thiacarbagermocane \(\text{Cl}_2\text{Ge(CH}_2\text{)}_3\text{S}\) prepared by a similar method is also low (12\%) while its o-analogue \(\text{Cl}_2\text{Ge(CH}_2\text{)}_3\text{O}\) could not be isolated\(^{531}\). Both chlorine atoms in dichloride 175 may be substituted with \(\text{Ph}_3\text{SiO}\) groups by the reaction of 175 with \(\text{Ph}_3\text{SiONa}\) in toluene\(^{531}\).

A different type of germocanes are the spirogermocanes 178, that are prepared by the reaction of polygermaniumsesquioxide \((\text{HOOCCH}_2\text{CH}_2\text{GeO}_{1.5})_n\) with triethanolamine or N-substituted diethanolamines\(^{444,532}\).

![Diagram](image-url)

Similar derivatives of ethylene glycol 179\(^{533}\) and 2-hydroxy-2,2-diphenylacetic acid 180\(^{534}\) were also reported. The former was formed in the reaction of \(N\)-methyl diethanolamine and \(\text{GeO}_2\) or \((n\text{-PrO})_4\text{Ge}\) in the presence of ethylene glycol\(^{533}\).

Spiroyclic ‘double germocanes’ 181 and 182 were prepared by the ligand exchange reactions from dihydroxygermocanes 172a and 172b and the derivatives of dithiols \((\text{HSCH}_2\text{CH}_2)_2\text{D}\) \((D = \text{O, S})\) in boiling methanol\(^{527}\).

Recently, the molecular structures of several germocanes and spirogermocanes were determined. Tables 38 and 39 provide selected structural parameters of the TBP structures.
16. Hypervalent compounds of organic germanium, tin and lead derivatives

TABLE 38. Structural parameters for germocanes XYGe(ZCH₂CH₂)₂D (X = Y)

<table>
<thead>
<tr>
<th>Compound (D/X/Z)</th>
<th>D → Ge(Å)</th>
<th>Ge–X(Å)</th>
<th>D–Ge–X (deg)</th>
<th>ΔGe¹ (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>171a (MeN/2-Thi/O)</td>
<td>2.446</td>
<td>1.954</td>
<td>162.1</td>
<td>0.266</td>
<td>526</td>
</tr>
<tr>
<td>177 (i-BuN/Cl/CH₂)</td>
<td>2.389</td>
<td>2.319</td>
<td>177.2</td>
<td>0.182</td>
<td>530</td>
</tr>
<tr>
<td>172a (HN/OH/O)</td>
<td>2.123</td>
<td>1.993</td>
<td>177.9</td>
<td>0.172</td>
<td>529</td>
</tr>
<tr>
<td>173 (O/Cl/S)</td>
<td>2.355</td>
<td>2.212</td>
<td>172.8</td>
<td>0.293</td>
<td>535</td>
</tr>
<tr>
<td>174 (S/Cl/S)</td>
<td>3.005</td>
<td>2.208</td>
<td>177.8</td>
<td>0.354</td>
<td>536</td>
</tr>
</tbody>
</table>

¹Deviation of the Ge atom from the equatorial plane toward the X substituent.

including bond lengths of germanium to the two apical ligands, the D–Ge–X angles and the displacement (Δ) of the Ge atom from the central plane defined by the three equatorial ligands.

The Ge atoms in the germocanes (Table 38) are pentacoordinated due to hypervalent D → Ge–X interaction. The coordination environments of these atoms are distorted TBP with the donor D (D = N, O, S) and the X in axial positions. The intramolecular coordination D → Ge bond belongs to both 5-membered heterocycles.

The D → Ge–X angles in all structures fall in the range of 173–178°, with the only exception of the 2-thienyl derivative 171a. The distortion of the TBP configuration in the latter compound is the most prominent. Despite the significant increase of the O–Ge–O angle, the oxygen atoms still occupy equatorial positions while the nitrogen atom is axial, which is also the case in its Si analogue Ph₂Si(OCH₂CH₂)₂NH. This contrasts with the structure of the Sn analogue (t-Bu)₂Sn(OCH₂CH₂)₂NMe (see below) where the oxygen atoms occupy axial positions.

The Ge atom in germocanes is shifted from the equatorial plane toward the X substituent. Both axial bonds are elongated as predicted by the concept of the 3c–4e hypervalent bond. The D → Ge distance is larger than the sum of covalent radii of these elements but is still significantly shorter than the sum of their van der Waals radii (Table 1).

At present, a detailed discussion of the influence of different factors on the strength of intramolecular coordination in germocanes is lacking due to insufficient experimental data. However, there is a tendency of weakening the coordination upon replacement of chlorine substituent at the Ge atom with a less electronegative 2-thienyl group as well as by the replacement of a donor nitrogen atom by oxygen and further with sulfur.

The ΔGe values in the spirocyclic derivatives (Table 39) are smaller than those in regular germocanes. Thus the TBP coordination polyhedra of the Ge atoms in the former are less distorted. The N → Ge distances in spirocyclic germocanes are also smaller, which indicate a stronger coordination in these compounds.

Both spirocyclic ‘double germocanes’ 181 and 182 have distorted tetrahedral geometry of the central atom. Four chalcogen atoms occupy a pseudo-equatorial plane. The

TABLE 39. Structural parameters for spirogermocanes XYGe(OCH₂CH₂)₂NR

<table>
<thead>
<tr>
<th>Compound (R/X,Y)</th>
<th>N → Ge (Å)</th>
<th>Ge–X (Å)</th>
<th>N → Ge–X (deg)</th>
<th>ΔGe¹ (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>178a (n-Bu/OCOCH₂CH₂)</td>
<td>2.161</td>
<td>1.895</td>
<td>171.0</td>
<td>−0.02</td>
<td>537</td>
</tr>
<tr>
<td>178b (HOCH₂CH₂/OOCOCH₂CH₂)</td>
<td>2.143</td>
<td>1.958</td>
<td>—</td>
<td>−0.03</td>
<td>538</td>
</tr>
<tr>
<td>178c ((EtO)₂P(O)CH₂/OOCOCHMeCH₂)</td>
<td>2.286</td>
<td>1.889</td>
<td>171.4</td>
<td>0.051</td>
<td>539</td>
</tr>
<tr>
<td>179 (Me/OCH₂CH₂O)</td>
<td>2.159</td>
<td>1.808</td>
<td>178.6</td>
<td>0.134</td>
<td>533</td>
</tr>
<tr>
<td>180 (Me/OOCOPh₂O)</td>
<td>2.080</td>
<td>1.870</td>
<td>171.0</td>
<td>0.046</td>
<td>534</td>
</tr>
</tbody>
</table>

¹Deviation of the Ge atom from the equatorial plane toward X.
distortion may be attributed to the formation of two eight-membered chelating rings and probably to weak interactions between the Ge and free O or S atoms of the ligands (the Ge―O distances in 181 are 2.915 and 2.955 Å; the Ge―S distances in 182 are 3.236 and 3.453 Å).

In the case of 178b, when the nitrogen atom is substituted by \( R = CH_2CH_2OH \), the spirocyclic structure remains intact in water, but in aprotic solvents the compound is present in the tautomeric equilibrium germocane-germatrane (equation 46)\(^{538,542,543}\). Both forms exist in DMSO solution at room temperature and at higher temperatures the equilibrium shifts toward the germatrane\(^{538}\) (see Section VI.C).

Organogermocane-3,7-diones \( R^1R^2Ge(OCOCH_2)_2NCH_3 \) [\( R^1, R^2 = Me_2, Ph_2, (OSiMe_2CH_2) \)] have been prepared from the corresponding organogermanes and MeN(\( CH_2COOH \))\(^{2544}\). For 183, \( R^1 = R^2 = Me \) both NCH\(_2\) protons and R groups are nonequivalent on the NMR time scale. At higher temperatures in DMSO-\( d_6 \) a coalescence of both resonances is observed with an activation barrier for the enantiomerization (equation 47) of \( \Delta G^\neq = 19.1 \) kcal mol\(^{-1}\). For a similar tin derivative (\( R^1 = R^2 = t\)-Bu) \( \Delta G^\neq = 20.9 \) kcal mol\(^{-1}\)\(^{1544}\).

The dipeptide derivatives, Me\(_2\)GeGlyGly (184)\(^{546}\) and Me\(_2\)GeGlyMet (185)\(^{547}\), are examples of pentacoordinated germanium compounds with dianionic N,N,O-chelate ligands. X-ray determinations reveal that the polyhedron around Ge in both 184 and 185 is a distorted TBP with the peptide nitrogen and two Me groups in equatorial positions and an oxygen of the unidentate carboxylate group and the amino nitrogen in the apical positions. The axial bond angles are 161.4° and 161.8°, respectively and the tridentate dipeptide ligands have a nearly planar skeleton. The N\(_{eq}\)―Ge distances are shorter than the N\(_{ax}\)―Ge ones (1.888 and 1.889 Å against 2.110 and 2.103 Å, in 184 and 185, respectively). However, the latter distances are shorter than those found for organogermatranes (2.19 to 2.24; Section VI.C.1.b) which, like 184 and 185, contain pentacoordinated Ge but tertiary and not a primary N(amino) as a donor atom.

Short intermolecular N⋯O distances in 185, 2.851 and 2.875 Å, indicate the presence of hydrogen bonds. In contrast, in 184 no intermolecular interactions via a hydrogen bond exist.

A number of dibutylgermanium complexes 186 containing a dianionic N,O,S-chelating ligand was recently synthesized by the reaction of the sodium salt of the corresponding
C. Tricyclic Complexes

Discovery of silatranes in 1961 and their amazing biological activity initiated active investigations of the analogous derivatives of other group 14 elements. The first germatranes and stannatranes were prepared in 1965 and 1967–1968, respectively. The most distinctive features of the atranes and their tricyclic analogues with tripodal fragments of triethanolamine and its carba- and hetero-substituted derivatives are the unusual cage structure with near-TBP environment of the central atom, with intramolecular interaction of the latter with the heteroatom. Recently, the germatranes are the most studied derivatives of hypervalent germanium with N→Ge coordination.

1. Germatranes and their C-organo-substituted derivatives

a. Synthesis and reactivities. The most common examples of germatranes and their C-organo-substituted (usually 3,7,10-trimethyl) analogues are compounds 187–195.

These compounds can be prepared either by formation of the atrane framework at the central atom or by substitution reactions of other atranes. The most common method of the atrane fragment formation is trans-alkoxylation reactions that proceed under moderately mild conditions (equation 48). In this way the following derivatives 188–191 were prepared: X=OMe, OEt, OP, OP-t, Cl, Br, Me, Et (188a), t-Bu (188b), and other alkyls, 1-Ad, CPh3, Vin, All (188c), CH=CH-Ph (188d), CH2SiMe3, CH2Cl (188e), CH2I (188f), CH2CONHAlk, CH(Me)N(CH2)3C=O (188g), CH2NHC6H4Cl-p (188h) and other amidomethyl and imidomethyl groups, CH2CH2OMe,
CH₂CH₂COOMe (188i) , CH₂CHMeCOOMe (188j) , CH₂CH₂CONH₂ (188k) , CH₂CH₂CN, Ph (189a) , o-, m- and p-Tol (189b–d) , 1-Naphthyl (189e) , 2- and 3-Fu, 2-(5-COOC₂H)₃ (189g) , 3-Thi (189h) and others; R′ = Me, Et, Pr, i-Pr.

\[
X-\text{Ge(OR′)}_3 + (\text{HOCH}_2\text{CH}_2)_3\text{N} \longrightarrow X-\text{Ge(OCH}_2\text{CH}_2)_3\text{N} + R′\text{OH}
\]  

(48)

In contrast to silatranes, the reaction in equation 48 proceeds without a base (NaOH, KOH) catalyst. For example, 1-trifluoromethylgermatrane (196) and 1-isothiocyanatogermatrane (197) were prepared from triethanolamine (TEAA) and CF₃Ge(OEt)₃ or SCNGe(OEt)₃ at room temperature in THF or CH₂Cl₂, respectively. 6-(Gerimatranylethyl)-substituted β-carbolyne and E-β-styrylgermatrane were prepared recently by a GeBr₂ insertion into the C–Br bond of β-bromostyrene, subsequent alcoholysis of the tribromide to triethoxygermyl derivative and re-etherification of the latter with TEAA.

1-(1-Trimethylsilylcyclopropyl)germatrane, the first example of cyclopropylgermatranes, was prepared by cyclopropanation of 1-trimethylsilyl-1-trimethoxygermylethylene with CH₂I₂ in the presence of a Zn-Cu catalyst and subsequent re-alkoxylation with TEAA.

The applicability of the method is limited by the instability (including hydrolytic) of some initial alkoxygermanes. However, hydrogermatranes may be prepared from stable TEAA or alcohol complexes of trialkoxygermanes that do not exist in the uncomplexed form.

Reaction of tetraalkoxygermanes with large excess of TEAA gives N[CH₂CH₂OGe(OCH₂CH₂)_3N]₃ with the three germatrane fragments. Subsequent hydrolysis leads to 1-hydroxygermatrane. However, better yields of 190a as well as its 4-ethyl (198) and 3,7,10-trimethyl (194a) derivatives may be achieved by exothermic reaction of GeO₂ with TEAA or 2-hydroxybutyl-bis(2-hydroxyethyl)amine in the presence of a catalytic amount of water.

The products of partial hydrolysis of organyltrichlorogermanes, i.e. polyorganogermesquioxanes, react with TEAA under more drastic conditions (refluxing xylene/KOH) and are suitable for synthesis of the 1-organylgermatranes with thermally and hydrolytically stable Ge–C bonds (equation 49).

\[
1/n(R-\text{GeO}_{1.5})_n + (\text{HOCH}_2\text{CH}_2)_3\text{N} \longrightarrow R-\text{Ge(OCH}_2\text{CH}_2)_3\text{N} + \text{H}_2\text{O}
\]  

(49)

This reaction was recently used for the preparation of new types of germatranes (R = CHR′CHR′CONHCH₂COOEt; R′, R′ = H, Me) containing α-amino acid fragments.

A less common method of atrane fragment formation is based on amino derivatives. Reaction of (Me₂N)₃SiCH₂Ge(NMe₂)₃ with TEAA in the presence of methanol leads to 1-(1-silatranymethyl)germatrane.

Tetrahalogermanes and organotrihalogermanes are more readily available reagents than the corresponding alkoxy and amino derivatives. However, their direct reactions with TEAA are almost unknown. A rare exception is the synthesis of the CF₃-germatrane from TEAA and CF₃GeCl₃; the by-product HCl forms an adduct with TEAA. In contrast, metallated (Na, SnR₃) and organoelement (B, SiMe₃) derivatives of trialkanolamines are widely used (e.g. equation 50).

\[
X-\text{GeHal}_3 + (\text{Alk}_3\text{MOCH}_2\text{CH}_2)_3\text{N} \longrightarrow X-\text{Ge(OCH}_2\text{CH}_2)_3\text{N} + \text{Alk}_3\text{MHal}
\]  

(50)

X = Hal, Alk, Ar; M = Si, Sn
16. Hypervalent compounds of organic germanium, tin and lead derivatives

Esters of α-germatranylcarboxylic acids $R''\text{OOCR}'\text{Ge(OCH}_2\text{CH}_2)_3\text{N}$ (199) ($R = H, \text{Me}; R' = \text{Me, Ph, COOEt, SiMe}_3$) and their 3,7,10-trimethyl-substituted analogues (200) were prepared recently by using organotin derivatives of trialkanolamines from the corresponding organotrichloro- and tribromogermanes$^{576}$. The structures of compounds 199a ($R = H, R' = \text{Ph, R''} = \text{Me}$), 199b ($R = H, R' = \text{SiMe}_3, R'' = \text{Me}$) and 199c ($R = R' = R'' = \text{Me}$) were determined by X-ray diffraction. By the same method 1-(phenylalkynyl)germatrane (201) was synthesized from $\text{Cl}_3\text{GeC≡CPh}$ while the corresponding organotribromogermanes served as precursors to 1-allylgermatrane (188c)$^{578}$ and its 3,7,10-trimethyl analogue$^{579}$, 1-diphenylmethyl-, 1-(phenyl)(trimethylsilyl)methyl- and 1-(1-indenyl)germatranes$^{572}$, 1-(9-fluorenyl)germatrane (202)$^{577}$ and its 9-Me$_3$Si (203a) and Me$_3$Ge (203b) derivatives$^{580}$, 1-(9-fluorenyl)-3,7,10-trimethylgermatrane (204), its 9-Me$_3$Si (205a) and 9-Me$_3$Ge (205b) derivatives$^{581}$.

The organotin method was also used for preparation of 1-hydrogermatrane 187 from the trichlorogermane complex with ether$^{572}$. A reductive dehydrochlorination with in situ generated trisodium salt of TEAA was used for the synthesis of carbofunctional germatranes (equation 51)$^{582}$.

$$\text{RCH}_2\text{CHR}'\text{GeCl}_3 + (\text{HOCH}_2\text{CH}_2)_3\text{N} + \text{NaH} \rightarrow \text{RCH}_2\text{CHR}'\text{Ge(OCH}_2\text{CH}_2)_3\text{N}$$ (51)

A series of 2-germatranylmethyl-N-arylsuccinimides 206 was obtained by the addition of trichlorogermane to the corresponding 2-methylenesuccinimides and subsequent reaction with TEAA$^{583}$. The structure of 2-germatranylmethyl-N-p-tolylsuccinimide 206a was confirmed by X-ray crystallography$^{584}$.

Boratrane was used as initial compound in one of the most effective syntheses of 1-ethoxygermatrane (190b)$^{585}$. Another type of reaction that lead to new germatranes but retains the original atrane framework was studied with hydrogermatrane 187, alkoxygermatranes 190 and especially 1-hydroxygermatrane (190a)$^{555}$, 586, 587. Reaction of 190a or 194a with amides of silicon, germanium and tin$^{557,555}$ and hydrides of silicon and germanium$^{588,589}$ leads to cleavage of the M–N or M–H bond in the precursors and gives the corresponding organoelement derivatives, in particular siloxygermatranes (2-Thi)$_n\text{Me}_3\text{SiOGe(OCH}_2\text{CH}_2)_3\text{N}$ ($n = 0$ (207a), 1 (207b), 2 (207c), 3 (207d))$^{588,589}$, 1-triphenylsiloxygermatrane (208)$^{588}$ and 1-TMSO-3,7,10-trimethylgermatrane (209). The same compounds may be prepared with lower yields from the reaction of 190a with triorganohalides of silicon, germanium and tin in the presence of Et$_3$N$^{557}$.

Reaktion of 1-methoxygermatrane (190c) with acetic acid in the presence of acetic anhydride leads to 1-acetoxygermatrane with nearly quantitative yield$^{554}$.

Triflates 210 with (a) $R = H$ and (b) $R = \text{Me}$ were prepared recently according to equation 52$^{590}$.

$$\text{Me}_3\text{SiOGe(OCH}_2\text{CHR})_3\text{N} + \text{Me}_3\text{SiOTf} \rightarrow \text{TfOGe(OCH}_2\text{CHR})_3\text{N} + (\text{Me}_3\text{Si})_2\text{O}$$ (210) (52)

The first germatran with amino substituent at the Ge atom, 211a, was synthesized from the hydroxygermatrane 190a according to equation 53. The authors suggest that
(Me₃Si)₂NSnO-germatrane is formed as an intermediate⁵⁹¹.

\[
\text{HOGe(OCH₂CH₂)₃N + Me₃SiOTf} \xrightarrow{\text{Sn[N(SiMe₃)₂]₂}} (\text{Me₃Si})₂N\text{Ge(OCH₂CH₂)₃N}
\]

(190a) \hspace{1cm} (211a) \hspace{1cm} (53)

Halogenating reagents (HF, SOCl₂, Et₃SiBr, Me₃SiI) lead to cleavage of the exocyclic O−Ge bond in alkoxy- and TMSO-germatranes 190b, 207a and 209 and form the corresponding halogermatranes 191 and 195⁵⁵⁷,⁵⁸⁷. In general, the Hal−Ge bond in the latter compounds is rather inert. However, reactions of bromides 191c and 195a with triorganoalkoxystannanes gives the corresponding alkoxides 190 and 194, including (−)-1-menthoxygermatrane 190d, with high yields⁵⁹²,⁵⁸⁷.

Recently, it was shown that the atrane fragment in germatranes is sometimes stable toward organolithium reagents⁵⁹⁰. For example, aminogermatrane 211a and its 3,7,10-trimethylamino analogue 211b may be prepared from the reaction of LiN(SiMe₃)₂ with bromides 191c and 195c, triflates 210a and 210b, and TMSO derivatives 207a and 209. Systematic study of the reactions of these atranes with cyclopentadienyl-, indenyl- and fluorenyllithium allowed one to determine the optimal reaction conditions. The most versatile substrates for the synthesis of indenyl and fluorenyl derivatives are siloxygermatranes 207a and 209. However, an excess of the more nucleophilic BuLi, t-BuLi or LiNMe₂ reagents leads to cleavage of both SiO−Ge and endocyclic O−Ge bonds and to formation of the corresponding alkyl- or amidogermanes (in particular, Bu₄Ge and (Me₂N)₄Ge). The exocyclic O−Ge bond seems to be the primary target of nucleophilic attack of organolithium reagents, so that the reaction of 207a with one equivalent of t-BuLi gives 1-t-butylgermatrane (188b).

Reaction of 1-allylgermatrane (188c) with polyhalo- and halo-alkanes (BrCCl₃, CCl₄, PrI) under UV irradiation leads to halogermatranes 191⁵⁵⁵ while the CH₂N₂/Pd(OAc)₂ system efficiently gives cyclopropanation products⁵⁷⁸. Addition of Br₂ to (phenylalkyl)germatrane 201 also retains both the atrane fragment and the Ge−C bond and leads to the dibromide PhCBr=CBrGe(OCH₂CH₂)₃N (212)⁵⁷². This is a rare example of a near-quantitative formation of a cis-dibromide (as determined by X-ray data) on Br₂ addition to acetylenes.

A number of new C-functionalized germatranes was reported. The reaction of alkynylgermatrane 201 with two equivalents of N-bromosuccinimide and subsequent hydrolysis lead to α-germatranylketone PhCOCBr₂Ge(OCH₂CH₂)₃N⁵⁷². Metalation of fluorenylgermatranes 202 and 204 proceeds smoothly and gives the corresponding 9-trimethylstannyl derivatives 203c and 205c⁵⁸⁰,⁵⁸¹.

1-(2-Furyl)germatrane can be quantitatively converted into 1-dichloromethylgermatrane (213) by irradiation in CHCl₃ solution⁵⁹³. Ethylgermatrane 187a and CH₃I form the quaternary salt EtGe(OCH₂CH₂)₃NMe⁺I⁻⁵⁵⁴.

The atrane fragment is also retained in the reaction of di-n-butyltin oxide and germatranyl-substituted propionic acids in a 1 : 2 molar ratio which leads to new di-n-butyltin dipropionates n-Bu₂Sn[OOCCH₂CHRGe(OCH₂CH₂)₃N]₂·H₂O (214) (R = H, Me, Ar)⁵⁹⁴. The structure of compound 214a (R = p-ClC₆H₄) was confirmed by X-ray diffraction.

Reactions that affect the atrane fragment are relatively rare. Among the products of hydrogermatrane 187 with Br₂, CH₃I or CH₂I₂, trihalo derivatives of TEAA were detected. Similar results were reported for the reaction of 1-allylgermatrane with I₂⁵⁵⁷.

b. Structure and physical properties. Recently the structures of about 50 germatranes and their C-substituted analogues have been reported. The Ge atom is pentacoordinated due
to hypervalent N → Ge–X interaction. The coordination polyhedron of the germanium is a distorted TBP with nitrogen and ligand X in axial positions. Intramolecular N → Ge coordination is the common bond for three condensed five-membered heterocycles. The Ge atom is shifted from the equatorial plane toward the X substituent. Similar to silatranes, both axial bonds in germatranes are weakened due to the presence of a three-center four-electron hypervalent bond.

These structures were discussed in reviews and papers. Some crystallographic data of their TBP fragments (the two apical bond lengths of the germanium and, where available, the displacement (Δ) of the Ge atom from the plane of three equatorial ligands) are summarized in Table 40.

The structure of 1-methyl-2-(1-germatranyl)-1,2-dicarba-closo-dodecaborane was recently determined. The N → Ge and C–Ge bond lengths were found to be 2.171 and 2.004 Å, respectively; the N–Ge–C angle is 177.7°.

The interatomic N → Ge distance is longer than the sum of the covalent radii by a significantly greater amount than the sum of the van der Waals radii of these elements (Table 1). After redetermination of the structure of 1-fluorogermatrane (191a), the shortest N → Ge distance (2.09 Å) was found in 1-fluorogermatrane (201 Å) in di(1-germatranyl)methane (215). These values are similar to those in neutral silatranes: the shortest Si–N distance (2.01 Å) was found in 1-fluorosilatrane and the longest (2.38 Å) in 2-(1-silatranyl)ethylsilatrane. In Si and Ge analogues with the same substituents, the N → M (M = Si, Ge) distance is generally 0.03–0.08 Å longer for germanium (the covalent radii of Ge is longer by 0.05 Å, Table 1). For example, in 1-ethylatranes the corresponding distances are 2.24 Å (Ge) and 2.21 Å (Si).

Gradual increase of the electron withdrawing effect of the substituent X at the central atom, e.g. from C2H5 to ICH2 to Br, leads to shortening of the N → Ge distance (2.24 → 2.19 → 2.09 Å, respectively). However, similar to the (O–M)-chelate derivatives of amides with the HalMe2MCH2N(M = Si, Ge) fragment (Section VI.A.1.c) and to 1-fluoro- and 1-chlorosilatranes, the N → Ge bond length in haloatranes increases in the series of Br < Cl < F, i.e. not in accordance with the electronegativity of the halogens but in the order of their ability to act as a leaving group in the nucleophilic substitution reactions. The N → Ge–X angle in germatranes is close to 180° and in most cases falls in the range of 176–179°. The only exception is p-tolylgermatrane (189d), where the angle is 144.2°.

It was suggested that the decrease of the C–Ge–O angles and ΔGe values in the crystal lead to intramolecular interaction between one of the O atoms of the atrane fragment and the H atom of the methyl group, which results in the noticeable distortion of the N → Ge–C bond.

An important characteristic of the geometry of the atrane fragment and the strength of the N → Ge interaction is the deviation of the Ge atom (ΔGe) from the plane of equatorial oxygen atoms toward the apical X substituent. For the germatranes studied (Table 40) the ΔGe values are in the range of 0.10–0.30 Å and increase with the N → Ge distance. For neutral silatranes the ΔSi range is ca. 0.10–0.24 Å. The correlation between the d(N → Ge) and ΔGe values is described by equation 54a:

\[
\Delta Ge = 0.72d(N-Ge) - 1.37 \quad r = 0.960 (n = 14) \quad (a)
\]

\[
\Delta Si = 0.61d(N-Si) - 1.24 \quad r = 0.970 (n = 32) \quad (b)
\]

Strengthening of the N → Ge interaction in Ge-substituted germatranes leads to a gradual decrease in the GeOC valent angles from 121.0 to 115.8° and to irregular changes of torsion OCCN (34.5–45.3°) and OGeNC (10.6–20.5°) angles. The nearly constant
### TABLE 40. Main structural parameters of germatranes XGe(OCH₂CH₂)₃N

<table>
<thead>
<tr>
<th>Compound</th>
<th>X</th>
<th>N → Ge(Å)</th>
<th>Ge–X(Å)</th>
<th>ΔGeᵦ (Å)</th>
<th>Reference</th>
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</thead>
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<tr>
<td>197</td>
<td>NCS</td>
<td>2.081</td>
<td>0.917</td>
<td>0.085</td>
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<tr>
<td>191c</td>
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<tr>
<td>191b</td>
<td>Cl</td>
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<td>2.209</td>
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<td>596</td>
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<td>191a</td>
<td>F</td>
<td>2.104</td>
<td>1.751</td>
<td>—</td>
<td>596</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2.011)</td>
<td>(1.781)</td>
<td></td>
<td>586</td>
</tr>
<tr>
<td>207d</td>
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<td>208</td>
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<td>—</td>
<td>—</td>
<td>588</td>
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<tr>
<td>199b</td>
<td>CH(SiMe₃)COOMe</td>
<td>2.209</td>
<td>1.975</td>
<td>0.23</td>
<td>576</td>
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<tr>
<td>189b</td>
<td>3-Thi</td>
<td>2.210</td>
<td>—</td>
<td>0.23</td>
<td>569</td>
</tr>
<tr>
<td>188j</td>
<td>CH₂CHMeCOOMe</td>
<td>2.210</td>
<td>—</td>
<td>—</td>
<td>483</td>
</tr>
<tr>
<td>189a</td>
<td>Ph</td>
<td>2.212</td>
<td>1.947</td>
<td>0.24</td>
<td>566</td>
</tr>
<tr>
<td>189c</td>
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<td>2.214</td>
<td>1.947</td>
<td>0.25</td>
<td>566</td>
</tr>
<tr>
<td>188d</td>
<td>E-CH=CHPh</td>
<td>2.215</td>
<td>1.939</td>
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<tr>
<td>189d</td>
<td>p-Tol</td>
<td>2.217</td>
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<td>566</td>
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<tr>
<td>199c</td>
<td>C(Me₂)COOMe</td>
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<td>2.006</td>
<td>0.24</td>
<td>576</td>
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<tr>
<td>214a</td>
<td></td>
<td>2.222</td>
<td>1.958</td>
<td>0.24</td>
<td>594</td>
</tr>
<tr>
<td>188g</td>
<td>CH(Me)N(CH₂)₃C=O</td>
<td>2.223</td>
<td>1.980</td>
<td>0.24</td>
<td>563</td>
</tr>
<tr>
<td>189b</td>
<td>o-Tol</td>
<td>2.230</td>
<td>1.94</td>
<td>0.26</td>
<td>566</td>
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<tr>
<td>188b</td>
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<td>2.238</td>
<td>1.971</td>
<td>0.27</td>
<td>559, 595</td>
</tr>
<tr>
<td>188a</td>
<td>Et</td>
<td>2.240</td>
<td>1.970</td>
<td>0.23</td>
<td>558, 595</td>
</tr>
<tr>
<td>189e</td>
<td>1-Naph</td>
<td>2.240</td>
<td>1.940</td>
<td>0.25</td>
<td>567, 595</td>
</tr>
<tr>
<td>212</td>
<td>C(Br)=C(Br)Ph</td>
<td>2.228</td>
<td>1.981</td>
<td>0.24</td>
<td>572</td>
</tr>
<tr>
<td>206a</td>
<td>CH₂-2-(N-p-tolyl)succinimide</td>
<td>2.239</td>
<td>1.977</td>
<td>0.264</td>
<td>577</td>
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<tr>
<td>188k</td>
<td>CH₂CH₂CONH₂</td>
<td>2.240</td>
<td>1.970</td>
<td>0.25</td>
<td>565, 595</td>
</tr>
<tr>
<td>211a</td>
<td>N(SiMe₃)₂</td>
<td>2.242</td>
<td>1.845</td>
<td>0.26</td>
<td>591</td>
</tr>
<tr>
<td>205c</td>
<td>(Me)ᵇ</td>
<td>9-SnMe₃-9-fluorenyl</td>
<td>2.247</td>
<td>1.97</td>
<td>0.25</td>
</tr>
<tr>
<td>205b</td>
<td>(Me)ᵇ</td>
<td>9-GeMe₃-9-fluorenyl</td>
<td>2.268</td>
<td>1.974</td>
<td>0.27</td>
</tr>
<tr>
<td>215</td>
<td>CH₂Ge(OCH₂CH₂)₃N</td>
<td>2.29</td>
<td>1.950</td>
<td>0.29</td>
<td>595, 599</td>
</tr>
</tbody>
</table>

ᵃDeviation of the Ge atom from the equatorial plane toward X.
ᵇFor -Ge[OCH₂CH₂]₂[OCH₂CH(C₂H₅)]₃N.
ᶜFor -Ge[OCH₂CH₂]₃N.
ᵈTwo independent molecules in the unit cell.
ᵉ-n-Bu₂Sn[OOCCH₂CHRGe(OCH₂CH₂)₃N]₂ · H₂O (214a) (R = p-CIC₆H₄).

<references>
distance of the N atom from the equatorial plane of the three O atoms (1.97–2.00 Å) and from the plane of the neighboring C atoms (0.37–0.42 Å) testifies to the conservation of the atrane (OCH₂CH₂)₃N fragment. Thus, the length of the transannular N → Ge bond is mostly affected by the deviation of the Ge atom from its equatorial plane.

The length of the Ge–X bond (the shortest value of 1.757 Å for siloxygermatrane 206d⁵⁸⁹, the longest value of 2.360 Å for bromogermatrane 191c⁵⁹⁵) depends on the nature of the ligand and changes in reverse order of the N → Ge distance. The strength of the N → Ge interaction has almost no effect on the equatorial bond lengths (1.77 ± 0.01 Å); however, the latter values are slightly longer than that in tetraalkoxygermanes (1.75 Å). The close values of the Ge–Oₐx and Ge–Oₑq distances in organoxygermatranes 181a and 198 impede the interpretation of the N → Ge–O axial fragment geometry within the theory of hypervalent interaction⁶⁰¹. According to the theory, the equatorial Ge–O bonds should be shorter than axial⁵⁷³. Similar behavior was demonstrated by 1-methyl-2-carbagermatrane for Ge–C distances (see below).

Introduction of additional acceptor thienyl substituents at the silicon in siloxygermatranes 207 increases the SiOGe angle (133.0° for 207a, 134.8° for 207b, 139.6° for 207c and 180° for 207d)⁵⁸⁹.

Two crystallographically independent molecules of 1-hydroxygermatrane (190a)⁵⁹⁷ and 1-hydroxy-4-ethylgermatrane (198)⁵⁷³ are associated into dimers. Relatively longer N → Ge bond lengths (2.166 and 2.185 Å) in 198⁵⁷³ compared with 190a (2.146 Å) may be due to a steric effect of the 4-ethyl group. 3,7,10-Trimethyl-substituted germatranes⁵⁷²,⁵⁸¹, silatranes⁶⁰² and stannatranes⁶⁰³ consist of a mixture of diastereomers⁶⁰⁴,⁶⁰⁵ which hinders the interpretation of the X-ray data for these compounds.

A linear dual substituent relation between the chemical shifts of the germatrane protons (extrapolated to infinite dilution in CDCl₃) and the inductive (σ₁) and resonance (σ₀) substituent parameters at the Ge atom was found (equations 55, r = 0.99)⁶⁰⁶.

\[
\begin{align*}
\delta\text{OCH}_2 &= 3.809 + 0.391\sigma_1 + 0.035\sigma_0^0 \\
\delta\text{CH}_2\text{N} &= 2.840 + 0.322\sigma_1 + 0.043\sigma_0^0
\end{align*}
\]

(55)

The variation in the proton shielding results from the inductive influence of the X substituent and is approximately the same for both OCH₂ and CH₂N protons. Thus, the influence is transmitted not only through the system of covalent bonds but also through the N → Ge intramolecular coordination.

The inductive and resonance constants of the pentacoordinate -Ge(OCH₂CH₂)₃N moiety (σ₁ = –0.23 and σ₀ = 0.053) and the tetracoordinate -Ge(OCH₂CH₃)₃ group (σ₁ = 0.29 and σ₀ = 0.136) were obtained from the correlation of the δ¹³C values of the meta and para carbon atoms in mono-substituted benzenes⁶⁰⁷. The difference between the σ₁ values (Δσ₁(Ge) = 0.52) was attributed to the N → Ge intramolecular interaction in the former. A smaller value for the corresponding silicon compounds (Δσ₁(Si) = 0.43)⁶⁰⁸ is related to the higher N → M interaction in germatranes (M = Ge) as compared to silatranes (M = Si).

The ¹⁵N chemical shifts of 1-substituted germatranes in DMSO vary linearly with the σ* constants of the substituent X (equations 56), which influence is transmitted through the X–N → Ge hypervalent bond⁶⁰⁹. The decrease of the ¹⁵N shielding on the increase of both the electronegativity of X and the solvent polarity indicate a strengthening of the transannular bond⁶¹⁰–⁶¹². The smaller slope for Taft’s equation in germatranes (2.52)⁶⁰⁹ compared with silatranes (3.54)⁶¹³, as well as the smaller difference of the ¹⁵N chemical shifts for the solvent changes [(δ¹⁵N(CCl₄) → δ¹⁵N(DMSO)], reflect a stronger N → Ge than N → Si interaction in atranes⁶¹⁴,⁶¹⁵.
\[ \delta^{15}\text{N}(\text{Ge}) = 2.52\sigma_X^* - 367.2 \quad r = 0.99, n = 9 \]  
\[ \delta^{15}\text{N}(\text{Si}) = 3.54\sigma_X^* - 356.8 \quad r = 0.99, n = 10 \]  

The chemical shifts of the equatorial \(^{17}\text{O}\) atoms in alkoxygermatranes are very close to those in tetraethoxygermane. However, the shielding of the axial oxygen in ethoxygermatranes is by 14 ppm lower than that in tetraethoxygermane, indicating the predominant trans-influence of the \(\text{N} \rightarrow \text{Ge}\) coordination in germatranes.

In alkoxygermatranes the \(\delta^{73}\text{Ge} = -55.2\) (R = H), -60.6 (R = Me), -63.4 (R = Pr), -73.8 (R = SiMe\(_3\)) are shifted upfield compared with \(\delta^{73}\text{Ge} = 36.0\) ppm for the tetrahedral Ge(OMe)\(_4\). Similar upfield shifts of \(^{29}\text{Si}\) signals were detected for the corresponding silatranes. However, mass spectrometric studies of these compounds indicate either a weakening or absence of such interaction in the gas phase.

The transannular interaction in germatranes is explained by the model of hypervalency that assumes the formation of a three-center four-electron \(\text{N} \rightarrow \text{Ge} \rightarrow \text{X}\) hypervalent bond. This model successfully explains the trans-influence in such fragments, i.e. the inverse interdependence and the constancy of the sum of \(\text{Ge} \rightarrow \text{X}\) and \(\text{Ge} \rightarrow \text{N}\) bond orders. The calculated energies of the transannular bonds in some germatranes are higher than those in the corresponding silatranes.

The MNDO method gives a satisfactory explanation for the relatively close values of the \(\text{N} \rightarrow \text{Ge}\) distances in the calculated isolated molecules and in the crystals of germatranes. Due to the crystal field effect the \(\text{N} \rightarrow \text{Ge}\) bond lengths in the crystals are somewhat shorter than that in isolated molecules. The extremely short \(\text{N} \rightarrow \text{Ge}\) bond in the fluorogermatrane can be ascribed not only to the presence of electron-acceptor substituents but also to a strong crystal field influence.

There is a linear correlation between the calculated \(\text{N} \rightarrow \text{Ge}\) bond length and the effective charge on the nitrogen atom \(|q_N|\) calculated by MNDO (equations 57).

\[ d(\text{N-Ge}) = 13.589|q_N| - 3.322 \quad r = 0.994\quad(n = 7) \] (57)

Some geometric characteristics of some metallatranes \(\{\text{N(}CH_2CH_2O)\}_3\text{M} \rightarrow \text{X}; \text{M} = \text{Si, Ge, Sn}; \text{X} = \text{F, Cl, Br, H, Me}\} \) were calculated by the DFT method and linear correlations between bond lengths \(d(\text{M-Ge})\) and \(\sigma_1\) constants of X were revealed (equations 58). These data indicate an increase in the strength of the coordination in the three-center bond in the series of Si < Ge < Sn.

<table>
<thead>
<tr>
<th>1-R</th>
<th>MNDO</th>
<th>X-ray</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>2.742</td>
<td>1.811</td>
<td>—</td>
</tr>
<tr>
<td>F</td>
<td>2.578</td>
<td>1.822</td>
<td>1.739</td>
</tr>
<tr>
<td>Cl</td>
<td>2.618</td>
<td>1.801</td>
<td>2.268</td>
</tr>
<tr>
<td>Br</td>
<td>2.643</td>
<td>1.799</td>
<td>2.388</td>
</tr>
<tr>
<td>I</td>
<td>2.704</td>
<td>1.799</td>
<td>2.565</td>
</tr>
<tr>
<td>Me</td>
<td>2.732</td>
<td>1.814</td>
<td>1.941</td>
</tr>
<tr>
<td>Ph</td>
<td>2.759</td>
<td>1.814</td>
<td>1.915</td>
</tr>
</tbody>
</table>
16. Hypervalent compounds of organic germanium, tin and lead derivatives

\[
d(N-Si) = -0.406\sigma_1 + 2.485 \quad r = 0.998 \; (n = 4)
\]
\[
d(N-Ge) = -0.189\sigma_1 + 2.393 \quad r = 0.989 \; (n = 5) \quad (58)
\]
\[
d(N-Sn) = -0.086\sigma_1 + 2.416 \quad r = 0.987 \; (n = 5)
\]

Assuming that the sum of the X–Ge and Ge–N bond orders is constant and equal to 1, the calculated N → Ge bond order is equal to 0.33, a value slightly higher than that in silatranes (0.30)\(^{621}\).

2. Homogermatranes, germatranones, carbagermatranes, thia- and azagermatranes

Tricyclic germatran analogues may be prepared by the same methods as germatranes. 1-Substituted 3-homogermatranes \((216)\) were synthesized from 3-hydroxypropyl-di(2-hydroxyethyl)amine. Reactions of the latter with MeGe(OEt)\(_3\) or organogerma-sesquioxanes lead to 1-methyl-3-homogermatrane in the first case or to 1-phenyl- and 1-(1-naphthyl)-3-homogermatranes in the second. The N-TMS derivative of the amine reacts with trifunctional germanes RGeX\(_3\) (X = Cl, Br, I, OEt; R = Alk, Ar, X) to give a series of homogermatranes \((220)\)\(^{624}\).

\[
\begin{align*}
\text{(216)} & \\
\text{(217)} & n = 3 \\
\text{(218)} & n = 2 \\
\text{(219)} & n = 1
\end{align*}
\]

\[
\begin{align*}
\text{(220)} & \\
\text{(223)}
\end{align*}
\]

The ability of the pentacoordinated Ge atom in atrane to further extend its coordination number was demonstrated by the formation of adducts of aminotriacetic acid derivatives (germatranones) with DMSO, DMF or H\(_2\)O. For example, germatrane-3,7,10-triones XGe(OOCCH\(_2\))\(_3\)N (\((217a)\) (X = Me, Et, Ph) were isolated as 1 : 1 adducts with DMF and DMSO from transalkoxylation reaction between aminotriacetic acid and XGe(OEt)\(_3\)\(^{444,557}\), and also from the reaction of the tris(trimethylsilyl) ester of the acid with RGeCl\(_3\) (R = Cl, Me, Et)\(^{625}\). At high temperatures the adduct \((217a)\)-DMF(R = Me) undergoes elimination.
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of DMF molecule and forms 1-methylgermatran-4,7,10-trione. Similar reactions of the corresponding aminoacetic acids or their TMS analogues lead to germatran-3,7-diones XGe(OOCC)2(OCH2CH2)N (218) and germatran-3-ones XGe(OOCC)2(OCH2CH2)2N (219) (X = Cl, Me, Et, Ph).

According to X-ray data, the substitution of one OCH2 group in the germatrane framework with an OCO fragment in 219a (X = Ph) does not affect the transannular N→Ge bond length (Table 42). However, further increase in the number of OCO fragments in compound 217b·H2O leads to shortening of the N→Ge bond, although the ΔGe value (0.17 Å) remains almost the same as in 189a·H2O (0.16 Å, Table 42). In these two compounds the Ge atom is hexacoordinated as a result of interaction with the H2O molecule.

The first carbagermatanes, 2-carbagermatanes 220 (X = Me, Et, Ph), were prepared from 3-chloropropylgermanes X(EtO)2Ge(CH2)3Cl and diethanolamine in the presence of Et3N.

In 1-methyl-2-carbagermatrane (220a) replacement of one oxygen atom with the less electronegative and bulkier CH2 group (with a van der Waals radius of 2.00 Å) elongates the N→Ge bond by 0.10 Å. However, the unexpectedly longer equatorial Ge−C distance (1.979 Å) compared with the axial bond (1.957 Å) indicate that steric factors and rigidity of the CGeC valent angle (which is only by 3° smaller than tetrahedral) affect significantly the geometry of the atrane framework.

The ionic component of the axial covalent Ge−X bond in the hypervalent N→Ge−X fragment increases on strengthening the N→Ge coordination. For example, the Ge−C bond length in 1-t-Bu-germatrane 118b (1.971 Å) is longer than that in 1-methyl-2-carbagermatrane 220a (1.957 Å) while the N→Ge coordination in the former (2.238 Å) is stronger than in the latter (2.436 Å). In turn, the Ge−X bond length in 1-bromo- (2.369 Å) and 1-chloro-germatrane (2.209 Å) is also longer than in the tetracoordinate GeBr4 (2.27 Å) and MeGeCl3 (2.135 Å).

TABLE 42. Selected structural parameters of tricyclic germatrane analogs

<table>
<thead>
<tr>
<th>Compound</th>
<th>X</th>
<th>N→Ge (Å)</th>
<th>Ge−X (Å)</th>
<th>ΔGea (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>217b·H2O</td>
<td>OH (trione)</td>
<td>2.084</td>
<td>1.762</td>
<td>0.17</td>
<td>626</td>
</tr>
<tr>
<td>219a</td>
<td>Ph (one)</td>
<td>2.203</td>
<td>1.952</td>
<td>0.25</td>
<td>627</td>
</tr>
<tr>
<td>220a</td>
<td>Me (monocarba)</td>
<td>2.436</td>
<td>1.957</td>
<td>0.37</td>
<td>628</td>
</tr>
<tr>
<td>223a</td>
<td>CH2CH2COOH (trithia)</td>
<td>2.63</td>
<td>—</td>
<td>—</td>
<td>542</td>
</tr>
</tbody>
</table>

aDeviation of the Ge atom from the equatorial plane toward the X substituent.
16. Hypervalent compounds of organic germanium, tin and lead derivatives

Synthesis of 1-chloro-2,8,9-carbagermatrane (221) by trans-metallation reaction of trialkylamine and GeCl₄ in the presence of zirconium compounds (equation 59) was reported recently. Subsequent reactions with organomagnesium or organolithium derivatives lead to 1-organyl-2,8,9-carbagermatranes (222) (e.g. R = Bu, Ph, Vin, All).

\[
(CH_2=CHCH_2)_3N \xrightarrow{1. \text{Cp}_2\text{ZrHCl, THF, 0 °C}} \xrightarrow{2. \text{GeCl}_4} \text{Cl}\text{GeNClGeN}(\text{221})
\]

\[
\text{RMgBr or RLi} \rightarrow \text{R}\text{GeN}(\text{222})
\]

In reaction with aryl bromides in the presence of Pd₂(DBA)₃·CHCl₃/PAr₃ (DBA = dibenzylideneacetone) the carbagermatranes 222 displayed higher reactivities than the corresponding tributylgermanes. It was suggested that this is a result of the presence of transannular N→Ge bond in the atrane compounds.

Reaction of tris(2-mercaptoethyl)amine with carbofunctional trialkoxygermanes or organogermasesquioxanes gives trithiagermatranes (X = OH, OMe, OEt, NH₂; R = H, Ph). They are more hydrolytically stable than their oxygen analogues. According to X-ray data, trithiagermatrane (223a) (X = OH, R = H) has atrane structure while the corresponding oxygen analogue exists in the solid state as a spirocyclic lactone. The Ge-N distance in 223a (2.63 Å) is longer than that in aminocarbonyl and methoxycarbonylgermatranes 188i and 188k (2.19 and 2.24 Å) as a result of a decreasing electron supply to germanium due to the low electronegativity of sulfur compared with oxygen.

The first azagermatranes 224, namely 1-alkylazagermatranes 224a,b,d–f, were prepared in 1993 by transamination reactions (equation 60). By the same method n-butyl and allylazagermatranes 224c, 224g–i and haloazagermatranes 224j–m were prepared later. Haloazagermatranes 224j and 224l were isolated as relatively stable complexes and the reaction by-product was Me₂NH. Halo-N,N',N''-trimethylazagermatranes 224k and 224m are more stable than their unsubstituted analogues and may be isolated as moisture-sensitive compounds.

Recently, only few reactions of azagermatranes have been reported. In the presence of (H₂NCH₂CH₂)_3N the N,N',N''-trimethylazagermatranes 224b and 224e were converted into azagermatranes 224a and 224d, respectively. Reactions of azagermatranes 224a,b,d,e with TEAA lead to replacement of the azatran ligand by an atrane fragment. Reaction of the bromide 224m with BuLi demonstrates the possibility of substitution of the halogen in 1-haloazagermatranes by alkyl groups.
VII. PENTACOORDINATE INTRAMOLECULAR NEUTRAL TIN AND LEAD COMPOUNDS

A. Monocyclic Complexes

The most intensive studies in higher coordinated tin and lead compounds were carried out in the 1970–1990 period and the topic has been extensively reviewed up to 1992, particularly the investigations of complexes containing monoanionic C,D-chelating ligands (D = N, O). These compounds with the hypervalent pattern XSnC3D are good model substances for nucleophilic substitution at the tin atom and map the tetrahedron (T)–trigonal-bipyramidal (TBP) path. A comprehensive survey exists on organotin complexes containing bidentate imidazole- and pyrazole-type ligands.

1. Derivatives with bidentate C,N- and C,P-chelating ligands

a. Tetraorgano compounds. In contrast to germanium, higher-coordinated tetraorganotin compounds are known when electron-donating built-in ligands are present in a suitable position. Earlier examples, in particular of compounds with an intramolecular N → Sn interaction, were discussed in reviews. Among them, two series of compounds were reported containing the 8-(dimethylamino)-1-naphthyl (Np N) and 3-(2-pyridyl)-2-thienyl (PyTh) ligands. Most recently, chiral nonracemic tetraorganotins containing one or two (−)-(1R,2S,5R)-menthyldimethylsilyl (Men) substituents were obtained by reaction of an excess of NpNLi with MenPh2SnF or Men2PhSnI, respectively. The tetraorganotin derivative with 2-(4-dimethylamino-2-methyl-2-azabutyl)phenyl (PhNN) ligand was also described.

X-ray crystallography of tetraorganotin compounds show a five-coordinated tin with a strongly distorted TBP geometry due to a weak intramolecular N → Sn coordination, with three of the carbon atoms at approximately equatorial positions and the nitrogen atom and the fourth carbon atom at the axial sites (Table 43). The N → Sn coordination bonds are extremely long (2.84–2.90 Å), and the Sn–C bonds...
trans-orientated with respect to the nitrogen are slightly elongated (at ca. 0.035 Å) as compared with the other bonds.

The electron lone pair at N in 227 points toward Sn (N···Sn distance of 3.153 Å) and the coordination tetrahedron at Sn is only slightly distorted toward a TBP \(^{641}\). This interaction is weaker than those in tetraorganostannanes 225a, 225b and 226a. The Mossbauer spectra of 226 are in agreement with the pentacoordinated tin atom in these compounds\(^{639}\). In compound [Me\(_2\)(Cl)SnOC\(_6\)H\(_4\)CH\(_2\)N(Me)CH\(_2\)CH\(_2\)NHMe\(_2\)]Cl \cdot HCl, a much stronger N→Sn interaction is found (2.574 Å) and the inner nitrogen atom is trans to the electronegative chlorine substituent (169.3°). An interaction of the second amino group with the Sn atom is not possible because the Lewis basic center is blocked by the addition of HCl.\(^{641}\)

In solution, the tin centers in 225 and 226 are also pentacoordinated, as indicated by an increase of the \(^1J(\text{\textsuperscript{119}Sn}-\text{\textsuperscript{13}C})\) value in the \textsuperscript{13}C NMR spectra and the high-field shift of the \textsuperscript{119}Sn resonance in the \textsuperscript{119}Sn NMR spectra\(^{638,639}\) (Table 43). Besides, the \(^1H\) and \textsuperscript{13}C NMR spectra of chiral 225b show two resonances for the diastereotopic NMe\(_2\) group, indicating the absence of pyramidal inversion of the nitrogen\(^{638}\).

In contrast, according to the \textsuperscript{119}Sn chemical shifts and the \(^1J(\text{\textsuperscript{119}Sn}-\text{\textsuperscript{13}C})\) or \(^2J(\text{\textsuperscript{119}Sn}-\text{\textsuperscript{1}H})\) values, a tetrahedral geometry at tin is suggested for Me\(_2\)N(CH\(_2\))\(_3\)SnPh\(_3\) (228)\(^{644}\), and for the ferrocenyl derivative 2-Me\(_3\)SnFcCH\(_2\)NMe\(_2\) (229) and its analogues with potential C,P- and C,O-coordinating ligands, 2-Me\(_3\)SnFcCH\(_2\)PPh\(_2\) (230) and 2-Me\(_3\)SnFcCH\(_2\)POPh\(_2\) (231)\(^{643}\). The geometry of 230 in the solid state displays a P···Sn contact longer than 4 Å (Table 1).
### Table 43. Selected structural and NMR data for tetraorganotin compounds and triorganotin hydrides containing a potential C,N- or C,P-chelating ligand

<table>
<thead>
<tr>
<th>Compound</th>
<th>N → Sn (Å)</th>
<th>Sn–Cax (Å)</th>
<th>N → Sn–Cax (deg)</th>
<th>ΔSn(^a) (Å)</th>
<th>δ(^{119})Sn (ppm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>225a(^b)</td>
<td>2.884</td>
<td>2.183</td>
<td>168.5</td>
<td>0.45 (347.2)</td>
<td>−155.3 (C(_6)H(_5)CD(_3))</td>
<td>638</td>
</tr>
<tr>
<td>225c(^b)</td>
<td>2.882</td>
<td>2.162</td>
<td>170.2</td>
<td>0.50 (344.7)</td>
<td>−107.1 (C(_6)H(_5))</td>
<td>640</td>
</tr>
<tr>
<td>226a</td>
<td>2.841</td>
<td>2.183</td>
<td>166.6</td>
<td>0.51 (343.5)</td>
<td>−176.3 (CDCl(_3))</td>
<td>639</td>
</tr>
<tr>
<td>227</td>
<td>3.154</td>
<td>2.166</td>
<td>170.1</td>
<td>0.54 (341.9)</td>
<td>−148 (CDCl(_3))</td>
<td>641</td>
</tr>
<tr>
<td>(R(_{Sn}))-235b(^b)</td>
<td>2.931(^c)</td>
<td>2.214(^d)</td>
<td>162.3</td>
<td>0.52 (337.4)</td>
<td>−91.3 (C(_6)D(_5))</td>
<td>642</td>
</tr>
<tr>
<td>(S(_{Sn}))-235b(^b)</td>
<td>2.885(^e)</td>
<td>2.212(^d)</td>
<td>162.6</td>
<td>0.57 (335.4)</td>
<td>−94.8 (C(_6)D(_5))</td>
<td>642</td>
</tr>
<tr>
<td>230(^b)</td>
<td>4.038(^f)</td>
<td>2.15</td>
<td>161.0</td>
<td>0.68 (331.3)</td>
<td>−12.0 (CDCl(_3))</td>
<td>643</td>
</tr>
<tr>
<td></td>
<td>4.134(^f)</td>
<td>2.14</td>
<td>161.9</td>
<td>0.66 (331.9)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Deviation of the tin atom from the quasi-equatorial plane toward the pseudo-axial carbon atom; the sum of the ‘equatorial’ angles is given in parentheses.

\(^b\) Two independent molecules in the unit cell.

\(^c\) Sn–H 1.52 Å.

\(^d\) Sn–C(Me\(_3\)).

\(^e\) Sn–H 1.63 Å.

\(^f\) P···Sn.

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Examples of enhanced reactivity in halodemetalation reactions of mixed tetraorganotin compounds, in which potentially coordinating groups, in particular the Np N ligand, are present in the \(γ\)-position with respect to tin, are discussed in a review\(^{636}\) and papers\(^{645–647}\). It is suggested that the intramolecular assistance by those groups facilitates the cleavage of Sn–C bonds \(trans\) to them.

**b. Triorganotin hydrides.** The examples of surprisingly relatively stable triorganotin hydrides containing one monoanionic C,N-chelating ligand that have been studied are depicted in Scheme 11. These compounds include the following ligands: \(3\)-(dimethylamino)propyl (Pr\(_N\)) in \(^{232}\)\(^{648}\), \(2\)-[(dimethylamino)methyl]phenyl (Ph\(_N\)) in \(^{233a–d}\)\(^{648}\), the chiral \(2\)-[(1S/R)-1-dimethylaminoethyl]phenyl (Ph\(_N^*\)) in \(^{234a–c}\) and \(2\)-[(1S)-1-dimethylamino-2,2-dimethylpropyl]phenyl (Ph\(_N^*\)) in \(^{234d}\) and \(^{234e}\), NpN in \(^{235a–d}\)\(^{648}\), \(2\)-(4,4-dimethyl-2-oxazolinyl)-5-(methyl)phenyl (Ox\(_N\)) in \(^{236a}\) and \(^{236b}\), and the chiral 2-(4-isopropyl-2-oxazolinyl)-5-(methyl)phenyl (Ox\(_N^*\)) in \(^{237a}\) and \(^{237b}\). These hydrides are generally obtained from the LiAlH\(_4\) reduction of the corresponding triorganotin bromides and the NaBH\(_4\) reduction of the chlorides\(^{640,650}\).

Among the organotin hydrides, the chiral compounds have received considerable attention in recent years as enantioselective free radical reducing agents\(^{650,651}\). The first representative of the optically active tin hydrides containing a potentially bidentate chelating ligand, \(^{235b}\), including a stereogenic tin atom with the NpN ligand and the chiral Men substituent, was synthesized by Schumann and coworkers\(^{642}\). Starting from (−)-methyl chloride, the corresponding Grignard reagent reacts stereospecifically with Me\(_3\)SnCl to give Me\(_3\)MenSn which was derivatized by selective bromodemetalation, alkylation and finally hydrogenation to yield \(^{235b}\) as a mixture of epimers differing in the absolute configuration at the tin center in a 40 : 60 ratio in solution. X-ray crystallography of \(^{235b}\) revealed a pair of \(R_{Sn}/S_{Sn}\) epimers, with the coordination geometry around tin for the two molecules in the asymmetric unit being ‘a trigonal-bipyramidal-like monocapped tetrahedron’.

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\(^{636}\) Deviation of the tin atom from the quasi-equatorial plane toward the pseudo-axial carbon atom; the sum of the ‘equatorial’ angles is given in parentheses.

\(^{645–647}\) Two independent molecules in the unit cell.

\(^{648}\) Sn–H 1.52 Å.

\(^{649}\) Sn–C(Me\(_3\)).

\(^{650}\) Sn–H 1.63 Å.

\(^{651}\) P···Sn.
A main feature of the arrangement at tin is a quasi-equatorial position of hydrogen and a quasi-axial position of the \( t \)-butyl group as well as the coordinating nitrogen atom, suggesting an early stage of an \( S_N2 \)-like approach of the donor atom toward the central atom \( \text{trans} \) to the \( \text{Sn}–\text{CMe}_3 \) bond. This feature relates 235b to the N-donor-substituted tetraorganotin compounds discussed above, taking into account similar N–Sn bond distances in all these compounds (Table 43). These distances are close to the limiting nonbonding distance between tin and nitrogen, 3.08 Å, defined by Dräger.535.

The estimation of the position of 235b along the \( T \rightarrow \text{TBP} \) pathway by using the difference between the sums of the equatorial and axial angles with values between 0 (ideal T) and 90° (ideal TBP)652 gives values of 21° and 14° for \( R_{\text{Sn}} \) and \( S_{\text{Sn}} \) epimers, respectively642.

The NMR spectral data of 232 indicate a coordination sphere of the Pr\( _\text{N} \) substituted organotin hydride similar to that of an unsubstituted hydride648. In particular, the two \( ^{117}\text{Sn}[^1\text{H}] \) resonances at \(-88.8 \) and \(-92.1 \) ppm are within the region of resonances of the likewise tetrahedrally coordinated tin, e.g., as in \( \text{Me}_2\text{MenSnH} \) (\(-96.8 \) ppm).
The $^{119}\text{Sn}$ NMR shifts of the tin hydrides 233 and 234 (δ about −120 to −130 ppm) are generally in the region of the values found for diaryl(monoalkyl)tin hydrides\textsuperscript{640,648,650}. Analogously, the absence of a high-field shift of the two $^{117}\text{Sn}$$^1\text{H}$ resonances of 235a at −108.5 and −125 ppm compared with those of unsubstituted MeMenNaphSnH (−117.0 and −121.6 ppm) is significant\textsuperscript{648}. These results suggest the absence of a significant donor–acceptor interaction between the tin and nitrogen atoms. Moreover, the $^{13}\text{C}$- and $^1\text{H}$-NMR spectra of 234b and 234b\textsuperscript{′} in C\textsubscript{6}D\textsubscript{6} at room temperature indicate equivalence of the nitrogen-bonded methyl groups of the PhN\textsuperscript{*} ligand for each diastereomer of 234b and 234b\textsuperscript{′}; indicating either no N → Sn coordination or a fast N → Sn association/dissociation on the NMR time scale\textsuperscript{640}.

Nevertheless, all $^1J(^1\text{H}−^{117,119}\text{Sn})$ coupling constants of the tin hydrides 233–235 are generally large compared to noncoordinated tin hydrides with similar substituents, showing a trend toward an intramolecular coordination at the tin atom and being in good agreement with the X-ray analysis of 235b\textsuperscript{642}, which indicates that the hydrogen atom is bound to the tin center in the equatorial position. Furthermore, in the case of the methylmethyl derivative, the methyl coupling constants, $^1J(^{13}\text{C}−^{117,119}\text{Sn})$ and $^2J(^1\text{H}−^{117,119}\text{Sn})$ are decreased, while the methyl coupling constant, $^1J(^{13}\text{C}−^{117,119}\text{Sn})$, is increased. This indicates also a distortion of the tetrahedral coordination around the tin toward the TBP geometries in these compounds, with the methyl group occupying a quasi-axial and the methyl group a quasi-equatorial positions\textsuperscript{648}. The tin hydride 234c shows an extremely high-field shift (δ = −188.8 ppm) as a result of a slightly stronger coordinative interaction due to the negative inductive effect of the additional phenyl substituent\textsuperscript{650}.

When compared to the PrN, PhN and PhN\textsuperscript{*} substituted organotin hydrides, the N → Sn coordination in the NpN derivatives 235c and 235d is stronger, as evidenced by NMR spectroscopy\textsuperscript{640}. In particular, the $^1\text{H}$- and $^{13}\text{C}$-NMR spectra of 235c at 20 and 100 °C in C\textsubscript{6}D\textsubscript{5}CD\textsubscript{3} contain two separate singlets and the $^1\text{H}$-NMR spectra of the two diastereomers of 235d at room temperature in C\textsubscript{6}D\textsubscript{6} contain four singlets, all associated with the two nonequivalent methyl groups attached to the nitrogen in the NpN moiety in each of the species.

Finally, the chemical $^{119}\text{Sn}$ NMR shifts of the extremely unstable organotin hydrides 236 and 237\textsuperscript{651} containing an oxazoline substituents are in the ranges of δ ca −62 to −64 and −122 to −148 ppm for the dimethyl and diphenyl derivatives, respectively. The $^{13}\text{C}$- and $^1\text{H}$-NMR spectra of the diastereomeric mixture of 236b display four separate signals corresponding to the two diastereomeric methyl groups of each isomer on the oxazoline ring, indicating that dissociation of the N−Sn bond is slow on the NMR time scale.

It is therefore evident that the weaker coordination of the tin hydrides compared to the tin halides (see below) is the result of the reduced Lewis acidity of the tin atom. The diastereomeric ratios of the triorganotin hydrides and the precursors tin halides in solution generally differ from unity (Table 44). In most cases the diastereomeric ratios are modest and higher for 234a\textsuperscript{650}. In the methyl derivatives 232, 233b and 235a, the diastereomeric ratios, which reveal an optical induction from the menthyl ligand to the asymmetric tin center, increase in an order of increasing rigidity of the potentially bidentate ligand, (PrN) < (PhN) < (NpN)\textsuperscript{648}.

Two different diastereomeric mixtures of (Rc)-234a were obtained, depending on the solvent used for the reduction\textsuperscript{650}. The ratios of both diastereomeric mixtures did not change for weeks, showing that the stereogenic tin center is configurationally stable. In addition, the tin hydrides 232, 233b and 235a show constant optical rotation values, indicating a constant ratio of diastereomers which are most likely stable toward interconversion\textsuperscript{648}. Moreover, heating a toluene solution of 235d at 100 °C for 20 minutes causes no change in the 66 : 34 diastereomeric ratio\textsuperscript{640}. Thus, the diastereomeric ratios of
16. Hypervalent compounds of organic germanium, tin and lead derivatives

TABLE 44. Diastereomeric ratios of the chelate tin halides and hydrides with a stereogenic tin atom containing a chiral tin atom and N-donor substituent

<table>
<thead>
<tr>
<th>Type of compound</th>
<th>X</th>
<th>Number</th>
<th>Diastereomeric ratio</th>
<th>X</th>
<th>Number</th>
<th>Diastereomeric ratio</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeMenP₅N₅SnX Br</td>
<td>Br</td>
<td>238</td>
<td>a</td>
<td>H</td>
<td>232</td>
<td>51 : 49 b</td>
<td>648</td>
</tr>
<tr>
<td>MeMenP₅H₅SnX Br</td>
<td>Br</td>
<td>243</td>
<td>53 : 47 b,c</td>
<td>H</td>
<td>233b</td>
<td>54 : 46 b</td>
<td>648</td>
</tr>
<tr>
<td>(R₆)-MePhP₅N₅Br</td>
<td>Br</td>
<td>245a</td>
<td>60 : 40 d</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>*SnX (R₆)-MePhP₅N₅</td>
<td>Br</td>
<td>246</td>
<td>60 : 40 d</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>*SnX</td>
<td>Br</td>
<td>247</td>
<td>80 : 20 d</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>*SnX</td>
<td>Br</td>
<td>248a</td>
<td>&gt; 98 : &lt; 2 d</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(S₅C)-t-BuPhP₅N₅ Br</td>
<td>Br</td>
<td>(S₅C)-245b</td>
<td>69 : 31 d</td>
<td>H</td>
<td>(S₅C)-234a</td>
<td>80 : 20 e,f</td>
<td>650</td>
</tr>
<tr>
<td>*SnX</td>
<td>Br</td>
<td>(R₅C)-245b</td>
<td>30 : 70 d</td>
<td>H</td>
<td>(R₅C)-234a</td>
<td>80 : 20 e</td>
<td>650</td>
</tr>
<tr>
<td>*SnX</td>
<td>Br</td>
<td>248b</td>
<td>75 : 25 d</td>
<td>H</td>
<td>234d</td>
<td>66 : 34 e</td>
<td>650</td>
</tr>
<tr>
<td>(S₅C)-n-BuPhP₅N₅ Br</td>
<td>Br</td>
<td>248c</td>
<td>84 : 16 d</td>
<td>H</td>
<td>234e</td>
<td>51 : 49 e</td>
<td>650</td>
</tr>
<tr>
<td>*SnX</td>
<td>Br</td>
<td>248d</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeMenP₅N₅*SnX Cl</td>
<td>Cl</td>
<td>244a</td>
<td>73 : 27 g</td>
<td>H</td>
<td>234b</td>
<td>64 : 36 g</td>
<td>640</td>
</tr>
<tr>
<td>MeMenP₅N₅SnX Br</td>
<td>Br</td>
<td>251a</td>
<td>54 : 46 h,c</td>
<td>H</td>
<td>235a</td>
<td>62 : 38 b</td>
<td>648</td>
</tr>
<tr>
<td>t-BuMenP₅N₅SnX Br</td>
<td>Br</td>
<td>251c</td>
<td>55 : 45 b</td>
<td>H</td>
<td>235b</td>
<td>60 : 40 b</td>
<td>642</td>
</tr>
<tr>
<td>MenPhP₅N₅SnX Br</td>
<td>Br</td>
<td>251d</td>
<td>60 : 40 g</td>
<td>H</td>
<td>235d</td>
<td>66 : 34 g</td>
<td>640</td>
</tr>
<tr>
<td>MenPhO₅N₅SnX Cl</td>
<td>Cl</td>
<td>252b</td>
<td>50 : 50 g,h</td>
<td>H</td>
<td>236b</td>
<td>50 : 50 g</td>
<td>651</td>
</tr>
<tr>
<td>MenPhO₅N₅*SnX Cl</td>
<td>Cl</td>
<td>254b</td>
<td>45 : 55 g</td>
<td>H</td>
<td>237b</td>
<td>34 : 66 g</td>
<td>651</td>
</tr>
</tbody>
</table>

*a Only one broad ¹¹⁷Sn resonance at −3.7 ppm is observed, indicating a fast dynamic process.
*b Determined by ¹¹⁷Sn[¹H] NMR.
*c Only one diastereomer was found in a freshly prepared solution, (Rₛₘ) for (R₅C)-MePhP₅N₅SnBr and MeMenP₅N₅SnBr.
*d Sₛₘ/Rₛₘ.
*e In Et₂O at 0 °C, the same ratio of the two isomers was obtained at −70 °C.
*f The ratio of the diastereomers is 58 : 42 for the reduction in THF at room temperature.
*g Determined by ¹¹⁹Sn NMR.
*h 30 : 70 (Sₛₘ/Rₛₘ) for a freshly prepared sample from methanol, 50 : 50 after 3 days.

The tin hydrides are usually the result of a kinetically controlled and stereospecific reduction of the corresponding tin halides. This distinguishes the diastereomeric tin hydrides from the corresponding diastereomeric tin halides, which are in a dynamic equilibrium (see below).

Nevertheless, epimerization was observed when the tin hydride (R₅C)-234a was treated with an excess of LiAlH₄ in THF. Furthermore, using THF as the solvent at room temperature, the reduction of the corresponding bromide gave a 58 : 42 diastereomeric ratio, i.e. under these conditions the reaction is thermodynamically controlled.

The almost nonselective formation of the tin hydrides 232, 234e and 236b is remarkable. In particular, in the case of 234e the authors suggest that the reduction occurs stereospecifically and that the minor diastereomer (S₅C,Rₛₘ)-t-BuPhP₅N₅*SnBr is reduced faster than the major diastereomer (S₅C,Sₛₘ)-t-BuPhP₅N₅*SnBr which is epimerized because of its configurational instability.
Data related to the enantioselectivity of organotin hydrides containing chiral PhN ligand in free radical reductions have been published. Reaction of the tin hydrides and with methanol was also reported to proceed with abstraction of H₂ and formation of the methoxy derivatives Me₂PhNSnOMe and MePhPhNSnOMe, respectively.

c. Triorganocompounds. Triorganotin halides containing one monoanionic C,N-chelating ligand have been well known since the 1970s as typical pentacoordinate compounds with a rather strong N → Sn coordination, mainly due to systematic investigations by Noltes, van Koten and Jastrzebski. The main representatives of these compounds include the following types of five-membered ring ligands (Scheme 12): PrN and PhN, chiral PhN, and chiral PhN. Triorganotin chlorides and bromides with the ligands shown in Scheme 12 are generally prepared by the reaction of 1 : 1 diorganotin dihalides with the PrN or ArN lithium reagents. In specific cases, arylcopper compounds or arylgoldlithium derivatives were used. Fluoride was obtained by treatment of chloride Men₂NpNSnCl with KF in acetone.

Early examples of related compounds, in particular those including 2-(phenylazo)phenyl ligand, i.e. 255a and 255b, or 2-{[(dimethylamino)methyl]phenyl}methyl and 8-(dimethylamino)methyl-1-naphthyl ligands, both containing a six-membered chelate ring, were discussed in a review. Various reactions, such as Grignard reactions, redistribution, halogenation, exchange of halide and phenylation, have been used for obtaining the series of compounds PrNPh₂SnX as well as the related derivatives (PrN)ₙPhₓSnClᵧ (x = 1–4, y = 0–3, z = 0–2), containing PrN as a potential intramolecular donor ligand. Note that attempts to substitute all the chlorine atoms of Ph₂SnCl₂ and PhSnCl₃ by the R group of the Grignard reagent failed and resulted in cleavage of a phenyl group, leading to the triorganotin derivatives, with KF in acetone.

The hydrochloride, compounds (X = Br, I, S₂CNR₂, OCO₂R, where R = Me, Et, Ph) containing 2-ethylpyrldyl ligand, as well as thienyl triorganotin species, in which the heterocycle contains 3-(2-pyridyl) or 2-(2-oxazolinyl) substituents, and 266 (R = Me, n-Bu, n-Hexyl, Ph, p-Tol; X = Cl, Br, I, OH, S₂CNMe₂) were recently described. X-ray crystallography of shows a TBP arrangement at the tin atom due to intramolecular coordination by the inner nitrogen atom, with a dangling CH₂CH₂NHMe₂⁺ group. A series of 2-stannyl-substituted ferrocenylmethyl-amine and -phosphine derivatives 2-XMe₂SnFcCH₂D (X = Me, Cl; D = NMe₂, PPh₂, POPh₂), with the ferrocenylene group spanning the two potential coordinating sites, were recently obtained.

The tetraorganotin was prepared from Me₂SnCl and 2-LiFcCH₂NMe₂; it was transformed into phosphine through intermediate methiodide according to equation 61. The tin monochlorides and were synthesized by the redistribution of and with Me₂SnCl or Me₂SnCl₂, respectively. The oxidation of with H₂O₂ in Et₂O leads to . The monochlorination of the latter to yield was achieved with HCl in ethanol.
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SCHEME 12. Triorganotin halides containing one five-membered C,N-chelating ligand
Earlier series of compounds containing a C,P-chelating ligand, the tertiary phosphine derivatives 271a–d, was also described\textsuperscript{201,204}.

The Pb analogue of 258a, i.e. the triphenyl derivative 272a, was prepared by phenylation of PbCl\textsubscript{2} with PhLi and subsequent reaction with 3-dimethylaminopropyl chloride\textsuperscript{658}. One phenyl group from 272a was cleaved with HCl, HBr or HI to yield the monohalides 272b–d, respectively.

Selected crystallographic and NMR data pertinent to the TBP structures for pentacoordinate triorganotin and triorganolead complexes containing aliphatic and aromatic N-donor ligands are collected in Tables 45–47.

In the solid, all the compounds have essentially TBP coordination geometry with the carbon ligands at the equatorial sites and the more electronegative nitrogen and halogen or sulfur atom at the axial positions. The solid state geometries are largely retained in solution as deduced from \textsuperscript{1}H, \textsuperscript{13}C and \textsuperscript{119/117}Sn NMR spectroscopic studies. For instance, comparison of the \textsuperscript{119}Sn-NMR chemical shifts of tin bromides (\(S_c,S_{Sn}\)- and (\(S_c,R_{Sn}\))- 245b (−103.2 and −98.2, CDCl\textsubscript{3}), (\(S_c\))-245c (−121.7, C\textsubscript{6}D\textsubscript{5}CD\textsubscript{3}), (\(S_c,S_{Sn}\)- and (\(S_c,R_{Sn}\))-248b (−100.3 and −93.1, CDCl\textsubscript{3}) with the corresponding data for diphenyl(neomenthyl) tin bromide (\(\delta = −5.91\)) shows a large high-field shift of approximately 100–120 ppm\textsuperscript{650}. Additional examples of \textsuperscript{119}Sn-NMR chemical shifts for pentacoordinated triorganotin complexes with the Ar\textsubscript{N} moiety are given in Table 47.
SCHEME 13. Preparation of tin compounds containing the Me₂N(CH₂)₃(PR₃) moiety
\[ \text{(263)} \]

\[ \text{(264)} \quad \text{(264a)} \ X = S_2\text{NM Me}_2 \]

\[ \text{(265)} \]

\[ \text{(266)} \]

\[ \text{(266a)} \ X = \text{Cl}, \ R = \text{Ph} \]

\[ \text{(266b)} \ X = S_2\text{CN Me}_2, \ R = \text{Me} \]

\[ \text{(267a)} \ X = \text{Me}, \ D = \text{N Me}_2 \]

\[ \text{(267b)} \ X = \text{Cl}, \ D = \text{N Me}_2 \]

\[ \text{(268a)} \ X = \text{Me}, \ D = \text{P Ph}_2 \]

\[ \text{(268b)} \ X = \text{Cl}, \ D = \text{P Ph}_2 \]

\[ \text{(269a)} \ X = \text{Me}, \ D = \text{P O Ph}_2 \]

\[ \text{(269b)} \ X = \text{Cl}, \ D = \text{P O Ph}_2 \]

\[ \text{(271a)} \ R = R' = n\text{-Bu} \]

\[ \text{(271b)} \ R = R' = c\text{-C}_6\text{H}_{11} \]

\[ \text{(271c)} \ R = R' = \text{Ph} \]

\[ \text{(271d)} \ R = t\text{-Bu}, \ R' = \text{Ph} \]

\[ \text{(272a)} \ X = \text{Ph} \]

\[ \text{(272b)} \ X = \text{Cl} \]

\[ \text{(272c)} \ X = \text{Br} \]

\[ \text{(272d)} \ X = \text{I} \]
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TABLE 45. Selected structural parameters for pentacoordinated triorganotin and organolead complexes with PrN and related moieties

<table>
<thead>
<tr>
<th>Compound</th>
<th>N → Sn (Å)</th>
<th>Sn–X (Å)</th>
<th>N → Sn–X (deg)</th>
<th>ΔSn&lt;sup&gt;a&lt;/sup&gt; (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl&lt;sub&gt;2&lt;/sub&gt;SnCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;NMe&lt;sub&gt;2&lt;/sub&gt; (239b)</td>
<td>2.578</td>
<td>2.492</td>
<td>167.7</td>
<td>0.15</td>
<td>658</td>
</tr>
<tr>
<td>Br&lt;sub&gt;2&lt;/sub&gt;SnCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;NMe&lt;sub&gt;2&lt;/sub&gt; (239c)</td>
<td>2.555</td>
<td>2.659</td>
<td>167.8</td>
<td>0.15</td>
<td>658</td>
</tr>
<tr>
<td>iPr&lt;sub&gt;2&lt;/sub&gt;SnCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;NMe&lt;sub&gt;2&lt;/sub&gt; (239d)</td>
<td>2.541</td>
<td>2.888</td>
<td>167.9</td>
<td>0.14</td>
<td>658</td>
</tr>
<tr>
<td>(PhO)&lt;sub&gt;2&lt;/sub&gt;SnCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;NMe&lt;sub&gt;2&lt;/sub&gt; (239e)</td>
<td>2.569</td>
<td>2.094</td>
<td>167.9</td>
<td>0.14</td>
<td>658</td>
</tr>
<tr>
<td>[Me&lt;sub&gt;2&lt;/sub&gt;NCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CMe&lt;sub&gt;2&lt;/sub&gt;Sn(Ph)]&lt;sub&gt;2&lt;/sub&gt;S (277)</td>
<td>2.656</td>
<td>2.531&lt;sup&gt;b&lt;/sup&gt;</td>
<td>174.0</td>
<td>0.26</td>
<td>668</td>
</tr>
<tr>
<td>ClMe&lt;sub&gt;2&lt;/sub&gt;SnCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;PH&lt;sub&gt;4&lt;/sub&gt;But (271d)</td>
<td>3.079&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.493</td>
<td>169.8</td>
<td>0.21</td>
<td>204</td>
</tr>
<tr>
<td>iPr&lt;sub&gt;2&lt;/sub&gt;PbCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;NMe&lt;sub&gt;2&lt;/sub&gt; (272d)</td>
<td>2.677</td>
<td>2.974</td>
<td>165.4</td>
<td>0.16</td>
<td>658</td>
</tr>
</tbody>
</table>

<sup>a</sup>Toward the halide, oxygen or sulfur atom.

<sup>b</sup>Sn–P bond.

TABLE 46. Selected NMR data for pentacoordinated triorganotin and organolead complexes with PrN moiety in CDCl<sub>3</sub>

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ&lt;sup&gt;13&lt;/sup&gt;C(α-CH&lt;sub&gt;2&lt;/sub&gt;) (ppm)</th>
<th>1&lt;sup&gt;J&lt;/sup&gt;(&lt;sup&gt;119&lt;/sup&gt;Sn–&lt;sup&gt;13&lt;/sup&gt;C), (Hz)</th>
<th>δ(&lt;sup&gt;119&lt;/sup&gt;Sn/&lt;sup&gt;207&lt;/sup&gt;Pb), (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph&lt;sub&gt;3&lt;/sub&gt;SnCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;NMe&lt;sub&gt;2&lt;/sub&gt; (258a)</td>
<td>8.3</td>
<td>399</td>
<td>−101.9</td>
</tr>
<tr>
<td>FPh&lt;sub&gt;2&lt;/sub&gt;SnCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;NMe&lt;sub&gt;2&lt;/sub&gt; (239a)</td>
<td>9.0</td>
<td>599.0</td>
<td>−143.4&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Cl&lt;sub&gt;2&lt;/sub&gt;SnCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;NMe&lt;sub&gt;2&lt;/sub&gt; (239b)</td>
<td>14.4</td>
<td>585.6</td>
<td>−135.7</td>
</tr>
<tr>
<td>Br&lt;sub&gt;2&lt;/sub&gt;SnCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;NMe&lt;sub&gt;2&lt;/sub&gt; (239c)</td>
<td>16.0</td>
<td>571.0</td>
<td>−47.7&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>iPr&lt;sub&gt;2&lt;/sub&gt;SnCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;NMe&lt;sub&gt;2&lt;/sub&gt; (239d)</td>
<td>18.5</td>
<td>526.0</td>
<td>−168.0&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>(PhO)&lt;sub&gt;2&lt;/sub&gt;SnCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;NMe&lt;sub&gt;2&lt;/sub&gt; (239e)</td>
<td>9.2</td>
<td>595.0</td>
<td>−150.4&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Cl&lt;sub&gt;2&lt;/sub&gt;PhSnCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;NMe&lt;sub&gt;2&lt;/sub&gt; (259a)</td>
<td>28.1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>399</td>
<td>−169.1</td>
</tr>
<tr>
<td>Cl&lt;sub&gt;2&lt;/sub&gt;PhSn(CHO)&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;NMe&lt;sub&gt;2&lt;/sub&gt; (260)</td>
<td>13.4</td>
<td>537.4</td>
<td>−50.0</td>
</tr>
<tr>
<td>Cl&lt;sub&gt;2&lt;/sub&gt;N(CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;NMe&lt;sub&gt;2&lt;/sub&gt; (262)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>31.0</td>
<td>922.1</td>
<td>−180.9</td>
</tr>
<tr>
<td>ClSn(CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;NMe&lt;sub&gt;2&lt;/sub&gt; (261)</td>
<td>15.5</td>
<td>462.3</td>
<td>−2.4</td>
</tr>
<tr>
<td>Ph&lt;sub&gt;3&lt;/sub&gt;PbCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;NMe&lt;sub&gt;2&lt;/sub&gt; (272a)</td>
<td>21.7</td>
<td>387.0</td>
<td>−126.4</td>
</tr>
<tr>
<td>Cl&lt;sub&gt;2&lt;/sub&gt;PbCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;NMe&lt;sub&gt;2&lt;/sub&gt; (272b)</td>
<td>35.5</td>
<td>592.0</td>
<td>−37.1</td>
</tr>
<tr>
<td>Br&lt;sub&gt;2&lt;/sub&gt;PbCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;NMe&lt;sub&gt;2&lt;/sub&gt; (272c)</td>
<td>36.7</td>
<td>583.6</td>
<td>−34.9</td>
</tr>
<tr>
<td>iPr&lt;sub&gt;2&lt;/sub&gt;PbCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;NMe&lt;sub&gt;2&lt;/sub&gt; (272d)</td>
<td>38.2</td>
<td>572.0</td>
<td>−56.3</td>
</tr>
</tbody>
</table>

<sup>a</sup>Measured in CD<sub>2</sub>C<sub>2</sub>Cl<sub>2</sub>.

<sup>b</sup>Not obtained.

<sup>c</sup>Hexacoordinated tin.

With a Burgi–Dunitz-type of analysis<sup>261, 262, 475</sup>, which was discussed in Section VI.A.1.c, the variations in the geometry of the pentacoordinate neutral intra- and intermolecular complexes with TBP geometries were analyzed in detail<sup>636</sup>. The axial arrangement of a donor atom D, in particular nitrogen, and a substituent X in compounds with central coordination unit DSnC<sub>3</sub>X was considered as a representation of different points (a ‘snapshot’) along a hypothetical reaction coordinate of a S<sub>N</sub>2 pathway for substitution with inversion at tetrahedral tin. The experimental data in relation to the interdependence of the differences between D–Sn and Sn–X bond lengths in pentacoordinate and tetrahedral compounds, and the averaged DSnC and CSnX angles, fit very well the theoretical curves. The latter were deduced by using the Pauling relationship between bond length and bond order<sup>474</sup>, where \( d(n) \) is the bond length, \( d(l) \) is the single bond length and \( c \) depends on the type of bond (equation 62).

\[
\Delta d(n) = d(n) - d(l) = -c \log n
\] (62)
TABLE 47. Selected X-ray and NMR data for pentacoordinated triorganotin complexes with the ArN moiety and related compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sn–N</th>
<th>Sn–X</th>
<th>N–Sn–X</th>
<th>∆Sn°</th>
<th>$\delta^{119}$Sn</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me2PhN2SnCl (240a)</td>
<td>2.487</td>
<td>2.531</td>
<td>171.0</td>
<td>0.16</td>
<td>63.9 (CDCl3)</td>
<td>656</td>
</tr>
<tr>
<td>Men3PhN2SnCl (244a)</td>
<td>2.640</td>
<td>2.474</td>
<td>169.1</td>
<td>0.229</td>
<td>−75.2 (CH2Cl2)</td>
<td>640</td>
</tr>
<tr>
<td>263</td>
<td>2.575</td>
<td>2.501</td>
<td>169.3</td>
<td>0.16</td>
<td>−45 (CDCl3)</td>
<td>641</td>
</tr>
<tr>
<td>MePhPhN2SnBr (248a)</td>
<td>2.552</td>
<td>2.673</td>
<td>176.2</td>
<td>0.15</td>
<td>−102.7 (CD2Cl2)</td>
<td>654</td>
</tr>
<tr>
<td>Ph2PhN2SnBr (242)</td>
<td>2.512</td>
<td>2.630</td>
<td>171.0</td>
<td>0.19</td>
<td>—</td>
<td>659</td>
</tr>
<tr>
<td>(S,S)-MePhPhN*SnCl (245a)</td>
<td>2.476</td>
<td>2.683</td>
<td>168.9</td>
<td>0.11</td>
<td>65 (CD2Cl2)</td>
<td>653</td>
</tr>
<tr>
<td>MePhPhN2SnBr (249a)</td>
<td>2.492</td>
<td>2.664</td>
<td>171.3</td>
<td>0.20</td>
<td>65 (CDCl3)</td>
<td>660</td>
</tr>
<tr>
<td>MePhPhN2MenCl (244b)</td>
<td>2.64</td>
<td>2.486</td>
<td>166.7</td>
<td>0.173</td>
<td>—</td>
<td>640</td>
</tr>
<tr>
<td>(S,S)-MeMenNpNSnBr (244b)</td>
<td>2.58</td>
<td>2.496</td>
<td>166.3</td>
<td>0.189</td>
<td>−123.8 (CHCl3)</td>
<td>670</td>
</tr>
<tr>
<td>MeNpNpSnF (250)</td>
<td>2.645</td>
<td>2.023</td>
<td>164.3</td>
<td>0.200</td>
<td>−106.5 (CHCl3)</td>
<td>661</td>
</tr>
<tr>
<td>MePhPhN2SnBr (251b)</td>
<td>2.497</td>
<td>2.667</td>
<td>171.5</td>
<td>0.19</td>
<td>−97.5 (CD2CD3)</td>
<td>638</td>
</tr>
<tr>
<td>(R,S)-Me-MeMenNpNSnBr (251a)</td>
<td>2.554</td>
<td>2.641</td>
<td>168.1</td>
<td>0.19</td>
<td>−35.0 (CD2D6)</td>
<td>648</td>
</tr>
</tbody>
</table>

For selected compounds, $\delta^{119}$Sn relative integral ratio: 46 : 54.

Two correlations were established: as D–Sn becomes shorter, the Sn–X distance tends to become longer and the average DSnC angles tend to become larger.

Another parameter, which also served as a probe for the progress of the S12 reaction, is the deviation of tin atom from the equatorial plane, ∆Sn (Tables 43, 45 and 47). Thus,
the tetraorganotins and hydride 235b (Table 43) represent an early step in the reaction (ΔSn ca 0.45–0.57 Å), while for the triorganotin derivatives (Tables 45 and 47) the progress of the reaction is more advanced (ΔSn ca 0.20 Å). The highest extent of a goodness of a TBP environment at tin takes place for six-membered chelate 257b (ΔSn 0.06 Å).

Factors affecting the increase of coordination at Ge, Sn or Pb were discussed for the tin compounds 239, 258–260 containing the PrN moiety, and also for their Ge (Section V.A) and Pb analogues, in which the Me2N donor intramolecularly coordinates the central atom658. The X-ray and 13C, 119Sn and 207Pb NMR data (Tables 45 and 46), the model of the 3c–4e interaction N → M−Xax and the structure correlation results673 were used for this purpose. It is suggested that the nucleophilic coordination originates from the π-basicity and the charge flow from the ligands into the σ∗-LUMO at the central atom. The values of 119Sn NMR chemical shifts and spin–spin coupling constants support the arguments in favor of interactions of the frontier orbitals. The δ13C values of the α-methylene group in CDCl3 solution are shifted distinctly to high frequency, which indicates the approach of the Me2N donor to the central atom. The electronegativity decrease of the ligands at Ge, Sn or Pb inhibits intramolecular nucleophilic attack658. In the ligand sequences PhCl2 > Ph2Cl > Ph3 and Ph2I > Ph2Br > Ph2OPh > Ph2F the N → Ge/Sn/Pb distance becomes smaller. With regard to the halide substituents, the chemical shift sequences δ(119Sn) (Br ≫ Cl > F > I) and δ(207Pb) (Br > Cl > I) are similar.

The X-ray structures of 239b–e and 272d show an almost equal deviation of the central atom from an ideal TBP arrangement658. In particular, the latter is displaced 0.14–0.16 Å out of the equatorial plane in a direction away from Nax, with the XaxSnNax angle in the narrow range of 167.7–167.9° for X = Hal (Table 45). Moreover, the N–Sn/Pb distances transformed into Pauling bond orders are almost equal (0.21–0.23). Furthermore, the goodness of their TBP geometries, defined as the difference ΔΣ(θ) of the sums of equatorial and axial angles (see below), is 75–77° (ΔΣ(θ) = Σθeq − Σθax, ΔΣ(θ) = 0° for a perfect tetrahedron and 90° for a perfect TBP).

X-ray determinations of the dithiocarbamates 264a and 266b reveal a TBP structure, with the nitrogen and sulfur atoms in the axial positions664,665. The 2-ethylpyridyl and 3-thienyl-2-(3-oxazolinyl) ligand chelate the tin, while the dithiocarbamate is monodentate. The N → Sn interaction in the latter is weaker and the extent of distortion from a TBP structure is larger (Table 47).

Both crystal structure determinations and NMR studies in solution show for 267b, 268b and 269b molecular structures in which the tin atom approaches a TBP pentacoordination as a consequence of an intramolecular D → Sn interaction643. In contrast to the tetraorganotin derivative 268a, the P–Sn distance of 3.349 Å in chloride 268b is shorter than the sum of van der Waals radii (Table 1), indicating a weak P → Sn interaction and suggesting the ligand polyhedron at tin as a monocapped tetrahedron (T). This interaction is weaker than that in the related structure of 271d204 due to the higher donor capacity of the t-BuPhP group and the greater flexibility of the chelate ring in the latter compound.

The extent of distortion of 267b–269b on the pathway between the ideal T and the ideal TBP is determined by three parameters: (i) the difference Σθeq − Σθax (deg) between the three equatorial CSnC angles and three axial CSnCl angles at tin, namely 90° for the TBP and 0° for T652; (ii) the deviation ΔSn (Å) of the tin atom from the plane through the three equatorial ligands in the tin polyhedron, which ranges from 0.71 Å for T to 0 Å
for the TBP; and (iii) the bond length differences $\Delta d(D \rightarrow Sn) - \Delta d(D-Sn)$ (Å) 
$D = N, P, O$; $d(N-Sn) = 2.08$, $d(P-Sn) = 2.52$, $d(O-Sn) = 2.02$, which decrease 
with increasing donor strength of the functional group $D$. All three parameters indicate 
an increase of the intramolecular coordination for the donor group in 267b–269b in the 
sequence $\text{Ph}_2P < \text{Me}_2N < \text{Ph}_2PO$. The observed $\delta^{119}\text{Sn}$ and 
$2J^{(119}\text{Sn}-\text{CH})$ values suggest for 267b and 269b TBP geometries at tin, while the $\delta^{119}\text{Sn}$ value of 268b indicates only a small tendency for 
an increase in the coordination number of tin in this compound.

The P $\rightarrow$ Sn coordination in 271a–d is relatively weak, as could be concluded from the 
observation that intermolecular coordination of external donors like pyridine, HMPA and 
DMF could compete with intramolecular P $\rightarrow$ Sn interaction. In solution of 268b and 
271d a fast equilibrium exists between tetracoordinated open-chain and pentacoordinated 
cyclic structures.

Contrary to tetraorganotins and triorganotin hydrides, triorganotin halides are gener-
ally configurationally unstable. It is well known that their configurational stability is 
significantly enhanced due to the presence of intramolecularly coordinating substituents. 
This gives chiral pentacoordinate, triorganotin halides with the tin atom as the center 
of chirality, as well as optically active tin bromide containing the C,N-chelating chiral 
$\text{PhN}^*$ ligand, which structure was proved by X-ray diffraction. Such tin com-
ounds containing a stereogenic tin center or chiral ligand are of particular interest 
both from a stereochemical point of view and as reagents, e.g. the chiral organotin hydrides 
in asymmetric synthesis (see above). Stereochemical aspects and fluxional processes in 
triorganotin halides containing one monoanionic C,N-chelating ligand were discussed 
in detail.

Two basic processes are in common operative in solution: (1) N–Sn dissociation/association and (2) inversion of configuration of the tin center. On the NMR time 
scale the former becomes fast for bromide above 30°C, while the latter does not 
occur or is at least slow up to 125°C. Nevertheless, inversion of configuration of the tin 
center takes places at low temperature on the laboratory time scale. For example, on dis-
solving enantiomerically pure bromide ($R_c$,$R_{Sn}$)-245a in toluene, the $^1H$ NMR spectrum 
at $-30°C$ shows the presence of only one diastereomer. At $-13°C$ an epimerization 
process starts which finally results in the formation a 40:60 mixture of the ($R_c$,$R_{Sn}$) and 
($R_c$,$S_{Sn}$) diastereomers. In addition, the reaction of $\text{PhN}^*$ with MenPh$\text{SnCl}_2$ in 
$\text{Et}_2\text{O}$ results in the formation of the two diastereomers in a 70:30 ratio at both 0°C 
and $-78°C$. Thus, the ratios of the tin halide diastereomers shown in Table 4 result 
from a thermodynamically controlled reaction of the precursor diorganotin dihalides with 
$\text{ArN}^*$ compounds.

Flexibility of the chelate ring has an important influence on the rate of inversion of 
configuration at tin. For the $\text{PrN}$ derivative 238, $^1H$ and $^{13}C$ NMR investigations show the 
presence of only one broad resonance pattern at an ambient temperature, which displays 
a tendency to decoalesce to two resonance patterns for the two possible diastereomers at 
low temperature ($-60°C$). However, at $-60°C$, the lowest temperature studied, only 
broadening of the Me–Sn and the NMe$_2$ signals took place. This suggests a comparatively 
fast inversion of configuration at tin due to the much more flexible chelate ring present 
in 238 as compared to both 243 and 251a.

The ratio of the two diastereomers depends significantly on the bulk of the substituents 
at the chiral benzylic carbon center. In particular, for the $t$-Bu-substituted 248a only 
one diastereomer ($R_c$,$S_{Sn}$) and for the Me$_3$Si-substituted 249a only one enantiomeric 
pair ($R_c$,$R_{Sn}$)/($S_c$,$S_{Sn}$) are present in solution. According to X-ray study, the same
enantiomeric pair is found in the solid state, where the bulky Ph−Sn and Me₃Si groups are at opposite sides of the molecule. From the ¹H DNMR investigations, in triorganotin bromides containing a six-membered chelate ring, 256a, 256b, 257a and 257b, both the N−Sn dissociation/association and inversion of configuration at tin processes are operative on the NMR time scale. In particular, for bromide 256b, the N−Sn dissociation/association process becomes fast at −30°C, while inversion of configuration of the tin center takes place above 0°C. In triorganotin bromides 251 containing the NpN ligand, N−Sn dissociation on the NMR time scale does not occur even at high temperature (125 and >100°C, respectively). A detailed discussion of the mechanism of inversion of configuration at tin centers having a TBP coordination geometry can be found elsewhere.

As a consequence of the asymmetry of 1,2-disubstituted ferrocenes and a stereochemically stable TBP configuration at tin, the two tin methyl groups in 267b–269b should be diastereotopic. Indeed, the ¹H NMR of 267b and 269b show two separate signals for these groups. In contrast, the N−Me groups in 267b are equivalent at room temperature, suggesting a N→Sn dissociation/association process, while the configuration at tin is stable on the NMR time scale.

The geometries and energies of the two tin epimeric diastereomers of 252b and 254b were optimized at the AM1 semiempirical technique. The calculations are in good agreement with the molecular geometry in the solid state as well as with the diastereomeric ratios observed in solution. In particular, the calculated N−Sn distances in (R-Sn)-252b and (S-Sn)−252b are 2.62 and 2.59 Å, respectively, while the X-ray determined value is 2.55 Å for (R-Sn)-252b. The calculations predict that (R-Sn)-252b is more stable than (S-Sn)-252b by 0.14 kcal mol⁻¹, which corresponds to an approximately 1:1 ratio of the isomers at 25°C (see Table 44).

d. Diorgano and monoorgano compounds. Earlier examples of diorganotin dihalides containing Ph₅N and Ph₅N C,N-chelating ligands, i.e. 273a−c and 274, and their complexation with pyridine were discussed in detail in a previous review.

\[
\begin{align*}
\text{(273) (a)} & : X = Cl, R = Me \\
\text{(b)} & : X = Br, R = Me \\
\text{(c)} & : X = Cl, R = Ph
\end{align*}
\]

\[
\begin{align*}
\text{(274) (S, S)} & : R = Me \\
\text{(274) (S, R)} & : R = Br
\end{align*}
\]

Based on the NMR and molecular weight data, the tin atom in these compounds is pentacoordinate and likely to have a TBP coordination geometry at tin in which the aryl and R groups reside in the equatorial plane. Of special interest is dibromide 274 containing two chiral centers with (S) configuration of the chiral benzylic carbon while the configuration of the chiral tin center may be either (S) or (R). Only one resonance
pattern in the $^1$H NMR spectrum is observed from $-80$ to $100°C$. This is most likely in agreement with a process of inversion of configuration at tin, which is fast on the NMR time scale even at very low temperature.

A proposed mechanism resulting in inversion of configuration at tin in dihalides 273 and 274 includes an achiral dimeric intermediate 275 with hexacoordinate tin centers (equation 63)$^{653}$. Evidence for such an intermediate is the observation of two Sn–Me resonances in the $^1$H NMR spectrum of a mixture of dichloride 273a and dibromide 273b in toluene-$d_8$ at $<-80°C$, while only one resonance pattern is observed at higher temperatures.

More recently, dichloride 259a and the corresponding diphenoxo derivative 259b containing the Pr$\text{N}$ moiety$^{644,658}$, as well as dichloride MePhNSnCl$_2$ (276)$^{656}$ have been prepared. An X-ray study of 276 revealed a TBP arrangement at the tin center with the two carbon atoms and a chlorine atom in equatorial positions and the coordinating nitrogen and the second chlorine atom in axial positions. As compared to monochloride 240a, the axial bond lengths in 276 are shorter and the deviation of the tin atom from the equatorial plane ($\Delta$$\text{Sn}$) toward the chlorine atom is larger (Tables 47 and 48), in agreement with the higher Lewis acidity of the tin atom in the latter.

A sequence analogous to the preparation of 259b from Me$_2$N(CH$_2$)$_3$MgCl (Scheme 13) was used for transformations Me$_2$NCH$_2$CH$_2$CMe$_2$MgCl $\rightarrow$ Me$_2$NCH$_2$CH$_2$CMe$_2$SnPh$_3$ $\rightarrow$ Me$_2$NCH$_2$CH$_2$CMe$_2$SnPh(0Ph)$_2$.$^{668}$ The latter reacted with two equivalents of Na$_2$S·9H$_2$O to give the diorganotin dimer 277. A similar dimeric derivative 278 containing one chelate and one nonchelate Si-substituted 1-(8-quinolinyl)methyl ligand at each of the tin atoms has been reported.$^{679}$ In contrast, its Se and Te analogues are found to be the monomeric bis-chelate derivatives (see below).
Rare examples of monoorganotin trihalides containing a C,N-chelating ligand are two series of imine derivatives, \( \text{279a–d} \)\(^680\) and \( \text{280a–d} \)\(^681\). X-ray crystal determinations of \( \text{279c} \) and \( \text{280b} \) revealed a distorted TBP geometry as a result of intramolecular \( \text{N} \rightarrow \text{Sn} \) coordination. Shortening of the axial bonds in trichlorides \( \text{279c} \) and \( \text{280b} \) as compared to mono- and dichlorides (see above) was observed (Table 48).

All the phenyl groups are cleaved off when \( \text{258a} \) is treated with ethylene glycol or with pinacol, resulting in the formation of \( \text{[PrNSn]}_2(\text{OC}_2\text{H}_4\text{O})_3 \) (\( \text{281} \)) and \( \text{[Me}_2\text{N(CH}_2)_3\text{Sn]}_2(\text{OC}_2\text{Me}_4\text{O})_3 \) (\( \text{282} \)), respectively\(^644\). Tetraphenyltin does not react with these diols under the same conditions, thus indicating the activating role of the dimethylaminopropyl group in \( \text{258} \). Compounds \( \text{281} \) and \( \text{282} \) are transformed almost quantitatively into \( \text{283} \) by reaction with PhSH.

In the sulfur derivatives \( \text{277} \)\(^644\), \( \text{278} \)\(^679\) and \( \text{283} \)\(^668\), the Sn atoms have a distorted TBP coordination with N and S in axial and two C atoms and another S atom or C atom and two other S atoms, respectively, in equatorial positions. The deviation from the ideal TBP

**TABLE 48.** Selected structural parameters for mono- and di-organotin (N–Sn) chelates

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sn–N (Å)</th>
<th>Sn–X(_{\text{ax}}) (Å)</th>
<th>Sn–X(_{\text{eq}}) (Å)</th>
<th>NSnX(_{\text{ax}}) (deg)</th>
<th>ΔSn(^a) (Å)</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>276</td>
<td>2.47</td>
<td>2.445</td>
<td>2.351</td>
<td>168.0</td>
<td>0.21</td>
<td>656</td>
</tr>
<tr>
<td>278</td>
<td>2.484</td>
<td>2.527(^b)</td>
<td>2.421(^b)</td>
<td>168.6</td>
<td>0.29</td>
<td>679</td>
</tr>
<tr>
<td>279c</td>
<td>2.284</td>
<td>2.402(^c)</td>
<td>2.323, 2.335(^c)</td>
<td>173.2</td>
<td>0.23(^d)</td>
<td>680</td>
</tr>
<tr>
<td>280b</td>
<td>2.259</td>
<td>2.417(^c)</td>
<td>2.313, 2.319(^c)</td>
<td>173.0</td>
<td>0.20</td>
<td>681</td>
</tr>
<tr>
<td>283</td>
<td>2.605</td>
<td>2.480(^b)</td>
<td>2.419, 2.425(^b)</td>
<td>168.4</td>
<td>0.39</td>
<td>644</td>
</tr>
</tbody>
</table>

\(^a\)Toward the halide or sulfur atom.
\(^b\)Sn–S.
\(^c\)Sn–Cl.
\(^d\)Dimeric structure with an additional weak coordination to chlorine (3.58 Å).
structures is greater than in compounds of the type 239. In particular, the displacement of the tin atom from the equatorial plane in the direction of S axial is 0.26 Å for the dithia derivative 277 and 0.39 Å for the trithia derivative 283. Thus, in these compounds the intramolecular N → Sn coordination is weaker than that in 239, reflecting the poor Lewis acidity of a tin center containing the S-ligands.

2. Derivatives with bidentate C,O-chelating ligands and related compounds

a. Hydroxy, alkoxy and acyloxy groups as donor centers. These groups are effective intramolecular donor centers in mono-, di-, tri- and even tetra-organostannanes. The most favored and stable chelate ring size is the five-membered ring, but four-membered and six-membered chelate rings were also reported.

The α-D-allofuranose derivative 284, (Z)-2-methyl-3-triphenylstannyl-3-penten-1-ol 285, as well as a number of o-methoxyarylstanannanes including the o-anisylstannyl compounds 286 provide examples of particularly strained four-membered rings.

The vinylic compound 285 is a rare representative of tetraorganotin species with an O → Sn intramolecular interaction, as shown unambiguously by an X-ray diffraction
The O···Sn separation (3.012 Å) lies between the sum of van der Waals radii of Sn and O and the Sn−O covalent bond length (Table 1). Based on analogous data, a very weak O···Sn interaction leading to the formation of the four-membered ring can also be proposed in (2,3-O-isopropylidene-5-O-(triphenylmethyl)-α-D-ribofuranosyl)triphenylstannane (287) and 5-deoxy-1,2-O-isopropylidene-5-C-triphenylstannyl-α-L-xylofuranose (288), with O···Sn separations of 3.093 and 3.252 Å, respectively. However, intramolecular O···Sn separation up to 3.07 Å is usually considered as evidence for a similar interaction.

As a series of o-anisylstannanes, (o-An)$_n$SnX$_{4-n}$ ($n = 3, 4, X = Cl, Br; n = 2, X = Ph, Cl, Br; n = 1, X = Br) was most recently reported (289). The synthesis of (o-An)$_3$Sn (289) and (o-An)$_2$SnPh$_2$ (290) was provided by the reactions of the Grignard reagent from o-AnMgBr with SnCl$_4$ and Ph$_2$SnCl$_2$, respectively. Compounds (o-An)$_n$SnX$_{4-n}$ ($n \neq 4$) were obtained either from reactions of 289 with SnX$_4$ or X$_2$, or by halide exchange reactions.

The X-ray structural determinations of a number of o-methoxyarylstannanes, namely 289, 290, (o-An)$_3$SnI (291), (o-An)$_2$SnBr$_2$ (292a), (o-An)$_2$SnI$_2$ (292b) and o-AnSnBr$_3$ (293), as well as 5-Me-2-MeOC$_6$H$_4$SnCl$_3$ (294) and 2,6-(MeO)$_2$C$_6$H$_4$SnCl$_3$ (295), indicate only weak O···Sn interactions. The same conclusions were reached for 294, 295 and other 2-alkoxyaryltin trichlorides by $^{35}$Cl NQR studies.

The relative reactivities of aryl–tin bonds in (o-An)$_2$SnPh$_2$ (290) and (o-Tol)$_2$SnPh$_2$ toward iodine were determined. The lower [o-AnI]/PhI value (5.2 : 1) compared to the [o-Toll]/PhI ratio (68 : 5.1) is considered to indicate an enhanced reactivity of the Ph−Sn bond in 290, arising from the nucleophilic assistance by an o-anisyl group during the Ph−Sn bond cleavage.

Among the early reported saturated compounds containing a five- or six-membered chelate ring, representative examples for which the TBP structure in the solid state was established by X-ray crystallography are the γ-hydroxy and γ-methoxy tin derivatives, IPh$_2$Sn(CH$_2$)$_3$OH (296) and ClPh$_2$Sn(CH$_2$)$_3$OEt (297), the dimer 298 with four-membered SnO$_2$Sn cycle as well as the fluoride 299a and the chloride 299b.

The iodo compound 296 was prepared by the reaction of the tetraorganotin Ph$_3$Sn(CH$_2$)$_3$OH with I$_2$. The reaction proceeds ca 100 times faster than that with Ph$_3$Sn(CH$_2$)$_3$CH$_3$, both reactions leading to Ph−Sn bond cleavage. This difference in reactivities was considered to arise from the nucleophilic assistance afforded by the OH group in the first case.
n = 3, (b) n = 4, (c) n = 5), were obtained and their coordination behavior was investigated by X-ray diffraction, multinuclear NMR and semi-empirical AM1 quantum-chemical calculations. The routes to these functional organotin trichlorides include the formation of the corresponding organotricyclohexyltinyls by coupling of an organometal species with tricyclohexyltin chloride, by reaction of (tricyclohexylstannyl)lithium with an organic halide or by hydrostannation of alkenes. A subsequent treatment of organotricyclohexyltins with SnCl₄ yielded the corresponding organotin trichlorides. The latter were also used as key intermediates for the preparation of monoorgano- tin trialkoxides, which are precursors of organic—inorganic hybrid materials and clusters containing tin.

Recently, the structures of the dichloride Cl₂Sn[(CH₂)₃O(CH₂)₂OMe]₂ (302) and trichloride Cl₃Sn(H₂O)(CH₂)₃O(CH₂)₂OMe (303), both containing five-membered chelate rings but six-coordinated tin atoms, were established.

Carbohydrate tin derivatives have been produced in which the tin and carbohydrate units are directly linked via Sn–O bonds, as well as more indirectly via Sn–CH₂CH₂–C (sugar) bonds, and Sn–CH₂–O (sugar) bonds, and Sn–CH₂–C (sugar) units (for additional references see Reference). Most recently, the structure of furanoside was unambiguously determined by X-ray diffraction. Unlike in, the oxygen in the γ-alkoxide, the sulfur in thioethers ClPh-SnCH₂I, and IPh-SnCH₂I species with tricyclohexyltin chloride, by reaction of (tricyclohexylstannyl)lithium with an organometal toward I₂ indicate that at least the groups containing Sn separations are > 4.0 Å, while in, 6-O-benzylidene-3-deoxy-3-triphenyltin-α-D-altropyranose, even a weak intramolecular O → Sn interaction is absent (in the solid, the O • • • Sn separations are > 4.0 Å), while in, 4,6-O-benzylidene-3-deoxy-3-triphenyltin-α-D-altropyranose, a weak interaction can take place (the O • • • Sn separations are 3.24 and 3.35 Å, respectively).

Recently, a family of [α-D-galactopyranosyl]methyl]tin species Ph₅Sn(CH₂OR)₄–ₙ (305, n = 1–3), Ph₅Me₃–ₙSn(CH₂OR) (306, n = 0–3) and Bu₃SnCH₂OR were prepared from 1,2,3,4-di-O-isopropylidene-α-D-galactopyranose (ROH) and the iodomethyl tin compounds Ph₅Sn(CH₂I)₄–ₙ (n = 1–3), Ph₅Me₃–ₙSnCH₂I (n = 0–3) and Bu₃SnCH₂I. Several of the compounds 305 and 306 were transformed into iodoethers IPh₅Sn(CH₂OR)₃–ₙ (307) and IPh₅Me₂–ₙSnCH₂OR (308) by iododephenylation reactions with iodine. The rather high reactivities of 305 and 306 toward I₂ indicate that at least the groups containing oxygen within the carbohydrate unit(s) provide nucleophilic assistance in the cleavage step. X-ray diffraction shows the presence of the six-membered chelate ring in 307a (n = 1).

Like the oxygen in the γ-alkoxide, the sulfur in thioethers Cl₅SnS(CH₂OR)₄–ₙ and sulfide (Cl₅SnS(CH₂CH₂CH₂)₂S (309c) can act as an intramolecular donor. This was established by the X-ray studies of 309a and 309c and H-DNMR investigation of 309b.

A family of stannylvinyl compounds of the types (Z)-Ar₃–ₙXₙSnCH=CHC(OH)RR' (310, Ar = Ph, p-Tol; n = 0–2; X = Cl, Br, I, R, R' = Me, t-Bu, Ph, cycloalkyl), exhibiting a potential HO → Sn intramolecular interaction, were prepared and characterized by H, C, Sn NMR and Sn Mössbauer spectroscopy. Triaryltins 310 (n = 0) were synthesized by the addition of the corresponding triarylhalide to the appropriate terminal alkynyl. Subsequent reactions of the former with halogens in 1 : 1 or 1 : 2 molar ratio yield the corresponding mono- and dihalides, respectively. For some of these compounds, including the Ph₃Sn (310a–e) and (p-Tol)₃Sn (311) as well as IPh₅Sn (312), Cl(p-Tol)₂Sn (313) and Br₂(p-Tol)Sn (314) entities and also for Cl₅SnC[CH₂C(OH)PhCOPh]=CHCH₂COOEt (315), the structures in the solid state were established by X-ray crystallography. 315713
Polyfunctional ligand 316 (L-H, Scheme 14) contains two methoxy groups that are potentially capable of intramolecular coordination. A wide range of organotin compounds were prepared from the ligand, $n$-BuLi and Ph$_3$SnCl followed by reaction with formaldehyde and/or halogenation\textsuperscript{239,241}. These compounds, including tetraorganotins LSnPh$_3$ (317) and LCH$_2$SnPh$_3$ (318), triorganotin bromide LSnPh$_2$Br (319), diorganotin derivatives LSnPh$_2$X$_2$ (320) and LCH$_2$SnPh$_2$X$_2$ (322, 323), and monoorganotin trichlorides LSnCl$_3$ (324) and LCH$_2$SnCl$_3$ (325), are good models for comparison of the relative stability of five- and six-membered ring systems containing tin.

That the intramolecular O → Sn coordination in compounds 320 is relatively weak was also shown by replacing the intramolecularly coordinating oxygen by the external strong Lewis base Bu$_3$PO to yield 1 : 1 or 1 : 2 adducts\textsuperscript{239}. In the latter, the tin atom remains pentacoordinated and the added Lewis base displaces a halide group. The tendency to form the 1 : 2 adduct decreases in the sequence: I > Br > Cl. The Cl derivative forms no adduct.

A related series of heptacoordinate monoorganotin trichlorides 326a–d was prepared earlier by reducing tris(2,6-dimethoxyphenyl)methanol with the stannous halide in H$_2$SO$_4$ solution (equation 64)\textsuperscript{715}. X-ray crystallographic analysis of 326a–c revealed a capped octahedral arrangement at the central atom, with tin atoms covalently bonded to three halogens and the central carbon of the triarylmethyl unit and associated, in addition, with the three neighboring methoxy groups (anti to the halogens).

In view of the presence of tin atoms with a higher coordination number than five or six in 326a–c, these compounds are not discussed here in detail. Nevertheless, in contrast to two sequences of pentacoordinate triorganotin halides\textsuperscript{357,674} as well as to a sequence of pentacoordinate (O−Si)-chelate triorganosilicon halides\textsuperscript{502}, the O−Sn interaction in 326a–c is weakened on decreasing the Lewis acidity of the Sn center as the halogen substituents become less electronegative. An analogous trend was observed for the barriers $\Delta G^\ddagger$ to methoxy group site exchange in 326a–d, which decrease (being 19.8, 16.9, 15.5 and 14.1 kcal mol$^{-1}$, respectively) as the halogens change from F to I, i.e. in the order of decreasing electronegativity.

Tables 49 and 50 present some of the structural parameters pertinent to the geometry and hypervalency at tin for (O−Sn) chelates with hydroxy, alkoxy and acyloxy groups. These include the bond lengths of tin to the two apical ligands, the axial OsnAx angles, the displacement of the tin atom ($\Delta$Sn) from the central plane defined by three equatorial ligands and the bite angles of the chelate ligands. Changes in the latter parameter allow
SCHEME 14. Preparation of tin compounds containing substituted bis(2-methoxyphenyl)methyl moiety
one to discuss the chelate ring strains which generally lie in the range 49–52°, 66–73°
and 83–84° on going from four- to five- to six-membered rings, respectively. In particu-
lar, the deviation of the β-hydroxy derivative Ph₃SnC(CMe₂OH)=CHMe (285) from the
tetrahedral geometry is less marked than in the analogous γ-hydroxy compounds 310a–e,
where it is due to stronger intramolecular O → Sn interactions, of 2.73–2.77 Å as com-
pared with 3.01 Å in 285. This results from the presence of a less strained five-membered
ring in the latter compounds.

On going from tetraorgano- to triorganotin compounds the O → Sn interaction becomes
significantly stronger as a result of the higher Lewis acidity of the tin atom in the lat-
er compounds (e.g. compare the tetraorganotin derivatives 287 and 288 with the iodo
compound 284, and the γ-hydroxy compounds 310a–e with the halo compounds 312
and 313). In particular, the displacement of the Sn atom by 0.47 Å from the equato-
rial plane toward iodine in 284 represents a 39% distortion of its geometry toward a
TBP arrangement. Furthermore, the sum of the equatorial angles in 284 is 346.2° as
compared with the sum of an almost tetrahedral value of 329.8° for 288.

Comparisons of the O−Sn and Sn−I axial bonds in iodides 284, 296, 304 and 307a con-
taining 4-, 5-, 5- and 6-membered chelate rings, respectively, show that the longer O−Sn
bond lengths are generally associated with the shorter Sn−I distances. The strengthening
of the O → Sn interaction represented by the O−Sn distances and the ΔSn values follows
the order: 307a < 304 < 284 < 296.

The coordination behavior of alcohols 300a–c and acetates 301a–c depends on the
nature of a functional group, the length of the polymethylene chain between the tin
atom and the coordinating function, whether the compound is in the solid state or in
solution and the concentration in solution. In particular, based on multinuclear NMR
studies (selected data are given in Table 51), the C3 and C4 alcohols 300a and 300b
in the noncoordinating solvent, CD₂Cl₂, reveal a five- and six-membered ring structure,
respectively (Scheme 15), resulting from intramolecular HO → Sn coordination.¹¹⁹Sn
NMR spectroscopy resonances in trihalostannyl alcohols and esters are all shifted upward
with respect to nonfunctional alkyltin trichlorides. The effect is stronger with alcohols.

The NMR data for alcohols 300a–c in acetone-d₆ reveal a complex coordination behav-
ior involving five- and six-coordinated species in a fast equilibrium for which HO → Sn
and (CD₃)₂C=O → Sn interactions are in evidence. The crystal structure of alcohol
300c reveals a polymeric structure that arises from significant intermolecular HO → Sn
interactions of 2.356 Å. As a result, the tin atom is five-coordinate and exists in a distorted
TBP geometry with the oxygen and one of the chlorine atoms at the axial positions.
TABLE 49. Selected structural parameters for tin (O–Sn) chelates with hydroxy, alkoxy and acyloxy groups

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chelate ring size</th>
<th>O–Sn (Å)</th>
<th>Sn–Xax (Å)</th>
<th>OSnXax (deg)</th>
<th>OSnCeq (deg)</th>
<th>ΔSn (Å)</th>
<th>Reference</th>
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</thead>
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<td><strong>Tetraorganotin compounds</strong></td>
<td></td>
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<td>287</td>
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<td>2.119</td>
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<td>684</td>
</tr>
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<td>683</td>
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<td>0.48</td>
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</tr>
<tr>
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<td>2.186</td>
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<td>66.6</td>
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<td>707</td>
</tr>
<tr>
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<td>2.139</td>
<td>167.7</td>
<td>66.6</td>
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<td>307a</td>
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<td>2.401</td>
<td>174.0</td>
<td>73.5</td>
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<tr>
<td><strong>Monoorganotin compounds</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>303a</td>
<td>5</td>
<td>2.442</td>
<td>2.401</td>
<td>174.8</td>
<td>76.9</td>
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</tr>
<tr>
<td>301b</td>
<td>i</td>
<td>2.462</td>
<td>2.389</td>
<td>178.7</td>
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<td>0.34</td>
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<td>300c</td>
<td>j</td>
<td>2.356</td>
<td>2.447</td>
<td>174.6</td>
<td>—</td>
<td>0.24</td>
<td>96</td>
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</tbody>
</table>

a Bite angle of the chelate ligand.
b Deviation of the tin atom from the quasi-equatorial plane toward the pseudo-axial carbon atom or the halide atom.
c Intermolecular F···Sn interaction; the O–Sn separation is 5.43 Å.
d Sn–Oeq 2.060 Å.
e Sn–BrEq 2.472 Å.
f The sum of the CSnC ‘equatorial’ angles is 356.6°.
g Six-coordinated tin.
h For the second (H2)O–Sn–Cl fragment: O–Sn, 2.292 Å; Sn–Cl, 2.401 Å; OSnCl, 174.7°; the remaining Sn–Cl distance is 2.401 Å.
i Cyclodimer with carbonyl coordination; the remaining Sn–Cl distances are 2.324 and 2.333 Å.
j A polymeric structure with intermolecular HO → Sn interaction; the remaining Sn–Cl distances are 2.310 and 2.343 Å.
TABLE 50. Selected structural parameters for $\alpha$-methoxyarylstannanes and related compounds

<table>
<thead>
<tr>
<th>Compound $^a$</th>
<th>Chelate ring size</th>
<th>O–Sn (Å)</th>
<th>Sn–X$_{\text{ax}}$ (Å)</th>
<th>OSnX$_{\text{ax}}$ (deg)</th>
<th>OSnC$_{\text{b}}$ (deg)</th>
<th>$\beta^c$ (deg)</th>
<th>$\Delta$Sn$^d$ (Å)</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>Tetraorganotin compounds</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>289$^{1,e,f}$</td>
<td>4</td>
<td>3.045</td>
<td>2.143</td>
<td>161.3</td>
<td>49.7</td>
<td>117.9</td>
<td>0.71</td>
<td>687</td>
</tr>
<tr>
<td>289$^{1,e,f}$</td>
<td>4</td>
<td>3.043</td>
<td>2.139</td>
<td>158.2</td>
<td>49.3</td>
<td>119.1</td>
<td>0.71</td>
<td>688</td>
</tr>
<tr>
<td>290$^2$</td>
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<td>2.158$^g$</td>
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<td>49.1</td>
<td>118.0</td>
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<td>317$^{4,i}$</td>
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<td>3.023</td>
<td>2.122</td>
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<td>—</td>
<td>0.65</td>
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<tr>
<td>327$^3$</td>
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<td>3.241</td>
<td>2.164</td>
<td>164.1</td>
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<td>—</td>
<td>0.72</td>
<td>687</td>
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<td></td>
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<td></td>
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<td>4.406$^j$</td>
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<td>Triorganotin compounds</td>
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<td></td>
<td>4.329$^j$</td>
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<td>Diorganotin compounds</td>
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<td>2.481</td>
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<td>114.2</td>
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</tr>
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<td>292b$^b$</td>
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<td>2.914</td>
<td>2.683</td>
<td>158.0</td>
<td>51.9</td>
<td>114.9</td>
<td>0.63</td>
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<td>320b$^{5,i}$</td>
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<td>2.630</td>
<td>2.526</td>
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<td>67.4</td>
<td>—</td>
<td>0.494</td>
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<tr>
<td>320c$^{5,i}$</td>
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<td>2.736</td>
<td>162.9</td>
<td>67.4</td>
<td>—</td>
<td>0.494</td>
<td>239</td>
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<td></td>
<td>4.365$^j$</td>
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<td>Monoorganotin compounds</td>
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<td>2.316$^l$</td>
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<td>53.2</td>
<td>112.4</td>
<td>0.60</td>
<td>691</td>
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<td>2.848</td>
<td>2.293$^m$</td>
<td>168.7</td>
<td>53.0</td>
<td>113.0</td>
<td>0.67</td>
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<td></td>
<td></td>
<td></td>
<td>3.201$^j$</td>
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<tr>
<td>293$^5$</td>
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<td>2.884</td>
<td>2.463$^n$</td>
<td>162.1</td>
<td>52.3</td>
<td>114.3</td>
<td>0.67</td>
<td>686</td>
</tr>
<tr>
<td>326a$^{7,f}$</td>
<td>5</td>
<td>2.436$^o$</td>
<td>1.960$^o$</td>
<td>166.5$^o$</td>
<td>71.1$^o$</td>
<td>—</td>
<td>—</td>
<td>715</td>
</tr>
<tr>
<td>326b$^{6,e,f,i}$</td>
<td>5</td>
<td>2.596$^o$</td>
<td>2.387$^o$</td>
<td>172.2$^o$</td>
<td>66.5$^o$</td>
<td>—</td>
<td>—</td>
<td>715</td>
</tr>
<tr>
<td>326c$^{7,f,i}$</td>
<td>5</td>
<td>2.653$^o$</td>
<td>2.528$^o$</td>
<td>173.0$^o$</td>
<td>65.2$^o$</td>
<td>—</td>
<td>—</td>
<td>715</td>
</tr>
</tbody>
</table>

$^a$Types of environments of the atoms: $^1$tetrahedral; $^2$two capped tetrahedral (4 + 2 tetrahedral); $^3$four capped tetrahedral (4 + 4 tetrahedral); $^4$one capped tetrahedral (4 + 1 tetrahedral); $^5$distorted trigonal-bipyramidal; $^6$distorted octahedral; $^7$seven-coordinated.

$^b$Bite angle of chelate ligand.

$^c$Exocyclic SnCipsoO(Me).

$^d$Deviation of the tin atom from the quasi-equatorial plane toward the pseudo-axial carbon atom or the halide atom.

$^e$Two independent molecules in the unit cell.

$^f$Given parameters are for the SnCCO fragment with the shorter O⋯Sn separation.

$^g$Sn–C(Ph).

$^h$Sn–C($\alpha$-An).

$^i$Only one of the MeO groups in the ligand interacts with the tin center.

$^j$Sn⋯O(2) separation.

$^k$Sn–X$_{\text{eq}}$.

$^l$Remaining Sn–Cl bond lengths are 2.317 and 2.276 Å.

$^m$Remaining Sn–Cl bond lengths are 2.311 and 2.303 Å.

$^n$Remaining Sn–Br bond lengths are 2.449 and 2.450 Å.

$^o$Average value.
TABLE 51. Comparison of solid-state $^{117}$Sn NMR, and $^{119}$Sn and $^{17}$O solution-state NMR data in C$_6$D$_6$ for alcohols Cl$_3$Sn$(\text{CH}_2)_n$OH$^{96}$ and the Cl$_3$Sn$(\text{CH}_2)_n$OAc esters ($n = 3–5$)$^{110}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$($^{117}$Sn), (ppm)$^a$</th>
<th>$\delta$($^{119}$Sn), (ppm)$^b,c$</th>
<th>$\delta$($^{119}$Sn), (ppm)$^d,e$</th>
<th>$\delta$($^{119}$Sn), (ppm)$^f$</th>
<th>$\delta$(C=O), (ppm)$^b$</th>
<th>$\delta$($^{17}$O−R), (ppm)$^b,g$</th>
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</thead>
<tbody>
<tr>
<td>300a</td>
<td>−174</td>
<td>−137</td>
<td>−131</td>
<td>−112</td>
<td>—</td>
<td>17.4</td>
</tr>
<tr>
<td>300b</td>
<td>−224</td>
<td>−172</td>
<td>−174</td>
<td>−147</td>
<td>$^b$</td>
<td>34.7</td>
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<td>300c</td>
<td>−230</td>
<td>$^b$</td>
<td>$^b$</td>
<td>$^b$</td>
<td>$^b$</td>
<td>$^b$</td>
</tr>
<tr>
<td>301a</td>
<td>−80</td>
<td>−42</td>
<td>−32</td>
<td>−38</td>
<td>367.5</td>
<td>162.6$^i$</td>
</tr>
<tr>
<td>301b</td>
<td>−168</td>
<td>−35</td>
<td>−4</td>
<td>−47</td>
<td>359.3</td>
<td>166.5</td>
</tr>
<tr>
<td>301c</td>
<td>−168</td>
<td>−33</td>
<td>−2</td>
<td>−67</td>
<td>357.4</td>
<td>167.8</td>
</tr>
</tbody>
</table>

$^a$Solid state CP-MAS.

$^b$100 or 10 mg/0.5 mL. in C$_6$D$_6$.

$^c$119Sn chemical shifts of reference compounds: HexSnCl$_3$, −3, BuSnCl$_3$, −2.

$^d$10 mg/0.5 mL.

$^e$119Sn chemical shifts of reference compounds: HexSnCl$_3$, +5, BuSnCl$_3$, +1.

$^f$Concentrated solution in CDCl$_3$.$^{433}$

$^g$With respect to water.

$^h$Insoluble.

$^i$17O chemical shifts of reference compounds: Me$(\text{CH}_2)_3$OAc, 363.6, 165.2 (C$_6$D$_6$); butanol (CD$_2$Cl$_2$)1.0.

### SCHEME 15. Schematic representation of solid state and solution structure of alcohols 300a,b and acetates 301a,b

Unlike the alcohols 300a–c, the acetates 301a–c in C$_6$D$_6$ solution display fast equilibrium between a monomer with intramolecular coordination and an oligomer with intermolecular coordination$^{110}$. 301b$^{714}$ is a cyclodimer in the solid state (Scheme 15) with coordination from the carbonyl oxygen to the tin. During dynamic equilibrium in solution, the monomeric form of ester 301a with the methoxy oxygen coordinating to the tin is predominant, independent of the concentration. In contrast, for esters 301b and 301c the oligomeric form predominates increasingly upon concentration increase$^{716}$. Note that in the case of acetate Ph$_3$Sn$(\text{CH}_2)_3$OAc, the O−Sn interaction is absent in the solid state$^{717}$.

The chloride 299b and the related six-membered carboxylic tin species, in which an intramolecular O → Sn interaction stabilizes the 1,3-diaxial conformations$^{696}$, were discussed in detail in a review.$^{636}$ The corresponding trimethyltin derivatives in the absence of an O → Sn coordination exist predominantly as the 1,3-diequatorial conformers. Moreover, an X-ray structure determination of the fluoride 299a, the analogue of 299b, which
is monomeric in CHCl₃ solution and adopts a 1,3-diaxial conformation, reveals a fluorine-bridged polymeric structure containing a cyclohexyl ring with 1,3-diequatorial stannyl and benzyloxy groups.

An X-ray structure determination of IPhSn(CH₂OR)₂ 307a reveals that only one of the sugar moieties acts as a C₂O-bidentate ligand to form a six-membered chelate ring via the pyranose ring oxygen (Scheme 16)²⁶⁷. The tin center is five-coordinated and has a TBP geometry with I and O in the axial positions (Table 49). As indicated by the solid state and solution $\delta^{119}$Sn values (−177.8 and −130.7 ppm, respectively), the solid-state structure does not survive on dissolution. The $\delta^{119}$Sn and $^1J(^{119}\text{Sn}−^{13}\text{C})$ values for 305 and 306 are also as expected for a four-coordinate species, i.e. in solution the sugar units remain monodentate²⁶⁷.

As in alkoxide 297, in the sulfur derivatives ClPh₂Sn(CH₂)₃Stol-p (309)⁷⁰⁴ and (ClMe₂SnCH₂CH₂CH₂)₂S (328)⁷⁰⁵, the tin atom has a distorted TBP coordination geometry, with the S and Cl atoms in the axial positions (Table 49). The S−Sn distances
of 3.19 Å for 309 and 3.10 and 3.12 Å for 328 lie between the sum of the covalent radii for Sn and S (2.44 Å) and the sum of their van der Waals radii (3.9 Å). The weaker S–Sn interaction in 309 than in 328 reflects the weaker donor ability of alkyl aryl sulfides compared with dialkyl sulfides. According to Dräger535, the formal bond order for the S → Sn coordination bond in 309 is 0.22, while an analogous calculation for ClMe2Sn(CH3)2PPhBu−r294 provides a value of 0.44 for the P → Sn coordination bond compared to values of 0.6 to 0.7 for triorganotin halide complexes involving an intra- or intermolecular N → Sn or O → Sn coordination. The displacement of the Sn atom from the equatorial plane in the direction away from S is 0.27 Å, which represents a 63% distortion toward a TBP array. This distortion is slightly greater as compared with 297 (Table 49). By contrast, in triphenyl-(2-(p-tolylthio)ethyl)tin718 and (4-chloro-3-(2-nitrophenylthio)butyl)triphenylstannane719, intramolecular S → Sn interactions are absent, at an S···Sn separation of about 4.8 Å.

In the crystals of triarylstannylvinyl compounds 310a–c and 311 the tin atom exhibits a distorted tetrahedral SnC₄ geometry toward TBP as a consequence of a close intramolecular contact with the hydroxyl oxygen atom of 2.73–2.77 Å. A distorted TBP geometry is found in mono- and dihalides 312–314, in which significant O → Sn interactions are noted (2.41–2.50 Å) (Table 49). In particular, the O–Sn bond in 310c is shorter than that in 311, and the O → Sn interaction in 313 is significantly stronger than those in 314 and especially in 312, in parallel with the Lewis acidity of the Sn atoms in these compounds. Thus, the X-ray crystallographic data allow one to place the corresponding tin entities in the following order of their Lewis acidity: (p-Tol)3Sn < Ph3Sn ≪ IPh2Sn < Br2(p-Tol)Sn < Cl(p-Tol)2Sn.

The solution ¹H, ¹³C and ¹¹⁹Sn NMR spectral data for all compounds of the types 310 and 311 are consistent with their expected more or less distorted tetrahedral or TBP structures and with the available X-ray data discussed above711. The systematic high-frequency shift of the observed ¹¹⁹Sn resonance for all p-tolyl compounds relative to that for the corresponding phenyl compounds is noteworthy. In addition, the ¹J(¹³C–¹¹⁹Sn) coupling constants decrease to a comparable extent in the sequence Cl > Br > I for both mono- and dihalides, reflecting the decreasing apicophilicity on going from chloride to iodide.

The intramolecular O···Sn separations in (o-An)ₙSnX₄₋ₙ (n = 1–4, X = Br, I) are in the range 2.8–3.1 Å and generally decrease with increasing Lewis acidity of the tin center. The consequences of the O···Sn interactions are an increase in the coordination number of tin in the O-methoxyarylstannanes and distortions of their geometries from tetrahedral toward TBP or octahedral (Table 50). However, given the small C_pseSnO(Me) angles of about 50°, the geometries are far removed from the ideal TBP or octahedral geometries. In particular, the ‘axial-Sn-axial’ angles in O-AnSnBr₃ (293)686, 5-Me-2-MeOC₆H₃SnCl₃ (294)691 and 2,6-(MeO)₂C₆H₃SnCl₃ (295)692 of 162.1, 161.8 and 168.7°, respectively, are somewhat removed from the ideal 180° expected for a TBP structure. Furthermore, the sum of the three ‘equatorial angles’ of 333.6° in 293 is closer to the value expected for a tetrahedral (328.5°) than for a TBP geometry (360°)686.

A detailed analysis of the changes in the exocyclic angles α, β, γ and δ of the o-anisylstannyl fragment 286, as indications of the O···Sn interactions in the o-anisylstannanes, is given elsewhere686. The most significant variations are for the angle β. The decreasing value of β, i.e. as the Sn center progressively leans toward the oxygen, indicates a more positive O–Sn interaction (Table 50).

X-ray crystallography reveals distorted TBP geometries for the diorganotin derivatives 320a–c and 321, owing to the presence of significant O → Sn interactions that are in the range from 2.56 Å for 320a to 2.99 Å for 321. One of the oxygen atoms and one of the halogen or SPh moieties define the axial angle in this description, and the tin atom lies
bonyl group, a family of so-called ‘estertin’ compounds, i.e. species containing the bonyl group, a family of so-called ‘estertin’ compounds, i.e. species containing the

LSnPhI\(_2\) \((317, 318)\) NMR data (Table 52), compounds LSnPhBr\(_2\) \((320a)\) and LSnPhCl\(_2\) \((320b)\) geometry is found in the tetraorganotin derivative \(317\), with O···Sn separations of 3.02 and 4.40 Å as compared to the sum of the van der Waals radii of 3.5 Å for these atoms and the ΔSn value of 0.65 Å. For \((\omega\text{-AnCH}_2\text{)}\text{I}_4\) Sn \((327)\) (Table 50) a significant distortion of the tetrahedral coordination around the tin toward the TBP geometry does not take place (the O···Sn separation is 3.241 Å and ΔSn = 0.72 Å)\(^{687}\).

Thus, the magnitudes of the O→Sn interactions correlate with the Lewis acidity of the tin atoms in the X\(_2\)PhSn entities, i.e. Cl\(_2\)PhSn > Br\(_2\)PhSn > I\(_2\)PhSn > (PhS)\(_2\)PhSn\(^{239}\).

NMR spectroscopy indicates a similar correlation in solution. As evidenced by \(^{119}\)Sn NMR data (Table 52), compounds \(317, 318\) and \(321\) are essentially four-coordinate between \(+30\) and \(-100^\circ\)C. In compounds \(320a\)–\(c\), \(322, 323a, 323b\) and \(325\) both four- and five-coordinate tin species exist simultaneously at low temperature. At higher temperatures, an average of these two coordination states is observed.

The positions of these equilibria are affected not only by the Lewis acidity at tin, but also by the ring size. Unlike the five-membered ring analogues \(320a, 320b\) and \(324\), equilibria involving compounds \(322, 323a, 323b\) and \(325\) containing six-membered rings are fast on the NMR time scale at all temperatures measured and only averaged signals were observed. Finally, note that for neither series (L or CH\(_2\)L, Scheme 14) was there any evidence for intramolecular coordination of both methoxy groups to tin\(^{239}\).

\textit{b. Carbonyl and related groups as donor centers.} Among compounds with a carbonyl group, a family of so-called ‘estertin’ compounds, i.e. species containing the

<table>
<thead>
<tr>
<th>Compound</th>
<th>(T(\circ)C)</th>
<th>(\delta^{(119})Sn) (ppm)</th>
<th>Compound</th>
<th>(T(\circ)C)</th>
<th>(\delta^{(119})Sn) (ppm)</th>
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<td>+25</td>
<td>-114.6</td>
<td>LCH(_2)SnPh(_3) ((318))</td>
<td>+25</td>
<td>-109.8</td>
</tr>
<tr>
<td></td>
<td>-80</td>
<td>-114.0</td>
<td></td>
<td>-80</td>
<td>-105.3</td>
</tr>
<tr>
<td>LSnPhCl(_2) ((320a))</td>
<td>+100</td>
<td>-83.4(^a)</td>
<td>LCH(_2)SnPhCl(_2) ((322))</td>
<td>+25</td>
<td>-4.7</td>
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<tr>
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<td></td>
<td>-25</td>
<td>-69.5, -122.0</td>
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<td>-40.7</td>
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<td>-71, -125.5</td>
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<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>-80</td>
<td>-132.4</td>
<td></td>
<td>—</td>
<td>—</td>
</tr>
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<td>LSnPhBr(_2) ((320b))</td>
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<td>-82.7(^a)</td>
<td>LCH(_2)SnPhBr(_2) ((323a))</td>
<td>+25</td>
<td>-26.4</td>
</tr>
<tr>
<td></td>
<td>+25</td>
<td>no signal</td>
<td></td>
<td>-55</td>
<td>-53.0</td>
</tr>
<tr>
<td></td>
<td>-25</td>
<td>-60.2, -148.2</td>
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<td>-80</td>
<td>-64.0</td>
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<tr>
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<tr>
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<td>-80</td>
<td>-63.8, -150.7</td>
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<tr>
<td>LSnPhI(_2) ((320c))</td>
<td>+100</td>
<td>-153.9(^a)</td>
<td>LCH(_2)SnPhI(_2) ((323b))</td>
<td>+25</td>
<td>-163.3</td>
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<td></td>
<td>+75</td>
<td>-146.0(^a)</td>
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<td>-141.2</td>
</tr>
<tr>
<td></td>
<td>+25</td>
<td>-129.3(^a)</td>
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<tr>
<td></td>
<td>-90</td>
<td>-91.3(^a)</td>
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<td>—</td>
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<tr>
<td>LSnPh(SPh)(_2) ((321))</td>
<td>+25</td>
<td>12.0</td>
<td>LCH(_2)SnCl(_3) ((325))</td>
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<td>-107.2</td>
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<td>—</td>
<td>—</td>
<td></td>
<td>-80</td>
<td>-154.3</td>
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</tbody>
</table>

\(^{a}\)In toluene.
ROOCCH₂CH₂Sn moiety, has been most extensively studied. They are of particular interest due to both their use as precursors of potentially valuable organotin-based polyvinyl chloride stabilizers and the ability of the ROOCCH₂CH₂ unit to act as a chelating ligand by utilizing the carbonyl oxygen as an additional donor center. The main types of estertin compounds which are presented in Scheme 17 include halides (pseudohalides), namely trichlorides 329a, 329b, 330 and 331, adducts of trichlorides with O-donors 332a, 332b, 332c and 332d, the phenol and β-naphthol derivatives, 333 and 334, the itaconic species Cl₂SnCH₂CH(COOMe)₂CH₂COOME (335), dimeric hydroxide 336 with hydroxo-bridging, dichlorides 337a and 337b, with potentially bidentate dimethylthiocarbamate ligand (S₂CNMe₂ = DMT), dihalides (dipseudohalides) X₂Sn[CH₂CH₂COOME]₂ (338a–c X = Cl₇₂₂,₇₃₂, I₃₄⁷ and NCS₃₄⁷), including mixed chloride–bromide ClBrSn(CH₂CH₂COOME)₂ (339)₃₄⁷, the N-acetylaminomalonial ester derivative Br₂MeSnCH₂C(COOEt)₂NHCOMe (340), the dichloride and diisothiocyanate X₂Sn[HB(Pz)₃] (CH₂)₂COOME (341a, X = Cl, and 341b, X = NCS) where HB(Pz)₃ is the tridentate hydrido-tris(pyrazol-1-ylborato) ligand, as well as mono-halides, including iodide IP₇₂₃H₂Sn(CH₂)₂COOME (342)₇₃₅, the alane derivatives Cl₂SnCH₂CH(N=CPh₂)COOEt (343)₇₅₆ and Cl₂Ph₂SnCH₂CH(COOEt)NHCOMe (344)₇₃₇, the monochlorohalides ClSn(DMTC)((CH₂)₂COOME)₂ (345)₇₃₈ and ClₙSn(DMTC)₂(CH₂)₂COOME (346)₇₃₉ with DMTC ligand, ClₙSn[H₂B(Pz)₂](CH₂)₂COOME (347) with the bidentate dihydro-bis(pyrazol-1-ylborato) (BTB) ligand, the 8-hydroxyquinoline (8-HO-Qu) derivative ClₙSn(8-O-Qu)(CH₂)₂COOME (348)₇₄⁰ and the imine ClₙSn(L)(CH₂)₃COOME (349) containing the negative bivalent tridentate O,N,O-coordinating ligand L (LH₂ = N-(2-hydroxyphenyl)salicylaldimine)₇₄¹. Furthermore, the unsaturated species 350a–d have been described. In addition to the structures shown, in part, in scheme 17, hexa-coordinated species are given in Section X.B. The structures were established in these cases by X-ray crystallography. The structures of other representatives of estertin and related compounds with halide as a ligand were suggested only on the basis of spectral data. Estertins, in particular, adducts of trichlorides with O-donors and the 1 : 1 adducts with bidentate donors, have been prepared. Additionally, the reaction of trichlorides 329a and 335 with the DMTC ligand (taken as Me₂NCSNa·2H₂O) in appropriate molar ratios affording products of the type Cl₃–ₙ(DMT)nSn(CH₂)₂COOME (n = 1–3) including the dichloride 337a or 337b were carried out. The reaction of 337a with N-(2-hydroxyphenyl)salicylaldimine...
in the presence of Et$_3$N gave the monochloride 349. The latter reacted with the various alcohols ROH (e.g. R = Et, Pr, i-Pr, All, ClCH$_2$CH$_2$) yielding the appropriate transesterification products. The treatment of esterin trichloride 335 with 1,2-dianilinoethane gave a partial hydrolysis product 336 instead of the amine adduct of esterin $^{182}$.

\[(\text{329a) } n = 1, R = \text{Me} \quad \text{(329b) } n = 1, R = \text{i-Pr} \quad \text{(330) } n = 2, R = \text{Et} \quad \text{(331)}\]

\[(\text{332a) } D = \text{Ph}_3\text{PO}, R = \text{All}, R' = \text{H} \quad \text{(332b) } D = \text{Ph}_3\text{PO}, R = \text{Bu}, R' = \text{Me} \quad \text{(332c) } D = \text{Bu}_2\text{SO}, R = \text{Et}, R' = \text{H} \quad \text{(332d) } D = \text{Bz}_2\text{SO}, R = \text{Et}, R' = \text{H} \quad \text{(333)}\]

\[(\text{334) } R = \text{Bu}, R' = 1-(p-\text{TolN}=CH)\text{Naph-2} \quad \text{(336) } R = \text{CH}_2\text{COOMe} \quad \text{(337a) } R = \text{H} \quad \text{(337b) } R = \text{CH}_2\text{COOMe} \quad \text{(338a) } X = \text{Cl}, R = \text{H} \quad \text{(338b) } X = \text{I}, R = \text{H} \quad \text{(338c) } X = \text{NCS}, R = \text{H} \quad \text{(350a) } X = \text{F} \quad \text{(350b) } X = \text{Cl} \quad \text{(350c) } X = \text{Br} \quad \text{(350d) } X = \text{I} \quad \text{(350e) } X = \text{Me} \quad \text{350} = \text{XMe}_2\text{SnCH}^\text{"D"}\text{COOMe}\]

SCHEME 17. Estertin compounds containing halide or pseudohalide as ligand
Reaction of dithiocarbamatoestertin dichloride 337a with sodium sulfide resulted in the dimeric species 351, whereas the cognate reaction of dichloride 338a gave the trimeric complex 352.

According to equation 20 (Section IV.B.2.b), the reaction of 329a with the appropriate zinc salt gave the anionic derivatives 111a–c, 112c and 112d.

Another synthetic way to organotins involves the halodemetalation reactions of the related tetraorganotin derivatives by the action of halogens, Me2SnCl2 or SnCl4 as realized in the case of halides 330–345, 342, 735 and 350b–d. Treatment of 350d with potassium fluoride in acetone afforded fluoride 350a.

Transesterification reactions of 2-alkoxycarbonylethyltin trichlorides and their adducts with neutral donors proceed readily. This is attributed to the intramolecular Lewis catalysis by the electrophilic SnCl group owing to the coordination of the ester carbonyl group to the tin atom, C=O → Sn, which decreases the electronic density at the carbonyl carbon atom.

Details of the structures of a variety of estertin compounds in the solid state are given in Table 53. Complexes with either mono- or bidentate ROOCCH2CH2 groups are characterized by a ν(C=O) value between those for a coordinated and noncoordinated ester group (1670–1680 and 1730–1740 cm⁻¹, respectively). With the appropriate number of donor atoms, estertins exhibit a tendency to become six-coordinated as evident, in part, in the examples of adducts 332a–d and on going from trichlorides 329a and 329b to dichlorides 338a–d. In the cases of 341a and 341b, C6H5Sn(DMT)2(OMe)(CH2)2 (345) and Sn(DMT)2(CH2CH2COOMe)2 (356), the coordination number becomes even higher at seven if weak interactions are also considered. This value is somewhat outside the limit normally taken for hypervalent O–Sn bonding (ca 2.9–3.0 Å). Without regard for such interactions, the tin atom is tetracoordinate in trimer 352 and five-coordinate in dimer 351.

In the solid state, the Sn atom in the itaconic species 335 adopts a distorted octahedral arrangement with the five- and six-membered fused rings via the two carbonyl oxygen-to-tin coordinations. On the basis of IR and multinuclear NMR spectroscopy data it was suggested that one carbonyl group presumably involved in the six-membered chelate is released from the tin atom, which results in a five-coordinate tin atom in solution in both coordinating and noncoordinating solvents.

The bite angle of the RO2CCH2CH2 group in estertins correlates with the O–Sn bond length. The correlation applies not only for complexes in which the estertin group is clearly chelating, but for compounds with the O···Sn separation of 3.0–4.0 Å, too. Using this criterion, a very weak but definite ester-to-tin interaction for estertins with the O–Sn distance up to ca 4.0 Å can be proposed.

The crystal structure determinations and spectral data show that the carbonyl oxygen in the 1 : 1 adducts of trichlorides of the type 329 (R = Alk, Ar) with monodentate donors like pyridine is coordinated intramolecularly to tin. However, the intramolecular coordination can be broken in the 1 : 2 adducts with monodentate donors and with 1 : 1 bidentate donors like bipyridine.

Some crystallographic data for estertins containing pentacoordinate tin atom owing to O–Sn interaction are collected in Table 54. In these compounds the tin atom has a near TBP coordination geometry with the carbon atom and the two chlorines or the three carbon atoms at equatorial positions and the halogen and oxygen atoms at axial sites. In general, the goodness of a TBP array at tin is defined by the deviation of the Sn from the equatorial plane toward the halide atom (∆Sn), and by the difference (∆Σ(θ)) between the sums of the equatorial and axial angles. For the two series of chelates, trichlorides 329a–c and monohalides 350a–d, the values are rather close (∆Sn, ca 0.25–0.30 Å; ∆Σ(θ), 55–66°). In 350a–d, the lengthening of the Sn–Hal bond in relation to the
### Table 53. Some structural features and selected structural data for solid esterins and related compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Coordination No. of Sn</th>
<th>C=O</th>
<th>O–Sn (Å)</th>
<th>OSnC (deg)</th>
<th>ν(C=O) (cm⁻¹)</th>
<th>Ref.</th>
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</thead>
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<tr>
<td>Cl₃Sn(CH₂)₂COOMe (329a)</td>
<td>5</td>
<td>complexed</td>
<td>2.348</td>
<td>77.2</td>
<td>1658</td>
<td>722</td>
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<tr>
<td>Cl₃Sn(CH₂)₂COOPr-i (329b)</td>
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<td>complexed</td>
<td>2.338</td>
<td>78.0</td>
<td>1650</td>
<td>723</td>
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<tr>
<td>Cl₃Sn(CH₂)₂COOEt (330)</td>
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<td>complexed</td>
<td>2.405</td>
<td>82.6</td>
<td>1645</td>
<td>724</td>
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<tr>
<td>Cl₃Sn(CH₂)₂CH₂OCO (331)</td>
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<td>complexed</td>
<td>2.482</td>
<td>75.7</td>
<td>—</td>
<td>725</td>
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<tr>
<td>Cl₃Sn(CH₂)₂COOAll - Ph₂PO (332a)</td>
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<td>complexed</td>
<td>2.412</td>
<td>76.4</td>
<td>—</td>
<td>725</td>
</tr>
<tr>
<td>Cl₃Sn(CH₂)₂CHMeCOOBut - Ph₂PO (332b)</td>
<td>6</td>
<td>complexed</td>
<td>2.356</td>
<td>75.9</td>
<td>—</td>
<td>725</td>
</tr>
<tr>
<td>Cl₃Sn(CH₂)₂COOEt - Bu₂SO (332c)</td>
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<td>complexed</td>
<td>2.351</td>
<td>77.0</td>
<td>1654</td>
<td>726</td>
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<td>2.343</td>
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<td>—</td>
<td>727</td>
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<td>—</td>
<td>—</td>
<td>—</td>
<td>1741</td>
</tr>
<tr>
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<td>2.390</td>
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<td>1666</td>
<td>747</td>
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<tr>
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<td>1657</td>
<td>182</td>
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<td>Cl₂Sn(DMTC)(CH₂)₂COOMe(337a)</td>
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<td>one complexed</td>
<td>2.448</td>
<td>75.1</td>
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<td>182</td>
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<tr>
<td>COOMe (337)d</td>
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<tr>
<td>Br₂MeSnCH₂Cl(COOME)₂(340)</td>
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<tr>
<td>Cl₂Sn(H₂B(Pz)₂)(CH₂)₂COOMe(347)</td>
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<td>2.550</td>
<td>73.5</td>
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<td>735</td>
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<td>FMe₂SnCHDCOOMe (350a)</td>
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<td>2.607</td>
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<tr>
<td>ClMe₂SnCHDCOOMe (350b)</td>
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<td>complexed</td>
<td>2.470</td>
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<tr>
<td>BrMe₂SnCHDCOOMe (350c)</td>
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<td>complexed</td>
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<td>ClMe₂SnCH(N=CPh₂)</td>
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<td>Cl₂Sn(8-O-Qu)(CH₂)₂COOMe(347)</td>
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<td>one complexed</td>
<td>2.847</td>
<td>65.7</td>
<td>1712</td>
<td>740</td>
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<td>(348)</td>
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<tr>
<td>Cl₂Sn(L)CH₂CH₂COOMe (349)</td>
<td>6</td>
<td>complexed</td>
<td>2.356</td>
<td>78.1</td>
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<td>741</td>
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<tr>
<td>[(DMTC)Sn(CH₂)₂COOMe]₂(351)</td>
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<td>complexed</td>
<td>3.197</td>
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<td>[Sn(CH₂)₂COOMe]₂S(352)</td>
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<td>one complexed</td>
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<tr>
<td>Sn(8-O-Qu)₂(CH₂)₂COOMe(353)</td>
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<td>complexed</td>
<td>3.414</td>
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### TABLE 53. (continued)

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<th>Compound</th>
<th>Coordination No. of Sn</th>
<th>C=O</th>
<th>O−Sn (Å)</th>
<th>OSnC (deg)</th>
<th>ν(C=O) (cm⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>Sn(DMTC)<a href="CH%E2%82%82">(SCH₂CH₂)₂O</a>₂</td>
<td>6</td>
<td>uncomplexed</td>
<td>5.006</td>
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<td>COOMe (354)</td>
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<td>Sn(DMTC)[[(OCH₂CH₂)₂NMe]</td>
<td>6</td>
<td>uncomplexed</td>
<td>4.978</td>
<td>—</td>
<td>1717</td>
<td>751</td>
</tr>
<tr>
<td>(CH₂)₂COOEt (355)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn(DMTC)₂(CH₂CH₂COOMe)₂ (356)</td>
<td>7</td>
<td>one complexed</td>
<td>2.751</td>
<td>69.8</td>
<td>1693</td>
<td>752</td>
</tr>
<tr>
<td>Sn(DMIT)2(CH₂CH₂COOMe)₂ (357)</td>
<td>6</td>
<td>both complexed</td>
<td>2.628</td>
<td>72.7</td>
<td>1674</td>
<td>349</td>
</tr>
<tr>
<td>[Sn(DMIO)₂(CH₂)₂COOMe]⁻NEt₄⁺</td>
<td>6</td>
<td>complexed</td>
<td>3.111</td>
<td>60.8</td>
<td>1677</td>
<td>347</td>
</tr>
<tr>
<td>(111a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Sn(DMIT)₂(CH₂)₂COOMe]⁻NEt₄⁺</td>
<td>5</td>
<td>uncomplexed</td>
<td>4.837</td>
<td>—</td>
<td>1731</td>
<td>349</td>
</tr>
<tr>
<td>(112c)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Sn(DMIT)₂(CH₂)₂COOMe]⁻</td>
<td>5</td>
<td>complexed</td>
<td>3.371</td>
<td>55.6</td>
<td>1720</td>
<td>349</td>
</tr>
<tr>
<td>[MeNC₅H₄Me-4]⁺ (112d)</td>
<td>6</td>
<td>complexed</td>
<td>3.371</td>
<td>55.6</td>
<td>1720</td>
<td>349</td>
</tr>
</tbody>
</table>

* a Bite angle of chelate ligand.  
* b Additional data: ClMe₂SnCH₂CH[COPh]COOEt, 1629, 1718; ClMe₂SnCH₂CH[COOEt]₂, 1691, 1736; ClMe₂SnCH₂CH[P(O)(OPr-i)Ph]COOPr-i, 1726; ClMe₂SnCH₂CH[PO(OPr-i)₂]COOPr-i, 1740.  
* c Six-membered chelate ring.  
* d Given data for one ROOCCH₂CH₂ moiety.  
* e Anisobidentate dithiocarbamate ligand.  
* f Five-membered chelate ring.  
* g Without regard for weak interactions.  
* h For a description of “D” in the ligand XMe₂SnCH₂“D”COOMe see Scheme 17 below compounds 350a–e.  
* i Bridging F.  
* j With regard to weak interactions.  
* k Bidentate S₂CNMe₂.  
* l Bridging S.

Single bond distances increases in the order: F ≪ Cl < Br < I. The coordinating O → Sn distance is in the order: F > Cl = Br > I with the shortest O−Sn distances for 350d. A detailed analysis of the geometrical variables in 350a–d suggests that pπ−dπ back donation from the halogen to the tin in 350a–d could invert the order of tin Lewis acidities expected on the grounds of simple halogen electronegativity. 350e is the first tetraorganotin compound with a coordinative tin–oxygen bond for which the structure was unambiguously established by X-ray crystallography.  

Comparison of the O → Sn bond lengths in trichlorides 329a and 330 reveals a longer coordinate bond in 330 (2.347 and 2.405 Å, respectively). This indicates a stronger coordination in the five-membered chelate 329a than in the six-membered chelate ring of 330. From the formation constants for adducts of 329a and 330 with pyridine, aniline and quinoline it is seen that this is also true in solution.  

The ¹¹⁹Sn NMR resonances of 330a–d exhibit an upfield shift about 100 ppm with regard to values expected for uncoordinated halides, indicating pentacoordination of the tin atom in solution.  

Comparison of the intramolecular coordination behaviors of (PhC≡C)₃Sn(CH₂)₂ COOMe (358) and 329a was carried out, using multinuclear NMR, including ¹H−¹¹⁹Sn-HMQC spectroscopy. While 329a exhibits an intramolecular carbonyl...
**TABLE 54.** Selected structural parameters for estertin and related compounds containing a penta-coordinate tin atom due to O → Sn interaction

<table>
<thead>
<tr>
<th>Compound</th>
<th>O–Sn (Å)</th>
<th>Sn–Halax (Å)</th>
<th>OSnHalax (deg)</th>
<th>ΔSn (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$_3$Sn(CH$_2$)$_2$COOMe (329a)$^b$</td>
<td>2.348</td>
<td>2.358</td>
<td>176.7</td>
<td>0.32 (59)</td>
<td>722</td>
</tr>
<tr>
<td>Cl$_3$Sn(CH$_2$)$_2$COOPr-$i$ (329b)$^c$</td>
<td>2.338</td>
<td>2.390</td>
<td>175.3</td>
<td>0.30 (62)</td>
<td>723</td>
</tr>
<tr>
<td>Cl$_3$SnCH$_2$CH$_2$CH$_2$OCO (331)</td>
<td>2.482</td>
<td>2.342</td>
<td>176.4</td>
<td>0.32 (59)</td>
<td>735</td>
</tr>
<tr>
<td>IP$_2$Sn(CH$_2$)$_2$COOMe (342)</td>
<td>2.550</td>
<td>2.811</td>
<td>170.5</td>
<td>0.30 (59)</td>
<td>722</td>
</tr>
<tr>
<td>FMe$_2$SnCHDCOOOMe (350a)$^e,f$</td>
<td>2.52</td>
<td>1.974</td>
<td>165.4</td>
<td>0.33 (56)</td>
<td>674</td>
</tr>
<tr>
<td>ClMe$_2$SnCHDCOOOMe (350b)$^f$</td>
<td>2.470</td>
<td>2.432</td>
<td>172.1</td>
<td>0.34 (55)</td>
<td>674</td>
</tr>
<tr>
<td>BrMe$_2$SnCHDCOOOMe (350c)$^f$</td>
<td>2.470</td>
<td>2.588</td>
<td>173.4</td>
<td>0.33 (57)</td>
<td>674</td>
</tr>
<tr>
<td>IMe$_2$SnCHDCOOOMe (350d)$^f$</td>
<td>2.391</td>
<td>2.830</td>
<td>172.5</td>
<td>0.25 (66)</td>
<td>674</td>
</tr>
<tr>
<td>Me$_3$SnCHDCOOOMe (350e)$^f$</td>
<td>2.781</td>
<td>2.150$^f$</td>
<td>172.4$^g$</td>
<td>0.57 (24)</td>
<td>748</td>
</tr>
<tr>
<td>ClMe$_2$SnCH$_2$(N=CPh$_2$)COOEt (343)</td>
<td>2.517</td>
<td>2.448</td>
<td>171.1</td>
<td>0.29 (61)</td>
<td>736</td>
</tr>
<tr>
<td>L$^6$SnMe$_2$Cl (Sn-144d)</td>
<td>2.303</td>
<td>2.489</td>
<td>167.4</td>
<td>0.20 (72)</td>
<td>758</td>
</tr>
</tbody>
</table>

$^a$Deviation of the tin atom from the equatorial plane toward the halide atom; in parentheses, the difference between the sums of the equatorial and axial angles with values between $0^\circ$ (ideal T) and $90^\circ$ (ideal TBP)$^{652}$.  
$^b$An additional intermolecular Sn···Cl contact (3.96 Å).  
$^c$An additional intermolecular Sn···Cl contact (4.16 Å).  
$^d$Six-membered chelate ring; an additional intermolecular Sn···Cl contact (4.26 Å).  
$^e$An additional intermolecular Sn···F contact (3.64 Å).  
$^f$For a description of “D” in the ligand XMe$_2$SnCH“D”COOMe see Scheme 17 below compounds 350a–e.  
$^g$Sn=C(pseudo-axial).  
$^h$OSnC(pseudo-axial).  

oxygen-to-tin coordination in solution, unlike acetate 301a, which coordinates through the alkoxy oxygen (see above), no firm evidence has been obtained for the existence of such an interaction in 358. This is ascribed to the lower electronegativity of an alkynyl group than of a chlorine atom.

A series of compounds (Bu$_3$Sn)$_2$CHCHRCO$_2$Me (R = CH$_2$CH=CH$_2$, CH$_2$Ph, CH$_2$NMe$_2$) was obtained by reaction of the precursor with R = H with LiNPr$_2$-$i$, followed by treatment of the corresponding halide RBr or RI$^{756}$. The conformational dependence for these species on the temperature and concentration was studied by means of Karplus-type dihedral angle relations for $^3J(^{119}$Sn–$^{13}$C) couplings. The results point toward a dominant conformation in which a very weak carbonyl oxygen-to-tin interaction is possible.

The reaction of ClCH$_2$SnMe$_2$Cl with N-TMS amides and lactams requires more drastic conditions (o-xylene, 80–100 °C) than the analogous reactions of ClCH$_2$SiMe$_2$Cl and ClCH$_2$GeMe$_2$Cl (Section VI.A.1.c) and, in general, leads to a mixture of the O- and N-alkylation products$^{484,494,757}$. A multistage reaction scheme established by NMR monitoring includes the transmetallation products 359 followed by subsequent formation of O-stannylmethyl and finally N-stannylmethyl derivatives, 360 and 361, respectively (Scheme 18).

Chlorides 361b and 361c were isolated. The pentacoordination of the tin in 360a–c and 361a–c was confirmed by significant upfield shifts of the signals in the NMR $^{119}$Sn spectra (−73.5 ppm for 360a–c and −40.6, −42.8 and −35.3 ppm for 361a–c, respectively) in comparison to the CICH$_2$SnMe$_2$Cl signal (112.3 ppm).
SCHEME 18. Reaction of ClCH₂SnMe₂Cl with trimethylsilylated amides and lactams

An X-ray diffraction of 361b revealed a TBP arrangement at the tin center, with the axial oxygen and halogen atoms. Comparison with the corresponding Ge and Si analogues 144c and Si-101b suggests that the geometry of the hypervalent OMC₃Cl moiety retains a TBP shape but changes markedly in the series Si-101b → 144c → 101b. Both components of the hypervalent O−M−Cl bond increase with the increasing size of the M atom (Table 55), although in a different way: the O−M distance has a larger leap on Si and Ge interchange, while the M−Cl distance is more sensitive to the Ge by Sn replacement. The lengthening of the M−Cl bond in relation to the single bond distances increases on going from Sn to Ge to Si.

The general state of the OMC₃Cl fragment may be defined by the parameters ΔM and ΔΩ, defined above. These two parameters indicate that the deviation from the ideal TBP increases along the row of Si → Ge → Sn, more significantly so on the Si → Ge substitution.

Like the reaction of ClCH₂SnMe₂Cl with N-TMS amides and lactams (Scheme 18), its reaction with O-TMS N-acetylacetamide yields a mixture of the O-alkylation (not

TABLE 55. Comparison of selected structural parameters for chloride 361b and the corresponding Ge and Si analogues, 144c and Si 101b

<table>
<thead>
<tr>
<th>Compound</th>
<th>M</th>
<th>(O−M) (Å)</th>
<th>Δd(O−M) (%)a</th>
<th>(M−Cl) (Å)</th>
<th>Δd(M−Cl) (%)a</th>
<th>OMC (deg)</th>
<th>ΔM (Å)b</th>
<th>ΔΩ (deg)c</th>
</tr>
</thead>
<tbody>
<tr>
<td>361b</td>
<td>Sn</td>
<td>2.303</td>
<td>21</td>
<td>2.489</td>
<td>6</td>
<td>167.4</td>
<td>0.196</td>
<td>55</td>
</tr>
<tr>
<td>144c</td>
<td>Ge</td>
<td>2.181</td>
<td>25</td>
<td>2.363</td>
<td>9</td>
<td>170.6</td>
<td>0.147</td>
<td>45</td>
</tr>
<tr>
<td>Si-101b</td>
<td>Si</td>
<td>1.954</td>
<td>20</td>
<td>2.307</td>
<td>11</td>
<td>171.1</td>
<td>0.058</td>
<td>19</td>
</tr>
</tbody>
</table>

a Lengthening of the bond distance in relation to the single bond.

b Displacement of the central atom from the equatorial plane.

c Ω is a solid angle formed by three equatorial bonds of the central atom (see text). L^n is the n-membered lactamomethyl ligand with R^n = MeCON(CH(Ph)Me)CH₂.
shown) and N-alkylation products (362). In the latter the degenerate 1,5-migration of the ClMe₂Sn group, in which the tin atom is a constituent of the coordinate bond, takes place between two carbonyl oxygen atoms (equation 65) with an activation free energy $\Delta G^\#$ of 11.5 kcal mol$^{-1}$.

$$\text{(362)}$$

Based on the IR, $^{119}$Sn NMR and $^{119}$Sn Mössbauer spectroscopy, the tin atom in tetraorganotin derivative 363a is suggested to be tetracoordinate, but it is pentacoordinate both in the iodide 363b due to the O → Sn interaction and in the dithiocarbamate 363c due to the bidentate mode of the thiocarbamate ligand.

$$\text{(363a)} \quad X = \text{Ph} \quad \text{(363b)} \quad X = \text{I} \quad \text{(363c)} \quad X = \text{S}_2\text{CNMe}_2$$

Ketoorganostannanes $\text{R}_3\text{Sn}(\text{CH}_2)_n\text{COR}'$ and ketoorganohalostannanes $\text{ClR}_2\text{Sn}(\text{CH}_2)_n\text{COR}'$ ($n = 2, 3$; $R, R' = \text{Me, Ph}$) have been known for a long time but have been less extensively investigated, especially in regard to their coordination chemistry. Based on the IR, $^1\text{H}$ and $^{13}\text{C}$ NMR and $^{119}$Sn Mössbauer spectroscopy, a TBP structure with intramolecular O → Sn coordination for chlorides 364a, 364b and 365a–c was suggested. This coordination is relatively weak as shown by replacement of the intramolecular coordinating oxygen atom by external ligands like pyridine. As indicated by IR spectroscopy, diketone ClMe₂SnCH₂CH[COPh]₂ contains one intramolecularly tin-coordinated carbonyl group resulting in pentacoordinate tin, whereas the other carbonyl remains uncoordinated in the solid state ($\nu(\text{C} = \text{O}) = 1627$ and 1670 cm$^{-1}$, respectively).

Among organotin species incorporating (C=)O → Sn coordination, compounds including an (X=)O → Sn moiety ($X = \text{heteroatom, P or S}$) have been also reported. According to NMR data, a tetrahedral geometry at tin in solution is suggested for
2-Me₃SnFcCH₂POPh₂ (231). The tetraorganotin compounds 366 and 367 were recently prepared (equation 66).

\[
\begin{align*}
\text{EtO} & \text{O} \text{Et} \\
\text{P} & \text{O}
\end{align*}
\]

LDA, Ph₃SnCl

\[
\begin{align*}
\text{EtO} & \text{O} \text{Et} \\
\text{P} & \text{O}
\end{align*}
\]

(366)

\[
\begin{align*}
\text{Ph} & \\
\text{Sn} & \\
\text{OEt} & \text{OEt} \\
\text{Ph} & \text{Ph} \\
\text{Ph} & \text{Ph} \\
\text{Ph} & \text{Ph}
\end{align*}
\]

(367)

X-ray determinations show that the tin centers in these compounds have strongly distorted TBP geometries with weak O → Sn interactions of 2.80 and 2.79 Å, respectively. These are of the same order of magnitude as those in tetraorganostannanes 91, 285, 310a and 310b discussed earlier (see Tables 49 and 53).

The earlier examples of the five-membered chelate ring with triorganotin moiety include phosphoryl derivatives, e.g. chlorides 368a–d and 369a-d, the ferrocenyl species 269b (Section VII.A.1.c), the bromide BrMe₂SnCH₂CH₂POPhBu-t (370), ditin species(ClMe₂SnCH₂CH₂)₂POPh (371) as well as the fluoride 372a and the S and Se analogues of phosphine oxide, bromide 372b and chloride 372c. Bromides 369b and 369c were recently obtained by the reaction of tetraorganotin compounds 366 and 367 with 1 or 2 equivalents of bromine. Bromide 369c was also synthesized by treatment of 367 with an excess of Me₃SiBr.

Starting from tetraorganotin compounds Me₃SnCH₂CH(X=O)Y=O and HCl or Me₂SnCl₂, a family of 2,2-difunctional triorganotin chlorides of the type ClMe₂SnCH₂CH(X=O)Y=O (373, X=O, Y=O = P(O)R₂, COR, R = Ph, OEt, OPr-i) was recently prepared.

Crystal studies of 369a-d, 369b, 370, 371, 372a, 372b, 372c reveal a distorted TBP ligand arrangement at the tin atom owing to the intramolecular...
16. Hypervalent compounds of organic germanium, tin and lead derivatives

\[
\text{Sn}\xrightarrow{\text{P}=\text{O(S, Se)}}\text{Sn coordination where the heteroatoms are situated in the apical positions,}
\]

and the three carbon atoms define the equatorial plane. Selected structural data pertinent to the TBP structures are collected in Table 56.

In tetraorganotin compounds 366 and 367 and the bromide 369b the \( \text{P}=\text{O} \) groups are directed toward the tin atoms, resulting in real structures along the T → TBP path\textsuperscript{762}. The position along this path is given by the differences in the sum of the equatorial and axial angles (90° for ideal TBP, 0° for ideal T). It amounts to 36.8° for 366, 34.3 for 367 and 65.9° (average) for 369b.

The crystal structure determinations of difunctional 373a\textsuperscript{770} and 373b\textsuperscript{747}, IR spectroscopic data and NMR studies\textsuperscript{747} show that one of the two functional groups is intramolecularly coordinated to tin, resulting in its pentacoordination, whereas the other donor group remains uncoordinated in the solid state. The structure of 373a reveals that the POPh\textsubscript{2} group with the higher donor ability is coordinated at the tin atom and the PO(OPr-i)\textsubscript{2} group remains uncoordinated. Crystal structure determinations and spectroscopic data assign the following sequence of increasing donor strength for the corresponding functional group both in the solid state and in solution: COPr-i < COPh < PO(OPr-i)\textsubscript{2} < PO(OPr-i)Ph < POPh\textsubscript{2}\textsuperscript{747}.

The triorganotin compound 374 has been prepared by reaction of new functional Grignard reagent (EtO)\textsubscript{2}POCH\textsubscript{2}SiMe\textsubscript{2}CH\textsubscript{2}MgCl with Me\textsubscript{3}SnCl and subsequent treatment with Me\textsubscript{2}SnCl\textsubscript{2}\textsuperscript{771}. The crystal structure reveals a nearly ideal TBP coordination of the tin atom that results from a six-membered chelate ring having a chair conformation.
TABLE 56. Structural parameters for pentacoordinate chelates with P=O and related groups

<table>
<thead>
<tr>
<th>Compound</th>
<th>O−Sn (Å)</th>
<th>Sn−X (Å)</th>
<th>OSnX (deg)</th>
<th>ΔSn † (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Ph₃SnC₆H₃[PO(OEt)₂-2,4]₂ (366)</td>
<td>2.803</td>
<td>2.148</td>
<td>174.2</td>
<td>0.477</td>
<td>762</td>
</tr>
<tr>
<td>1.5-(Ph₃Sn)C₆H₃[PO(OEt)₂-2,4]₂ (367)</td>
<td>2.793</td>
<td>2.148</td>
<td>177.0</td>
<td>0.492</td>
<td>762</td>
</tr>
<tr>
<td>FMe₂SnCH₂CH₂POPh₂ (372a)</td>
<td>2.454</td>
<td>2.035</td>
<td>172.7</td>
<td>0.186</td>
<td>766</td>
</tr>
<tr>
<td>(ClMe₂SnCH₂CH₂)₂POPh (371)b</td>
<td>2.352</td>
<td>2.536</td>
<td>172.7</td>
<td>0.172</td>
<td>765</td>
</tr>
<tr>
<td>BrMe₂SnCH₂CH₂POPhBu-t (370)</td>
<td>2.323</td>
<td>2.684</td>
<td>172.5</td>
<td>0.162</td>
<td>763</td>
</tr>
<tr>
<td>BrMe₂SnCH₂CH₂PSPb₂ (372a)</td>
<td>2.872</td>
<td>2.650</td>
<td>175.1</td>
<td>0.141</td>
<td>767</td>
</tr>
<tr>
<td>ClMe₂SnCH₂CH₂PSePh₂ (372c)</td>
<td>3.022</td>
<td>2.500</td>
<td>173.2</td>
<td>0.141</td>
<td>768</td>
</tr>
<tr>
<td>Cl₂Me₂Sn[POPh₂-2] (369a)</td>
<td>2.357</td>
<td>2.452</td>
<td>171.5</td>
<td>0.190</td>
<td>764</td>
</tr>
<tr>
<td>1.5-(BrPh₂Sn)C₆H₂[PO(OEt)₂-2,4]₂ (369c)</td>
<td>2.379</td>
<td>2.600</td>
<td>174.6</td>
<td>0.245</td>
<td>762</td>
</tr>
<tr>
<td>2-ClMe₂SnFcCH₂POPh₂ (269b)</td>
<td>2.412</td>
<td>2.598</td>
<td>175.4</td>
<td>0.190</td>
<td>765</td>
</tr>
<tr>
<td>ClMe₂SnCH₂CH₂PO(OPr-i)₂ (374)</td>
<td>2.518</td>
<td>2.518</td>
<td>178.9</td>
<td>0.12</td>
<td>771</td>
</tr>
<tr>
<td>ClBrMeSnCH₂CH₂PO(OPr-i)₂ (378)b</td>
<td>2.427</td>
<td>2.587</td>
<td>—</td>
<td>—</td>
<td>141</td>
</tr>
<tr>
<td>Br₂MeSnCH₂CH₂PO(Pr-i)₂ (379)f</td>
<td>2.425</td>
<td>2.591</td>
<td>169.7</td>
<td>—</td>
<td>772</td>
</tr>
<tr>
<td>(ClMe₂Sn)₂CHCH₂CH₂SOEt (380a)b</td>
<td>2.301</td>
<td>2.572</td>
<td>176.1</td>
<td>0.03</td>
<td>773</td>
</tr>
<tr>
<td>(BrMe₂Sn)₂CHCH₂CH₂SOEt (380b)b</td>
<td>2.287</td>
<td>2.747</td>
<td>177.3</td>
<td>0.02</td>
<td>773</td>
</tr>
<tr>
<td>(Cl₂MeSn)₂CHCH₂CH₂SOEt (381a)b,g</td>
<td>3.117</td>
<td>2.367</td>
<td>174.1</td>
<td>0.42</td>
<td>773</td>
</tr>
<tr>
<td>(Br₂MeSn)₂CHCH₂CH₂SOEt (381b)b,g</td>
<td>2.215</td>
<td>2.690</td>
<td>171.5</td>
<td>0.06</td>
<td>773</td>
</tr>
<tr>
<td>Cl₂MeSn(2CH₃)₃SO₂ Tol-p (382)</td>
<td>2.625</td>
<td>2.809</td>
<td>177.1</td>
<td>0.25</td>
<td>774</td>
</tr>
</tbody>
</table>

† Toward the halide atom.
‖ Hypervalent fragment Hal−Sn(2)···Halbr.
§ Only the POPh₂ group is coordinated.
¶ Dimeric structure with six-coordinate tin atoms.
∥ Both P=O groups are coordinated.
†† Away from Halbr.
‡‡ An additional intermolecular Hal···Sn interaction.
As shown by DNMR investigations, a ligand exchange process occurs in solution of both the monofunctional chlorides \(368a-d\) and the difunctional halides \(373a\) and \(373b\). The barrier for \(368a-d\) decreases dramatically on lowering the donor strength of the P\(=\)O group, while the configurational stability of \(373a\) and \(373b\) increases with decreasing the donor strength of the functional groups X\(=\)O and Y\(=\)O. For compounds \(368a-d\) the hexacoordinated intermediates \(375\) are suggested as transition states in donor solvents (D), whereas in apolar solvents the process is expected to proceed via dimeric species like \(376\). In the case of the halides \(373\), it is suggested that the uncoordinated donor group induces a ligand exchange in a neighboring molecule by intermolecular O\(\cdots\)Sn interactions via hexacoordinated dimeric species of the type \(377\).

Unlike triorganotin phosphoryl compounds, the alkyldihalostannylibisphosphonates \(X_2RSnCH_2CH[PO(OPr-i)_2]_2\) (X = Cl, Br; R = Me, Bu-t) exist as dimers in the solid state with hexacoordinated tin, resulting from intramolecular P\(=\)O \(\rightarrow\) Sn coordination of one P=O group as well as an intermolecular P=O \(\rightarrow\) Sn interaction of the second P=O group with the tin atom of a neighboring molecule, as in ClBrMeSnCH_2CH[PO(OPr-i)_2]_2 (378). In solution, a concentration and temperature dependent equilibrium takes place between dimeric and monomeric species\(^{141, 775}\). However, if the hydrogen of the central CH group is substituted by a methyl group, as in Br_2MeSnCH_2C(Me)[PO(OPr-i)_2]_2 (379), both P=O groups act as a tridentate ligand in the octahedral ligand array at the Sn atom and the structure remains unchanged in solution\(^{772}\).
Examples of organotin complexes incorporating S=O → Sn coordination are the ditin sulfoxides, 380a and 380b, and 381a and 381b, as well as sulfone 382. Based on the X-ray studies (Table 56) due to O → Sn interaction all compounds contain a pentacoordinate tin atom in a six-membered chelate ring with the metal atom having a near-TBP coordination geometry. The second Sn atom in chloro and bromo 380 and 381 is also pentacoordinated by virtue of a weak intramolecular Hal···Sn interaction due to the Sn···Hal···Sn bridging. Moreover, both coordination sites in 381a and 381b are distorted owing to a weak additional interaction through halide bridging between two adjacent binuclear units.

In contrast, an intramolecular S=O → Sn interaction is absent in tetraorganotin compounds Ph3Sn(CH2)ₙTos-p (n = 2–4). Based on ¹H, ¹³C and ¹¹⁹Sn NMR studies it was suggested that the O of the sulfoxide group undergoes a rapid coordinative exchange between the two tin atoms in each of the compounds 380 and 381 in solution.

3. Monocyclic derivatives with other bidentate chelating ligands

Although organotin compounds with monoanionic C,N- and C,O-chelating ligands were most extensively studied in relation to hypervalency, complexes containing other monoanionic bidentate X,D-chelating ligands (X, D = N, O, S) have also been reported. Among them, the β-diketones, carboxylate and dithiocarbamate (DTC) derivatives are most widely known.

The organotin carboxylates may adopt a variety of structural modes depending on the nature of the organic substituent on the tin atom and/or the carboxylate
In the crystalline state, triorganotin carboxylates generally adopt either a polymeric structure with a five-coordinated tin atom (type 383) or a monomeric structure varying from a purely tetrahedral four-coordinate geometry (type 384) to a similar one with a weak additional intramolecular coordination from the carbonyl oxygen to the tin atom (type 385). The polymeric structure 383 is especially common in the crystalline state. However, sterically demanding groups apparently favor a monomeric structure (384 or 385). Furthermore, the electronegativity difference between the organic groups R and the carboxylate moiety plays an important role.

Some of the organotin DTC complexes are discussed above (see Table 53 and compounds 264a and 266b, Section VII.A.1.c). For the organotin dithiocarbamates, it has been found that small variations in tin-bound or nitrogen-bound organic substituents may lead to very different coordination geometries about the tin. In particular, for derivatives of the type ClPh₂SnDTC the complexes contain essentially four-coordinate tin, but with wide variations from the normal tetrahedral environment. For chlorides ClR₂SnDTC (R = Alk, Ph), the DTC ligand is generally bonded to the tin atom in an anisobidentate manner.

¹¹⁹Sn NMR spectroscopy is very useful for elucidating the nature of the coordination in DTC complexes of tin. There is an approximately linear dependence of the δ(¹¹⁹Sn) values on the coordination number of the complexes. Thus, the δ(¹¹⁹Sn) values are between −150 and −250 ppm in pentacoordinate, between −300 and −500 ppm in hexacoordinate and between −700 and −800 ppm in heptacoordinate compounds. Based on ¹¹⁹Sn and ¹⁵N NMR data, an intramolecular N → Sn coordination was detected analogously in the cases of N,N-TMS(trimethylstannyl)-2-aminopyridine, N,N-TMS(trimethylstannyl)-N-TMS-2,6-diaminopyridine and 2-[N,N-bis(trimethylstannyl)amino]pyridine.

Most recently, the hydroxylamine derivative Me₃SnONMe₂ (386) was found to be an exotic example of a triorganotin compound containing a three-membered chelate ring resulting from intramolecular coordination. A secondary interaction between the tin and nitrogen atoms has been detected on the basis of a gas-phase structure determination by electron diffraction, an X-ray crystallographic study in the solid and ab initio calculations (MP2/DZ(P)), with O···Sn distances of 2.731, 2.745 and 2.661 Å, respectively. In the crystal, the coordination sphere of tin is further enlarged by an intermolecular Sn···O contact (2.998 Å) and a 4 + 2 coordination geometry is achieved, as deduced from the distorted TBP with one of the axial substituents replaced by the two weak contacts. It is noteworthy that 386 is the first partially hypercoordinate tin compound studied in the gas phase.
Some crystallographic data for selected cases of organotin and organolead complexes of the type $\text{387}$ containing monoanionic X,D-chelating ligands ($X, D = N, O, S$) are given in Table 57; their structures are given in Chart 1. These compounds, however, are beyond the scope of this review and will not be discussed in detail.

### Table 57. Some structural parameters for selected tin and lead pentacoordinate compounds of the type $\text{387}$ containing a DMC$_2$XY moiety ($M = \text{Sn}, \text{Pb}$) with monoanionic X,D-chelating ligand

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<th>$Y$–$\text{Sn}$ (Å)</th>
<th>$X$–$\text{Sn}$ (Å)</th>
<th>$\text{DSnY}$ (deg)</th>
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16. Hypervalent compounds of organic germanium, tin and lead derivatives

### TABLE 57. (continued)

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S, O-cherlates

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S, S-chelates

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<td>2.511</td>
<td>2.345</td>
<td>163.2</td>
<td>87.6</td>
<td>0.25&lt;sup&gt;g&lt;/sup&gt;</td>
<td>814</td>
</tr>
<tr>
<td>XXI</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>2.795</td>
<td>2.489</td>
<td>2.573</td>
<td>150.7</td>
<td>67.0</td>
<td>0.25&lt;sup&gt;g&lt;/sup&gt;</td>
<td>815</td>
</tr>
<tr>
<td>XXIIb</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>2.957</td>
<td>2.466</td>
<td>2.433</td>
<td>160.6</td>
<td>65.4</td>
<td>0.41</td>
<td>816</td>
</tr>
</tbody>
</table>

### B. Bicyclic Complexes

#### 1. Stannocanes

Among the numerous pentacoordinated organotin derivatives reported so far, stannocanes are the most systematically studied. The three main types of stannocanes are 4,6-dioxastannocanes (388–390), 4,6-dithiastannocanes (391–393) and 4,6-dicapastannocanes (394–396). Depending on the donor (NR, O, S), each type may be further subdivided into groups of compounds with identical or different substituents (X and Y) at the tin atom.

Different stannocanes may be prepared by the reaction of organotin halides<sup>817,818</sup> or SnHal<sub>4</sub><sup>819</sup> with a suspension of disodium diolate in THF and disodium dithiolate in toluene and ethanol or with free diethiols in CHCl<sub>3</sub>. These reactions yield...
CHART 1. The structures of organotin and organolead complexes of the type containing monoanionic X,D-chelating ligands (X, D = N, O, S)
symmetrically \((X = Y)\) and unsymmetrically \((X \neq Y)\) substituted 1-aza-4,6-dioxo- and -4,6-dithiastannocanes (equation 67a,b)\(^{820}\). The symmetrically substituted compounds may be also synthesized from diorganotin dialkoxides or oxides in the presence of KOH as catalyst (equation 67c,d)\(^{817,820}\).

1-Oxa- and 1-thia-4,6-dioxo- and -4,6-dithiastannocanes \(389, 390, 392\) and \(393\) were prepared by similar methods from the respective organotin halides or \(\text{SnHal}_4\) and diolate or dithiolate salts \(\text{D(CH}_2\text{CH}_2\text{ZNa})_2\) \((\text{D} = \text{O}; \text{Z} = \text{O}, \text{S})^ {818-820}\).

High yields in some of these reactions indicate the formation of pentacoordinate tin intermediates whose structures may resemble \(397^ {820,821}\).

Some special types of stannocanes were prepared using the same common methods of stannocane framework generation. Similar to equation 67c,d, the reaction of
dialkyltin oxides or dialkyltin alkoxides with N-methyliminodiacetic acid gives 3,7-stannocanediones 398. Reaction of [CH₂(PhSnO)₂]ₙ with dithiol MeN(CH₂CH₂SH)₂ yields bis-stannocane 399. Separation of the mixture of oligomeric products from the reaction of [(t-Bu)₂Sn(OMe)₂] with RP(CH₂CH₂SH)₂ gave 16-membered Sn,P-heterocycles [(t-Bu)₂Sn(SCH₂CH₂PR]₂ 400 (R = Me, Ph) instead of the expected 8-membered derivatives 823.

Transannular interactions in compounds 400 and in the products of their reaction with sulfur or selenium [(t-Bu)₂Sn(SCH₂CH₂P(X)R]₂ 401 (X = S, Se) are absent. For 401 (R = Ph, X = S) this was confirmed by an X-ray study. However, according to NMR data (δ(¹¹⁹Sn) = −183.0 ppm, δ(³¹P) = −40.5 ppm, Jₘₙ₋ₚ = 1185 Hz), such interaction takes place in phosphastannocane ClPhSn(SCH₂CH₂)₂PPh (402), which was prepared from PhSnCl₃ and (NaSCH₂CH₂)₂PPh, similarly to the route in equation 67b 825.
Other suitable starting materials for stannocanes are eight-membered derivatives of tin(II), which may be readily transformed to the corresponding tin(IV) compounds according to equation 68.

\[
\text{Sn}(\text{ZCH}_2\text{CH}_2)_2\text{D} + \text{X}^- \rightarrow \text{X}_2\text{Sn}(\text{ZCH}_2\text{CH}_2)_2\text{D}
\]

\[\text{D} = \text{NR}, \text{PR}, \text{O}, \text{S}; \text{X} = \text{Cl, Br}, \text{I}, \text{SPh, OCOPh}; \text{Z} = \text{O, S} \quad (68)\]

Equation 69 illustrates the formation of spirocyclic ‘double stannocanes’ 403–405 from Sn(II) derivatives.

\[
\text{Sn(SCH}_2\text{CH}_2)_2\text{D} + (\text{HSCH}_2\text{CH}_2)_2\text{D} \rightarrow \text{H}_2\text{Sn}(\text{SCH}_2\text{CH}_2)_2\text{D}
\]

\[\text{D} = \text{NMe}(404) \quad \text{D} = \text{O}(405) \quad (69)\]

The spiro stannocanes 404 and 405 were also prepared by the reaction of SnCl\textsubscript{4} with 2 equivalents of the dithiolates (NaSCH\textsubscript{2}CH\textsubscript{2})\textsubscript{2}D (D = NMe, O, S)\textsuperscript{825}. Similar to spirocyclic ‘double germocanes’ 182 and 183, the distortion of the SnS\textsubscript{4} tetrahedral coordination is a result of weak transannular D···Sn (D = O, S) interactions. Thus, the coordination geometry at tin can be described as a bicapped tetrahedron\textsuperscript{825}. The lengths of transannular bonds are 2.84, 2.78 Å (O···Sn in 404) and 3.24, 3.074 Å (S···Sn in 405), respectively.

According to \textsuperscript{119}Sn NMR data, the tin atom in solutions of 403 is hexacoordinated while the coordination in the O and S analogues is closer to tetrahedral (\(\delta(\textsuperscript{119}\text{Sn}) = -198.9, -21.7, -17.1\), respectively, in 301K in Py)\textsuperscript{824}.

A general approach to 4,6-dicarbastannocanes 394–396 is based on the reaction of difunctional Grignard reagents with SnCl\textsubscript{4}, SnBr\textsubscript{4} or PhSnCl\textsubscript{3} in THF/toluene under sufficient dilution (equations 70a and 70b).

\[
\text{SnX}_4 + \text{D}(\text{CH}_2\text{CH}_2\text{CH}_2\text{MgX})_2 \rightarrow \text{X}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{D}
\]

\[\text{X} = \text{Cl, Br}; (394\text{a}) \text{ D} = \text{NR}, (395\text{a}) \text{ D} = \text{O}, (396\text{a}) \text{ D} = \text{S} \quad (70\text{a})\]

\[
\text{PhSnCl}_3 + \text{D}(\text{CH}_2\text{CH}_2\text{CH}_2\text{MgCl})_2 \rightarrow \text{ClPhSn}(\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{D}
\]

\[\text{D} = \text{NR}, (305\text{b}) \text{ D} = \text{O}, (396\text{b}) \text{ D} = \text{S} \quad (70\text{b})\]

The yield decreases drastically along the series NMe > O > S and in the case of RN donors also upon substitution of R = Me by other alkyl groups.

The symmetrically substituted tetraorganotin compounds 406a and 407a (R' = Me, \(t\)-Bu, Ph) were obtained in nearly quantitative yields from the reaction of their dichloro precursors with organolithium reagents (equation 71).

\[
\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{D} + 2\text{R'}\text{Li} \rightarrow \text{R'}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{D}
\]

\[\text{(406a)} \text{ D} = \text{NR}, (407\text{a}) \text{ D} = \text{O} \quad (71)\]
Analogous reaction of the dichlorides Cl₂Sn[(CH₂)₃]₂D 394a and 395a with Ph₃SiONa leads to the corresponding disilox derivatives (Ph₃SiO)₂Sn[(CH₂)₃]₂D 406b and 407b (R = Me, CH₂Ph, i-Bu; R’ = OSiPh₃)⁵³⁰.

One methyl group in the tetraorganotin compounds 406a and 407a (R’ = Me) may be cleaved easily by R’’₃SnX (equation 72)⁸²¹,⁸²⁸.

\[
\text{Me}_2\text{Sn(CH}_2\text{CH}_2\text{CH}_2\text{)}_2\text{D} + R’’₃\text{SnX} \rightarrow X\text{MeSn(CH}_2\text{CH}_2\text{CH}_2\text{)}_2\text{D} + R’’₃\text{SnMe}
\]

(72)

R’’₃SnX = Pr₃SnF, Me₃SnCl

(406c) X = F, Cl; D = NMe₂

(407c) X = Cl; D = O

The monofluoride 406c (X = F) that was isolated as a hydrate from the reaction in equation 72 is apparently the first and only example of a stannocane with fluoride substituent at the Sn atom⁸²⁸.

One methyl group in the dimethyl derivatives 406a (R = R’ = Me) may be also cleaved by the reaction with t-BuPO(OH)₂²⁴⁰. According to the X-ray data, the t-butylyphosphonic acid ligand in the resulting nonsymmetrically substituted stannocane [t-BuP(O)(OH)O]MeSn(CH₂CH₂CH₂)₂NMe 408 coordinates with the tin center only via the oxygen atom.

New types of carbostannocanes were prepared from the dichloride 394a and the monochloride 406c, X = Cl. Spirocyclic compound 409 was obtained in high yield by the reaction of 394a with H₂S in the presence of Et₃N⁸²⁷. Furthermore, the reaction of 394a with sodium naphthalenide in THF at −70°C yields the thermally stable distannane 410a⁸²⁹. Its Me analogue 410b was prepared by a similar method from 406c and Na/NH₃⁸²⁹.

Hexacoordinated stannocanes MeOOCCH₂CH₂(DMTC)Sn(ZCH₂CH₂)₂D 411a (Z = O, D = NMe) and 411b (Z = S, D = O) were prepared by the reaction of MeOOCCH₂CH₂(DMTC)SnCl₂ with (NaZCH₂CH₂)₂D⁷⁵¹.

The Pb analogues of germocanes and stannocanes are almost unknown. The rare examples known include 4,6-dithiaplumbocanes Ph₂Pb(SCH₂CH₂)₂D 412 (D = O) and 413 (D = S), which were prepared from lead diacetate and the corresponding disodium.
dithiolate\textsuperscript{200,830}. According to \textsuperscript{207}Pb NMR data, the 1,5-transannular \( S \rightarrow \text{Pb} \) interaction in \textbf{413} is weaker than the \( O \rightarrow \text{Pb} \) coordination in \textbf{412}. X-ray studies of \textbf{412} show that in the crystal there are two modifications (orthorhombic and triclinic) of the compound. Both contain four crystallographically independent 8-membered cycles that have three chair–chair and one boat–chair conformations. The tetrahedral \( \text{C}_2\text{PbS}_2 \) configuration is expanded by one 1,5-transannular \( O \rightarrow \text{Pb} \) interaction (2.85 to 3.08 \( \text{Å} \), monocapped). In one of the triclinic modifications an intermolecular \( S \cdots \text{Pb} \) interaction takes place (4.11 and 3.75 \( \text{Å} \), bicapped)\textsuperscript{830}.

Evidence for the 1,5-transannular \( D \rightarrow \text{Sn} \) interaction in stannocanes was obtained from X-ray data and Mössbauer spectroscopy in the solid state and in solution also from NMR spectroscopy, especially from the coupling constants \( 1J(\text{\textsuperscript{119}Sn}−D) \), \( D = \text{\textsuperscript{15}N} \), \( \text{\textsuperscript{31}P} \) and \( 2J(\text{\textsuperscript{119}Sn}−D−\text{C}−\text{H}) \). The high-field shift of these compounds in the \textsuperscript{119}Sn NMR spectra compared with compounds of coordination number four with similar substituents at tin as well as the change of the \( 1J(\text{\textsuperscript{119}Sn}−\text{\textsuperscript{13}C}) \) and \( 2J(\text{\textsuperscript{119}Sn}−\text{C}−\text{H}) \) coupling constants are in agreement with pentacoordination\textsuperscript{820,827,831}. It is noteworthy that the relationship between the increasing coupling constants and the increase in the coordination number of the tin atom is valid only for the equatorially bonded organic groups in a TBP arrangement. As a result of the \( D \rightarrow \text{Sn} \) donor–acceptor interaction, the configuration of the tin atom is more or less distorted TBP with two basic configurations, \textbf{414A} and \textbf{414B}, depending on the nature of the substituents.

![Diagram](image)

(\textbf{414A})

(\textbf{414B})

There is NMR evidence for each of the structures\textsuperscript{831–834}. Moreover, in some cases there is indication of the presence of an equilibrium mixture of the two forms in solution\textsuperscript{831}. At lower temperatures a fast intramolecular exchange (Berry-type pseudorotation) was assumed. At a higher temperature, a dissociation–inversion process shows the magnetic equivalence of the \( X \) and \( Y \) groups when \( X = Y \).

In particular, NMR data support the structure \textbf{414A} for \( \text{R}_2\text{Sn(SCH}_2\text{CH}_2)_2\text{NMe} \) \textsuperscript{(391, \( R = \text{Me, \textit{t}-Bu} \))\textsuperscript{833} and the structure \textbf{414B} for \( \text{(\textit{t}-Bu)}_2\text{Sn(OCH}_2\text{CH}_2)_2\text{NMe} \) (the \textbf{388} type)\textsuperscript{832,834}.

According to X-ray data, the molecules of all known 4,6-dicarba- and 4,6-dithiastannocanes (Tables 58 and 59) have configuration \textbf{414A}, where the donor atom \( D \) (\( \text{NR, O, S} \)) and \( X_{ax} \) (\( X = \text{Hal, OSiPh}_3\), \( \text{OPO(OH)Bu-t} \)) are axial ligands while two \textit{S} or \textit{C} atoms (\( Z \)) and \( Y_{eq} \) (\( X = \text{Hal, OSiPh}_3\), \( \text{Me, Ph} \)) occupy the equatorial positions. In the nonsymmetrically substituted alkyl halide or phenyl halide compounds, the halogen substituent is always axial. Furthermore, in the case of the methyl phenyl 4,6-dithiastannocane \textbf{392} (\( X = \text{Ph, Y} = \text{Me} \)) the more electronegative phenyl substituent also occupies the axial position. In the nonsymmetrical compounds, the axial bonds are always longer than the equatorial bonds.

The coordination environment of the tin atom in the three compounds \( \text{Cl}_2\text{Sn(CH}_2\text{CH}_2\text{CH}_2)_2D \) (\( D = \text{NMe, O, S} \)) is more or less distorted TBP due to the
presence of a D → Sn interaction. The donor D and one of the Cl atoms are axial while the second chlorine occupies an equatorial position. A peculiar feature of the structure of bis-stannocane 399 is nonsymmetrical configurations of the two stannocane fragments in the solid state. While both tin atoms have TBP geometries, one Ph group occupies an axial position and another one is equatorial. At the same time the N → Sn distances are almost the same (ca 2.65 Å). The spirostannocane 409 contains a nearly planar Sn₂S₂ four-membered ring with different Sn–S distances for the apical (2.53 Å) and the equatorial (2.40 Å) atoms.

While no short intermolecular contacts were detected in compounds [X₂Sn(SCH₂CH₂)₂O (X = Cl, Br, I)] and [X₂Sn(SCH₂CH₂)₂S (X = Cl, Br, I)], such expansion of the coordination sphere was assumed for compounds [X₂Sn(SCH₂CH₂)₂NMe (X = Cl, Br, I)] on account of their low stability and high melting points. This assumption is in accordance with the facile formation of an adduct of Cl₂Sn(SCH₂CH₂)₂NMe with HMPA. The ¹¹⁹Sn NMR data indicate a hexacoordinated tin atom in the adduct.

The ‘path’ from a tetrahedron to a trigonal bipyramid is controlled by four electronic factors (donor strength of D, electronegativity of the substituent Xₘ, lone pair interaction of Xₘ, type of equatorial ligands) and one steric factor (geometrical flexibility of X). These influences are discussed with respect to the structural and spectroscopic data (i.e. geometrical goodness of the trigonal bipyramid, Pauling-type bond orders BO(D → Sn) and BO(Sn–Xₘ), force constants f(Sn–Xₘ) and ¹¹⁹Sn-NMR chemical shifts). The D → Sn–Hal interaction in the compounds under discussion is given a qualitative MO description in terms of frontier orbitals (a related qualitative description of stannane anions is given elsewhere).

As for the influence of Xₘ, the electronegativity and lone pair interaction effects are counteractive and cancel each other, for the two heavier halides.

Finally, the donor strength of D in compounds [X₂Sn(SCH₂CH₂)₂D (D = NMe, O, S; X = Cl, Br, I)] decreases in the orders: NMe > S > O in the solid state and NMe > O > S in solution.

<table>
<thead>
<tr>
<th>D/X/Y, conformation</th>
<th>Sn–D (Å) (BO)⁶</th>
<th>Sn–X (Å) (BO)⁶</th>
<th>D–Sn–X (deg)</th>
<th>ΔSn⁷ (Å) (ΔΣ(θ))⁸</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBz/OSiPh₃/OSiPh₃</td>
<td>2.530 (0.240)</td>
<td>2.017 (0.95)</td>
<td>172.3</td>
<td>0.310</td>
<td>530</td>
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<tr>
<td>NBu-i/OSiPh₃/OSiPh₃</td>
<td>2.494 (0.269)</td>
<td>2.026 (0.92)</td>
<td>174.0</td>
<td>0.287</td>
<td>530</td>
</tr>
<tr>
<td>NBu-i/Cl/Cl</td>
<td>2.462 (0.299)</td>
<td>2.474 (0.691)</td>
<td>176.1</td>
<td>0.272</td>
<td>530</td>
</tr>
<tr>
<td>NBu-i/Cl/Cl (177)</td>
<td>2.389 (0.180)</td>
<td>2.319 (0.559)</td>
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<td>0.182</td>
<td>530</td>
</tr>
<tr>
<td>NBz/Cl/Cl</td>
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<td>2.487 (0.662)</td>
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<td>530</td>
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<tr>
<td>NMe/OPO(OH)Bu-t/Me</td>
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<td>2.083</td>
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<td>240</td>
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<td>NMe/Cl/Cl, BC</td>
<td>2.441 (0.320)</td>
<td>2.455 (0.735)</td>
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<tr>
<td>NMe/Cl/Ph</td>
<td>2.435 (0.326)</td>
<td>2.550 (0.540)</td>
<td>170.1</td>
<td>0.211</td>
<td>530</td>
</tr>
<tr>
<td>{MeN[(CH₂)₃]₂SnS}₂ (409)</td>
<td>2.553</td>
<td>2.520</td>
<td>176.2</td>
<td>—</td>
<td>835</td>
</tr>
<tr>
<td>O/Cl/CC</td>
<td>2.448 (0.234)</td>
<td>2.465 (0.711)</td>
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<td>S/Cl/BB</td>
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<td>2.449 (0.749)</td>
<td>178.9</td>
<td>0.320 (60.0)</td>
<td>530</td>
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</table>

⁶C, chair; B, boat.
⁷Pauling-type bond order, BO = 10¹⁻Δd⁻¹.⁴¹⁴
⁸Deviation of the Sn atom from the equatorial plane toward X.
⁹The difference between the sum of the equatorial and axial angles.
ⁱ⁰Ge–N, Ge–Cl, N–Ge–Cl and ΔGe.

TABLE 58. Selected structural parameters for 4,6-dicarbostannocanes XYSn(CH₂CH₂CH₂)₂D (394–396).
In most stannocanes the pentacoordination state of the tin atom is retained in solution. This was confirmed by the high-field shifts of the signals of these compounds in the $^{119}$Sn NMR spectra compared to model tetracoordinated compounds. This is confirmed by the increase in the coupling constants $J$ for the equatorially bonded carbon atoms in a TBP arrangement as in 4,6-dicarbastannocanes and also by the coupling constants $J$ for the TBP configuration is retained in solution, but also allow one to estimate the strength of the donor–acceptor interaction. This is especially important for compounds where X-ray data are not available.

The $^{119}$Sn spectra of Cl(n-Bu)Sn(SCH$_2$CH$_2$)$_2$O and Cl(n-Bu)Sn(SCH$_2$CH$_2$)$_2$S show unique $\delta$ values at $-10.93$ and $-8.85$ ppm, respectively. Such chemical shifts

<table>
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<tr>
<th>D/X/Y, conformation$^a$</th>
<th>Sn–D (Å) (BO)$^b$</th>
<th>Sn–X (Å) (BO)$^b$</th>
<th>D–Sn–X (deg)</th>
<th>$\Delta$Sn$^c$ (Å)</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>NMe/Me/Me, BC</td>
<td>2.566</td>
<td>2.159</td>
<td>165.8</td>
<td>0.366 (55.5)</td>
<td>652</td>
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<tr>
<td>NMe/Ph/CH$_2$Sn$^f$ (399)</td>
<td>2.651</td>
<td>2.178</td>
<td>166.4</td>
<td>—</td>
<td>822</td>
</tr>
<tr>
<td>NMe/CH$_2$Sn$^f$/Ph (399)</td>
<td>2.653</td>
<td>2.164</td>
<td>162.8</td>
<td>—</td>
<td>822</td>
</tr>
<tr>
<td>O/Me/Me, CC</td>
<td>2.774 (0.02)</td>
<td>2.133 (1.07)</td>
<td>163.6</td>
<td>0.57 (37)</td>
<td>818</td>
</tr>
<tr>
<td>O/Ph/Ph, M</td>
<td>2.660 (0.003)</td>
<td>2.147 (1.0)</td>
<td>168.8</td>
<td>0.519 (36)</td>
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<tr>
<td>O/Ph/Ph$^e$</td>
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<td>830</td>
</tr>
<tr>
<td>O/Ph/Me</td>
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<td>2.214</td>
<td>161.1</td>
<td>—</td>
<td>830</td>
</tr>
<tr>
<td>O/I/Me, CC</td>
<td>2.466 (0.22)</td>
<td>2.762 (0.85)</td>
<td>167.0</td>
<td>0.385 (53)</td>
<td>818</td>
</tr>
<tr>
<td>O/Br/Me, CC</td>
<td>2.440 (0.24)</td>
<td>2.561 (0.82)</td>
<td>166.5</td>
<td>0.353 (56)</td>
<td>818</td>
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<tr>
<td>O/Cl/Ie, CC and BC</td>
<td>2.423 (0.26)</td>
<td>2.413 (0.85)</td>
<td>168.3</td>
<td>0.32 (58)</td>
<td>818</td>
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<tr>
<td>O/Cl/n-Bu, BC</td>
<td>2.409 (0.26)</td>
<td>2.407 (0.85)</td>
<td>169.7</td>
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<td>O/Cl/Ph, D</td>
<td>2.412 (0.26)</td>
<td>2.420 (0.82)</td>
<td>167.3</td>
<td>0.295 (63)</td>
<td>839</td>
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<td>O/I/I, CC</td>
<td>2.431 (0.25)</td>
<td>2.738 (0.91)</td>
<td>166.4</td>
<td>0.36 (51)</td>
<td>819</td>
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<td>O/Br/Br, CC</td>
<td>2.41 (0.27)</td>
<td>2.536 (0.88)</td>
<td>165.8</td>
<td>0.29 (59)</td>
<td>819</td>
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<tr>
<td>O/Cl/Cl, CC</td>
<td>2.359 (0.31)</td>
<td>2.376 (0.94)</td>
<td>170.9</td>
<td>0.29 (61)</td>
<td>819</td>
</tr>
<tr>
<td>S/Me/Me$^i$, BC</td>
<td>3.514 (0.03)</td>
<td>2.147 (1.0)</td>
<td>169.3</td>
<td>0.720 (27)</td>
<td>818</td>
</tr>
<tr>
<td>S/Ph/Ph, BC</td>
<td>3.246 (0.06)</td>
<td>2.156 (0.98)</td>
<td>170.8</td>
<td>0.559 (31)</td>
<td>840</td>
</tr>
<tr>
<td>S/Cl/Ie, BC</td>
<td>2.863 (0.22)</td>
<td>2.444 (0.77)</td>
<td>168.6</td>
<td>0.208 (72)</td>
<td>818</td>
</tr>
<tr>
<td>S/Cl/Ph, BC</td>
<td>2.806 (0.28)</td>
<td>2.453 (0.74)</td>
<td>174.2</td>
<td>0.195 (73)</td>
<td>841</td>
</tr>
<tr>
<td>S/Br/Me, BC</td>
<td>2.836 (0.24)</td>
<td>2.582 (0.77)</td>
<td>168.5</td>
<td>0.18 (73)</td>
<td>818</td>
</tr>
<tr>
<td>S/Cl/n-Bu, BC</td>
<td>2.786 (0.29)</td>
<td>2.446 (0.74)</td>
<td>170.2</td>
<td>0.176 (81)</td>
<td>838</td>
</tr>
<tr>
<td>S/I/I, BC</td>
<td>2.779 (0.29)</td>
<td>2.786 (0.77)</td>
<td>177.6</td>
<td>0.21 (70)</td>
<td>819</td>
</tr>
<tr>
<td>S/Br/Br, BC</td>
<td>2.767 (0.30)</td>
<td>2.545 (0.85)</td>
<td>174.5</td>
<td>0.21 (70)</td>
<td>819</td>
</tr>
<tr>
<td>S/Cl/Cl, BC</td>
<td>2.760 (0.31)</td>
<td>2.392 (0.91)</td>
<td>165.6</td>
<td>0.21 (70)</td>
<td>819</td>
</tr>
</tbody>
</table>

$^a$C, chair; B, boat; D, diplanar; M, monoplanar.

$^b$Pauling-type bond order, BO = 10$^{-1}(\Delta d^{1.41})$.

$^c$Deviation of the Sn atom from the equatorial plane toward X.

$^d$The difference between the sum of equatorial and axial angles.

$^e$Average value.

$^f$CH$_2$Sn(SCH$_2$CH$_2$)$_2$NMe.

$^g$Pb–D, Pb–C, OPhC, Pb; two modifications with two independent molecules in each modification (CC, CC and CC, BC).

$^h$Heptacoordinate tin due to the two intermolecular coordination bonds.

$^i$4,6-Dioxastannocane t-Bu$_2$Sn(OCH$_2$CH$_2$)$_2$NMe; three molecules in the unit cell.
TABLE 60. $^{119}$Sn NMR chemical shifts $\delta(^{119}$Sn) and one-bond coupling constants $^1J(^{119}$Sn$-^{13}$C) of equatorial methylene groups in carbastannocanes $XYSn[(CH_2)_3]_2D$ 394–396$^{a,b}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1J$ (Hz)</th>
<th>$\delta$ (ppm)</th>
<th>Reference</th>
<th>Compound</th>
<th>$^1J$ (Hz)</th>
<th>$\delta$ (ppm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMe/Cl</td>
<td>$-14.3$</td>
<td>609.7</td>
<td>530</td>
<td>NMe/Me$_2$</td>
<td>$-28.0$</td>
<td>418.3</td>
<td>821</td>
</tr>
<tr>
<td></td>
<td>$-14.8$</td>
<td>612.4</td>
<td>821</td>
<td>NMe/(t-Bu)$_2$c</td>
<td>$-14.65$</td>
<td>313.4</td>
<td>821</td>
</tr>
<tr>
<td>NPr-i/Cl</td>
<td>$-2.9$</td>
<td>592.2</td>
<td>530</td>
<td>NMe/Ph$_2$</td>
<td>$-103.4$</td>
<td>459.0</td>
<td>530</td>
</tr>
<tr>
<td>NBu-i/Cl</td>
<td>$-1.5$</td>
<td>601.2</td>
<td>530</td>
<td>NBu-i/Ph$_2$</td>
<td>$-91.4$</td>
<td>448.7</td>
<td>530</td>
</tr>
<tr>
<td>NCH$_2$Ph/Cl</td>
<td>$-6.7$</td>
<td>598.2</td>
<td>530</td>
<td>NCH$_2$Ph/Ph$_2$</td>
<td>$-94.6$</td>
<td>448.6</td>
<td>530</td>
</tr>
<tr>
<td>NMe/(OSiPh$_3$)$_2$</td>
<td>$-123.9$</td>
<td>682.3</td>
<td>530</td>
<td>O/Cl$_2$</td>
<td>$+5.1$</td>
<td>599.0</td>
<td>530</td>
</tr>
<tr>
<td>NBu-i/(OSiPh$_3$)$_2$</td>
<td>$-114.3$</td>
<td>673.3</td>
<td>530</td>
<td>O/Br$_2$</td>
<td>$-28.8$</td>
<td>566.5</td>
<td>530</td>
</tr>
<tr>
<td>Nbn/(OSiPh$_3$)$_2$</td>
<td>$-117.1$</td>
<td>671.6</td>
<td>530</td>
<td>O/(OSiPh$_3$)$_2$</td>
<td>$-115.8$</td>
<td>670.5</td>
<td>530</td>
</tr>
<tr>
<td>NMe/Cl,Me</td>
<td>$+4.45$</td>
<td>509.0</td>
<td>821</td>
<td>O/Cl,Me</td>
<td>$+45.0$</td>
<td>477.3</td>
<td>821</td>
</tr>
<tr>
<td>NMe/Cl,Ph</td>
<td>$-54.8$</td>
<td>535.5</td>
<td>530</td>
<td>O/Me$_2$e</td>
<td>$-7.2$</td>
<td>393.2</td>
<td>821</td>
</tr>
<tr>
<td>NBu-i/Cl,Ph</td>
<td>$-35.4$</td>
<td>527.8</td>
<td>530</td>
<td>O/Ph$_2$</td>
<td>$-86.0$</td>
<td>430.2</td>
<td>530</td>
</tr>
<tr>
<td>NCH$_2$Ph/Cl,Ph</td>
<td>$-42.2$</td>
<td>528.3</td>
<td>530</td>
<td>S/Cl$_2$e</td>
<td>$+19.8$</td>
<td>561.0</td>
<td>821</td>
</tr>
</tbody>
</table>

$a$ Ambient$^{530}$ or 32°C$^{821}$ in CDCl$_3$ solution.

$b$ For comparison, data on some related compounds with 4-coordinated tin ($\delta(^{119}$Sn)) are: Bu$_4$Sn, $-11.5, 313.7$; Bu$_2$SnPh$_2$, $-65.9, -$; Bu$_2$SnCl$_2$, $+122.0, 424.0$; Bu$_3$SnCl, $+141.1, -$; Me$_4$Sn, $0.0, 337.8$; Me$_3$SnPh, $-28.6, 347.5$; Me$_2$SnPh$_2$, $-60.0, 365.0$; Me$_3$SnPh, $-93.0, 377.0$; SnPh$_4$, $-128.1, -$; Me$_2$Sn(CH$_2$CH$_2$)$_2$CH$_2$, $4.12, 349.4$.

$c$ In toluene- $d_8$ solution.

TABLE 61. Selected $^{119}$Sn NMR chemical shifts $\delta(^{119}$Sn) of stannocanes 388–393

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1J$ (Hz)</th>
<th>$\delta$ (ppm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i-Bu)$_2$Sn(OCH$_2$CH$_2$)$_2$NH</td>
<td></td>
<td></td>
<td>834</td>
</tr>
<tr>
<td>(i-Bu)$_2$Sn(OCH$_2$CH$_2$)$_2$NMe</td>
<td>305</td>
<td>Cl$_2$H$_2$</td>
<td>$-209.5$</td>
</tr>
<tr>
<td>Me$_2$Sn(SCH$_2$CH$_2$)$_2$NMe$^a$</td>
<td></td>
<td></td>
<td>833</td>
</tr>
<tr>
<td>Me$_2$Sn(SCH$_2$CH$_2$)$_2$O$^b$</td>
<td></td>
<td></td>
<td>818</td>
</tr>
<tr>
<td>Cl(n-Bu)Sn(SCH$_2$CH$_2$)$_2$O</td>
<td></td>
<td></td>
<td>838</td>
</tr>
<tr>
<td>Cl(n-Bu)Sn(SCH$_2$CH$_2$)$_2$S</td>
<td></td>
<td></td>
<td>838</td>
</tr>
<tr>
<td>ClPh$^b$Sn(SCH$_2$CH$_2$)$_2$NMe</td>
<td>302 K</td>
<td>Py-$d_5$</td>
<td>$-101.1$</td>
</tr>
<tr>
<td>ClPh$^b$Sn(SCH$_2$CH$_2$)$_2$O</td>
<td>302 K</td>
<td>CDC$_3$</td>
<td>$-77.1$</td>
</tr>
<tr>
<td>ClPh$^b$Sn(SCH$_2$CH$_2$)$_2$S</td>
<td>302 K</td>
<td>CDC$_3$</td>
<td>$-68.8$</td>
</tr>
<tr>
<td>ClPh$^b$Sn(SCH$_2$CH$_2$)$_2$PPh</td>
<td>302 K</td>
<td>CDC$_2$Cl$_2$</td>
<td>$-183.0$</td>
</tr>
<tr>
<td>Cl$_2$Sn(SCH$_2$CH$_2$)$_2$NMe</td>
<td></td>
<td></td>
<td>819</td>
</tr>
<tr>
<td>Cl$_2$Sn(SCH$_2$CH$_2$)$_2$O</td>
<td></td>
<td></td>
<td>819</td>
</tr>
<tr>
<td>Cl$_2$Sn(SCH$_2$CH$_2$)$_2$S</td>
<td></td>
<td></td>
<td>819</td>
</tr>
<tr>
<td>Br$_2$Sn(SCH$_2$CH$_2$)$_2$O</td>
<td></td>
<td></td>
<td>819</td>
</tr>
<tr>
<td>I$_2$Sn(SCH$_2$CH$_2$)$_2$O</td>
<td></td>
<td></td>
<td>819</td>
</tr>
<tr>
<td>Br$_2$Sn(SCH$_2$CH$_2$)$_2$S</td>
<td></td>
<td></td>
<td>819</td>
</tr>
<tr>
<td>I$_2$Sn(SCH$_2$CH$_2$)$_2$S</td>
<td></td>
<td></td>
<td>819</td>
</tr>
</tbody>
</table>

$a$ $^1J(^{119}$Sn$-^{13}$C$_{eq}) = 131$ Hz.

$b$ $^1J(^{119}$Sn$-^{13}$C$_{eq}) = 131$ Hz.

are outside the proposed range$^{542}$ for pentacoordinated tin (between $ca. -90$ and $-330$ ppm), although similar signals were detected for several other pentacoordinated compounds, such as O(CH$_2$CH$_2$)$_2$Sn(CH$_2$CH$_2$COOMe)Cl ($-18.4$ ppm)$^{738}$ and Br$_2$Sn(SCH$_2$CH$_2$)$_2$O ($-40.9$ ppm)$^{819}$. 

\[ \text{Reference} \]
Solid-state investigations show that stannocanes $\text{RR}^{'\prime}\text{Sn}((\text{SCH}_2\text{CH}_2)_2\text{D})$ ($\text{D} = \text{NMe}, \text{O}, \text{S}$) have either chair–chair (CC) and boat–chair (BC) conformations of the eight-membered cycles or some intermediate structures between these two conformations. CC and BC conformations were assumed for compounds $[\text{X}_2\text{Sn}((\text{SCH}_2\text{CH}_2)_2\text{O})]$ ($\text{X} = \text{Cl, Br, I}$) and $[\text{X}_2\text{Sn}((\text{SCH}_2\text{CH}_2)_2\text{S})]$ ($\text{X} = \text{Cl, Br, I}$), respectively. The molecules of stannocanes $\text{Cl}_2\text{Sn}((\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{D})$ ($\text{D} = \text{NMe}, \text{O}, \text{S}$) have CC, BC or boat–boat (BC) conformations, respectively.

Substitution of one chlorine atom in $\text{Cl}_2\text{Sn}((\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{NMe})$ by a second tin fragment in $[\text{ClSn}((\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{NMe})_2]$ shifts the conformation of the eight-membered cycle toward the BC state while the Sn–N distances in both compounds are nearly the same.

If the secondary bonding is strong enough, the conformation becomes boat–boat, but when the bond strength decreases, the preferred conformation is boat–chair and then a chair–chair arrangement.

A quantitative measure for the position of a given structure on the pathway between tetrahedron and TBP is the displacement ($\Delta_{\text{Sn}}$) of the central atom from equatorial plane and the difference between the sums of the equatorial and axial angles, $\Delta \Sigma (\theta)$. Selected structural parameters of known stannocanes are summarized in Tables 58 and 59.

The transition from the dimethylstannocanes $\text{Me}_2\text{Sn}((\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{D})$ ($\text{D} = \text{NMe, O}$) to the monochlorides $\text{ClMeSn}((\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{D})$ ($\text{D} = \text{NMe, O}$) leads to low-field shifts of the $^{119}\text{Sn}$ signals in the NMR spectra while the signals of the dichlorides $\text{Cl}_2\text{Sn}((\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{D})$ ($\text{D} = \text{NMe, O}$) are shifted upfield as a result of the so-called ‘U-shape’ dependence of $\delta(^{119}\text{Sn})$ on the number of electronegative substituents at the tin atom.

The dynamic processes observed by NMR studies are interpreted in terms of a dissociation–inversion (DI) mechanism or an ‘in-out’ equilibrium. The dynamic behavior of the 4,6-dicarbastannocanes is interpreted in terms of a combined DI and ring-inversion mechanism.

2. Bicyclic analogues of stannocanes

Diorganotin complexes containing a tridentate ligand are among hypervalent organotin compounds which are of interest owing to their antitumour activity and include $\text{N}_x\text{N}_y\text{O}_z$, $\text{N}_x\text{O}_y\text{O}_z$, $\text{N}_x\text{O}_y\text{S}_z$- and $\text{O}_x\text{C}_y\text{O}_z$-chelates. Early examples of dipeptide derivatives with the common structure established by X-ray studies are: $(\text{t-Bu})_2\text{Sn}(\text{Gly-GlyO})$, $\text{Ph}_2\text{Sn}(\text{Gly-GlyO})$, $(\text{c-Hex})_2\text{Sn}(\text{Gly-AlaO})$, $\text{Et}_2\text{Sn}(\text{Gly-ValO})$, $\text{Me}_2\text{Sn}(\text{Gly-MetO})$ and $\text{Et}_2\text{Sn}(\text{Gly-TyrO})$. The polyhedron around Sn in all complexes bearing a dianionic N,N,O-chelate ligand corresponds to that found in diorganogermainium derivatives of dipeptides (Section VI.B). It is a distorted TBP with the peptide nitrogen and two carbon atoms in equatorial positions and the oxygen of the unidentate carboxylate group and the amino nitrogen in the apical positions. The tridentate dipeptide ligands are usually nearly planar. The $\text{N}_{ax}$–Sn bond lengths at 2.25–2.30Å are significantly longer than the $\text{N}_{eq}$–Sn distances (around 2.10Å). The
latter are very short and even shorter than the sum of the N and O covalent radii (2.154 Å, see Table 1), indicating a strong bond. The analogous Sn—N(peptide) bond of Me₂(SnGlyGlyO) resists fast hydrolysis in solution, in contrast to the two apical bonds of Sn to the amino N and carboxylate O⁸⁵¹.

One of the two tin atoms in [Et₂Sn(Gly-HisO)]₂·MeOH has a TBP environment, as above, while the second is hexacoordinate⁸⁵². Recently, the molecular dynamics of tryptophan-containing dipeptide complexes, i.e. Me₂Sn(Trp-AlaO), Ph₂Sn(Trp-AlaO) and Me₂Sn(Trp-TyrO), were investigated by a variable-temperature ¹¹⁹Sn Mössbauer spectroscopy⁸⁵³. The complexes behaved as Debye solids and, in particular, the calculated mean-square displacements of the tin atom confirm the occurrence of monomeric structures. An X-ray diffraction of Me₂Sn(Trp-AlaO)·MeOH reveals a distorted TBP arrangement at the tin center, with the two methyl carbons (C—Sn—C123°) and the deprotonated peptide nitrogen (Neq—Sn 2.064 Å) in equatorial positions while the terminal amino nitrogen (N→Sn 2.272 Å) and the terminal carboxylate oxygen are in apical positions (O—Sn—Nax151.5°).

The pentacoordinate organotin compounds ⁴¹⁶a–c also contain a tridentate dianionic N,N,O-chelate ligand⁸⁵⁴,⁸⁵⁵. The structure of ⁴¹⁶c⁸⁵⁴ was determined by X-ray diffraction which conformed the rigid polycyclic structure proposed on the basis of ¹H, ¹¹B, ¹³C, ¹⁵N and ¹¹⁹Sn NMR data in solution (δ¹¹⁹Sn −150.4 ppm)⁸⁵⁵. In contrast, the dimethyltin compound ⁴¹⁶a displays a fluxional structure in solution.

Several series of bicycloazastannoxides bearing dianionic N,O,O-chelate ligands were described. Diorganotin 2,6-pyridinedicarboxylates 2,6-C₅H₃N(COO)₂SnRR¹ ⁴¹⁷ (R, R¹ = Me, Et, Pr, i-Pr, Bu, Ph) were investigated for antitumour activity⁸⁵⁶,⁸⁵⁷. Among them, organotin derivatives of 1,2- and 1,7-dicarba-closo-dodecaboranes, ⁴¹⁷a (R = R¹ = o-(C₂B₁₀H₁₁-9)) and ⁴¹⁷b (R = R¹ = m-(C₂B₁₀H₁₁-9)), were recently synthesized by the reaction of the corresponding ortho- and meta-carboranyl tin oxides with 2,6-pyridinedicarboxylic acid and their structures were proved by ¹¹⁹Sn Mössbauer, ¹H, ¹³C and ¹¹⁹Sn NMR spectroscopy⁸⁵⁸.

Other representatives of the N,O,O-chelates are diorganotin-N-arylidene-α-amino acid complexes (⁴¹⁸)⁸⁵⁹,⁸⁶⁰, including ⁴¹⁸a⁸⁵⁹ and ⁴¹⁸b⁸⁶⁰, for which five-coordinate monomeric structures were established by X-ray studies. The tridentate ligands in these compounds are near-planar. The tin centers have a distorted TBP geometry with the two
carbon atoms and the imino nitrogen in the equatorial positions and the two oxygens in the axial positions. The OSnO angles are 155.9°, 157.2° and 159.4°(av) for \(418\text{a}, 418\text{b}\) and \(418\text{c}\), respectively (see below). The two axial Sn—O bonds (2.15 and 2.08 Å in \(418\text{a}\), 2.12 and 2.09 Å in \(418\text{b}\) and 2.129 (av) and 2.061 (av) Å in \(418\text{c}\) and the corresponding equatorial N → Sn bond of 2.13, 2.14 and 2.189 (av) Å are among the shortest reported for related complexes. The shorter O—Sn bond length involves the phenolic oxygen.

![Diagram of \(418\text{a}\) and \(418\text{c}\)](image)

\(418\text{a}\) R = Bu, R\(^1\) = i-Pr, R\(^2\) = R\(^3\) = R\(^4\) = H
\(418\text{b}\) R = Ph, R\(^1\) = R\(^2\) = H, R\(^3\)R\(^4\) = o-C\(_6\)H\(_4\)
\(418\text{c}\) R = Ph, R\(^1\) = H, R\(^2\) = Me, R\(^3\) = R\(^4\) = H

A similar geometry is found for bicycloazastannoxide \(419\text{a}\) (OSnO 159.5°, O—Sn 2.103 and 2.085 Å, N → Sn 2.241 Å)\(^861\), the salicylhydrazone derivatives \(420\text{a}\) and \(420\text{b}\) (OSnO 153.5°, O—Sn 2.160 and 2.094 Å, N → Sn 2.174 Å in \(420\text{a}\)\(^862\), and OSnO 156.2° and N → Sn 2.152 Å in \(420\text{b}\)\(^863\) and for both tin atoms in the ditin species \(421\text{a}\) (OSnO 151.4°, O—Sn 2.059, O → Sn 2.210, and N—Sn 2.133 Å)\(^864\).

The reactions of mono-sodium or -potassium salts of \(N-(2\text{-hydroxyacetophenone})\)glycine with dichlorides \(R_2\text{SnCl}_2\) (R = t-Bu, Vin, Ph) were recently investigated yielding glycinate, \(418\text{c}\), only for R = Ph\(^865\). In the other cases, the adducts with (t-Bu)\(_2\)SnCl\(_2\), \(422\text{a}\), and with a water molecule, Vin\(_2\)Sn(2-OC\(_6\)H\(_4\)C(Me)==NCH\(_2\)COO)-H\(_2\)O \(423\), respectively, were isolated from the reaction mixtures. In turn, reaction of \(418\text{c}\) with Ph\(_3\)SnCl yielded the 1 : 1 adduct \(422\text{b}\) in which the two tin atoms, like in \(422\text{a}\), are joined via the carbonyl atom of the ligand to form a rare mixed diorganotin/triorganotin species.

X-ray structural determinations of \(418\text{c}\) reveal that the polyhedron around Sn in \(418\text{c}\) is a distorted TBP with nitrogen and two carbon atoms in equatorial positions and two
Oxygens of the phenolic and unidentate carboxylate groups in the apical positions. Similar features are found in structures 422a and 422b, except for the presence of bidentate bridging carboxylate residues. A comparison of chemically equivalent geometric parameters for 418c with those about the Sn1 atom in 422b shows remarkable consistency; the Sn1 atom lies 0.032 Å in 418c and 0.038 Å in 422b, respectively, out of the trigonal plane in the direction of the phenolic oxygen. Unlike in complexes 418c, 422a and 422b, the tin atom in 423 is six-coordinate and distorted octahedral due to the coordination of a water molecule. NMR data indicate that the 1 : 1 adducts 422a, 422b and 423 dissociate in noncoordinating solvents with formation of five-coordinate species.

Chelates 419b and 424 are examples of diorganotin complexes with a tridentate dianionic ligand bonding through three different donors — N, O and S. According to the X-ray data, the tin atom in these compounds is five-coordinate and has a distorted TBP arrangement with equatorial nitrogen and two carbons. A similar geometry was found for chelate, 425, which is a rare example of a diorganotin complex containing a tridentate trianionic ligand. Corresponding geometric parameters for 419b and its oxo analogue 419a are very similar (OSnS 157.4° against 159.5° for OSnO in 419a; 2.093 and 2.217 Å for O—Sn and N → Sn, respectively, against 2.085 and 2.241 Å in 419a). In the case of 425, the OSnO angle is 151.6° and both O—Sn and N—Sn distances are 2.111, 2.115 and 2.146 Å, i.e. close to the corresponding ordinary bonds in such complexes.
A special feature of chelates 421a\textsuperscript{864} and 424\textsuperscript{867} is a coordinative O → Sn bond, but not an N → Sn bond as in other chelates, with tridentate ligands discussed in this section. In consequence, the N–Sn distances of 2.133 and 2.147 Å in 421a and 424, respectively, are shorter than those, e.g., in 419a and 419b (see above) and the O → Sn bond lengths of 2.210 and 2.164 Å are correspondingly longer. The S–Sn distances in both thio complexes, 419b and 424, are practically equal (2.496 and 2.502 Å).

The five-coordinate complexes of type 421 possess a rigid structure, which is retained in solution as indicated by comparing the $^{119}$Sn NMR in solution and in the solid state\textsuperscript{864}. For 421a–c, isotope-induced chemical shifts $^1\Delta^{12/13}$C($^{119}$Sn) were determined for the first time for five-coordinate tin nuclei at natural abundance of $^{13}$C. A positive sign of $^1\Delta^{12/13}$C($^{119}$Sn) was found, in contrast with most tetracoordinate organotin compounds.

The synthesis of the first monoanionic O,C,O-pincer ligand 4-\textit{t}-Bu-2,6-[PO(OEt)$_2$]$_2$C$_6$H$_2$ and its application for the preparation of penta- and hexacoordinate species were reported most recently (Scheme 19)\textsuperscript{147,762,769}. Attempts to synthesize organotin cations starting from intramolecularly coordinated organotin compounds 426a and 426b resulted in an intramolecular donor-assisted cyclization reaction with elimination of EtCl (EtX, PhH or PhX) leading to neutral pentacoordinate 2,3,1-benzoxaphosphastannole derivatives 427a and 427b or hexacoordinate dihalides 428a and 428b. A similar dihalide was isolated by treatment of 427a with an excess of Me$_3$SiBr. Pentacoordinate cationic tin species of the type 429, which may be described by two resonance structures, are suggested as intermediates in these cyclizations.

X-ray crystallography of stannole 426a revealed a slightly distorted TBP center, with the two oxygens occupying axial positions (OSnO 160.2°, O–Sn 2.125, O → Sn 2.396 Å) and the three carbon atoms occupying equatorial positions\textsuperscript{769}. The configuration at tin can be classified as being located on the T → TBP pathway\textsuperscript{818,819}. The estimation of the position along this path by using the difference between the sums of the equatorial and axial angles (0° for the ideal T, 90° for ideal TBP) gives a value of 77.7° for 426a. The tin atom deviates from the equatorial plane by 0.136 Å away from the dative O → Sn bond.

The action of an excess Me$_3$SiBr on 426a led to its complete transesterification product, 4-\textit{t}-Bu-2,6-[PO(OSiMe$_3$)$_2$]$_2$C$_6$H$_2$SnPh$_3$. The subsequent treatment of the latter with water afforded 2,3,1-benzoxaphosphostannole 4-\textit{t}-Bu-2,6-[PO(OH)$_2$]$_2$C$_6$H$_2$SnPh$_2$ and benzene. As a result of the high donor capacity of the intramolecularly coordinated phosphonyl groups, the similar reaction of stannole 427a with Me$_3$SiBr proceeds with Sn–C rather than P–O(Sn) bond cleavage, yielding the hexacoordinate dibromide 4-\textit{t}-Bu-2-[PO(OEt)$_2$]-6-[PO(OEt)(OSiMe$_3$)]C$_6$H$_2$SnPhBr$_2$ which is related to dihalides 428a and 428b.
Finally, the hexacoordinate trichloride 430 also undergoes intramolecular cyclization by heating to provide the dimeric dichloro-substituted 2,3,1-benzostannole 431 as a mixture of the two diastereomers (equation 73). An X-ray crystal structure analysis of the major diastereomer of 431 shows that the tin centers adopt a distorted octahedral coordination geometry owing to both intermolecular and intramolecular O—Sn interactions with the phosphonyl group acting as a bidentate bridging ligand.

SCHEME 19. Intramolecular cyclization of organotin compounds bearing O,C,O-coordinating ligand
16. Hypervalent compounds of organic germanium, tin and lead derivatives

C. Tricyclic Complexes

1. Stannatranes and their analogues

a. Synthesis and reactivity. Several main types of stannatranes, 432–436,554,820 and their tricyclic analogues, such as tribenzostannatranes 437, 438,554,555,820, stannatranones 439,555,820,869 and azastannatranone 440,869, carbastannatranes 441 and 442,827,828, thia- stannatranes 443 and azastannatranes 444–447,870,871, have been described.

Generation of atrane framework in stannatranes and their analogues may be generally performed by the same methods applied to the corresponding derivatives of germanium (Section VI.C.1.a). For example, re-alkoxylation (similar to equation 48) was used for the preparation of 1-organostannatranes 432, 1-alkoxystannatranes 433 and 1-organoazastannatranones 439,554,603. Reactions of polyorganostannosesquioxides \( (RSnO_1)_n \) or polyorganostannonic acids \( [RSn(O)OH]_n \) with TEAA in aromatic solvents with and without KOH proceed similarly to equation 49 and lead to analogous products,554,820. 1-Organothiastannatranes 443 were prepared from polyorganostannonic acids and tris(2-mercaptoethyl)amine in the presence of KOH,554,820. Preparation of atranes 432 or 443 from polydiorganostannoxides includes elimination of one organic radical from the tin atom (equation 74),554,820.

\[
1/n(R_2SnO)_n + (HYCH_2CH_2)_3N \xrightarrow{\text{xylene, KOH}} RSn(YCH_2CH_2)_3N \quad (432) Y = O \\
(433) Y = S 
\]

Reaction of mixed polydiorganostannoxides (RPhSnO)_n with aminotriacetic acid proceeds with elimination of the phenyl group and gives stannatranones 439,869.

Use of other types of organotin compounds for the preparation of stannatranes is less common. Alcoholysis of aminostannane \( Sn(NMe_2)\_4 \) with TEAA and methanol was used for the synthesis of 1-methoxystannatranate 433 (R = Me),554. Reaction of tetraacyloxystannanes with \( (Et_3SnOCH_2CH_2)_3N \) leads to acyloxystannatranes 434 (R = Me),554 while 1-alkylstannatranes 432 were prepared from \( RSnCl_3 \), TEAA and MeONa,554.

Reaction between \( Me_2N(CH_2)_3Sn(OPh)Ph_2 \) (239e) and TEAA proceeds smoothly due to the high reactivity of hypervalently activated organotin compounds and gives stannatran 432 (R = (CH_2)_3NMe_2),644. Its \( ^{119}\text{Sn} \) NMR appears between those of stannatranes with penta- and hexacoordinated tin atoms. This fact was interpreted as a result of a fast equilibrium on the NMR time scale.
Similar reactions of $^{239}$e or Me$_2$N(CH$_2$)$_3$SnPh$_3$ (228) and nitrilotriacetic acid led to the formation of stannatranone 439 ($R = (\text{CH}_2)_3\text{NMe}_2$) and, unexpectedly, to the N-oxide derivative 439 ($R = (\text{CH}_2)_3\text{N(O)Me}_2$). According to X-ray data, the latter contains a pentacoordinate tin with intramolecular Sn–N and Sn–O distances of 2.231 and 2.101 Å, respectively$^{644}$.

The C–Ph bond in compounds 432 ($R = \text{Ph}$) or 438 may be cleaved easily by I$_2$ or HgI$_2$, leading to formation of PhI or PhHgI and the corresponding iodo derivatives or cation–anion complexes with tetrahedral tin in the cation and a HgI$_3^{–}$ anion$^{555}$.

Initial approaches to carbastannatranes 441 and 442 were based on the reaction of SnCl$_4$ with the trifunctional Grignard reagent N(CH$_2$CH$_2$CH$_2$MgCl)$_3$ or of Me$_2$SnCl$_2$ with tris(stannyl)amine N(CH$_2$CH$_2$CH$_2$SnMe$_3$)$_3$. Both methods led to chloride 442b (442,

---

(432) $X = R$
(433) $X = \text{OR}$
(434) $X = \text{OCOR}$
(435) $X = \text{Hal}$

(436) $X = \text{Ar, } Y = \text{Me}$

(437) $X = \text{Alk}$
(438) $X = \text{Ph}$

(439) $X = \text{R, } Y = O$
(440) $X = \text{R, } Y = \text{NMe}$

(441) $X = \text{R}$
(442) $X = \text{Hal}$

(443) $X = \text{R, } Y = S$
(444) $X = \text{R, } Y = \text{NH}$
(445) $X = \text{R, } Y = \text{NMe}$
(446) $X = \text{NMe}_2, Y = \text{NMe}$
(447) $X = \text{Hal, } Y = \text{NMe}$
X = Cl$^{827}$. Introduction of SnCl$_4$ into the last reaction gave the product under milder conditions in higher yields$^{872}$. Reaction of 442b with methylolithium gave 441, R = Me (441a)$^{826, 827}$. Carbastannatrane 441a was recently exchanged with Pr$_3$SnF and gave 1-fluorocarbastannatrane 442a; the latter was also prepared by exchange reaction of halides 442b–d ((b) X = Cl, (c) X = Br, (d) X = I) with Bu$_4$NF·H$_2$O$^{828}$. In all the reactions the fluoride 442a was isolated and characterized as monohydrate 442a·H$_2$O.

Due to the relative lability of the apical Sn–R bond in carbastannatranes 441, these compounds are interesting synths for further chemical transformations$^{636, 873}$. For example, under ultrasonic induction even methanol is capable of splitting the Me–Sn bond in carbastannatrane 441a$^{819}$.

Transamination reaction similar to equation 60 is also a general approach to azastannatranes. In the case of tin the reaction proceeds more readily (at room temperature and without catalyst) than for germanium derivatives and the yields of the desired products 444 and 445 (R = Me, n-Bu, t-Bu, Ph) and 446 are generally higher$^{820, 870, 874}$. The axial NMe$_2$ group in 446 is labile to substitution, affording either 1-haloazastannatranes 447 (Hal = F, Cl, Br, I) in reactions with corresponding ammonium salts or 1-(phenylalkynyl)-N,N',N''-trimethylazastannatrane and bis(N,N',N''-trimethylazastannatranyl)acetylene in reactions with phenylacetylene or acetylene, respectively$^{875}$.

Compound 445 (R = n-Bu) demonstrates the ability of azastannatranes to participate in transmetallation reactions with metal alkoxides N≡Mo(OBu-t)$_3$, OV(OPr-i)$_3$ or N-substituted tris(siloloy)vanadium(V) imides to prepare N≡Mo(NMeCH$_2$CH$_2$)$_3$N$^{874}$, O≡V(NMeCH$_2$CH$_2$)$_3$N$^{874}$ and RN≡V(NMeCH$_2$CH$_2$)$_3$N (R = SiMe$_3$, CMe$_3$)$^{871}$, respectively, in high yields.

Reaction of carbastannatrane 442b (Hal = Cl) with AgBF$_4$ yields the tetrafluoroborate salt [N(CH$_2$CH$_2$CH$_2$)$_3$Sn]$^+$BF$_4$$. Its ionic structure in solution was confirmed by $^{119}$Sn NMR chemical shift (103 ppm), which indicate a tetracoordinate tin atom$^{827, 876}$. However, reactions of azastannatranes 445 (R = Me, n-Bu, Ph) with BF$_3$·Et$_2$O lead to six-coordinated compounds 448 (equation 75)$^{877}$.

The tricyclic atrane framework is preserved under hydrolysis conditions and the hydrolysis product 449 is formally an adduct of 445, R = Me with HF and HBF$_4$ (equation 75). According to X-ray data, the ionic 449 contains a six-coordinate tin atom, with the cation stabilized by three coordinating amino groups$^{877}$.

The first stannatrane containing a tin–metal bond, the osmium derivative 450, was synthesized from TEAA and a triiodostannylosmium complex (Scheme 20)$^{878}$.

b. Structure and physical properties. In contrast to germatranes, the stannatranes without bulky substituents at the tin atom are capable of participating in additional intermolecular interactions. Most stannatranes form intermolecular associates in their crystals. These compounds are moderately stable in water and soluble in polar solvents. The solubility decreases at lower temperatures, possibly as a result of oligomerization. Molecules of stannatranes are noticeably associated in concentrated solutions. For example, 1-methylstannatrane (432a) forms trimers in nonpolar solvents whereas 1-t-butylstannatrane (432b) exists only as monomer in all solvents studied$^{554, 820, 879}$. In contrast to regular stannatranes, thiastannatranes 443 (R = Me, t-Bu) and azastannatranes 444–447 are always monomeric in solution$^{535, 820}$.

The structures of stannatranes in solution were deduced from the decreased $^2J(^{119}$Sn–C−$^1$H) coupling constants in comparison with similar tetracoordinated compounds (e.g. MeSn(CNMeCH$_2$CH$_2$)$_3$N (i.e. of type 445) $^2J(^{119}$Sn−C−$^1$H) = 61.0 Hz; MeSn(NEt$_2$)$_3$68.7 Hz; MeSn(SCH$_2$CH$_2$)$_3$N (i.e. of type 446) 60.0 Hz; MeSn(SEt)$_3$ 65.2 Hz)$^{879}$. The temperature dependence of the NMR spectra of 1-organostannatranes
SCHEME 20. Synthesis of stannatrane 450 containing the tin—osmium bond
substituted by sterically bulky substituents on Sn indicate molecular association in organic solvents. The associates are assumed to have a trimeric cyclic structure. The increase in size of the substituent R (e.g. R = t-Bu, o-MeC₆H₄) decreases the stability of the associates.

Stannatranes (Table 62) were studied less by X-ray diffraction than germatranes (see Table 40). Only some stannatranes have ‘regular’ atrane structures with pentacoordinated tin atom. Compound 432b (R = 2-MeOC₆H₄) was the first monomeric stannatrane for which atomic coordinates were reliably determined. The central atom has a distorted TBP environment, opened slightly toward the methoxy group. Comparison of stannatrane 432b and 1-phenylgermatrane 189a (in particular, the ∆M (M = Ge, Sn) values; see Table 40) suggests a weaker coordination in the tin derivative.

A trimeric structure of 1-methylstannatrane (432a) with a roughly pentagonal bipyramidal central and distorted octahedral terminal atoms of tin has been discussed. Strong association between the molecules results from the presence of bridged oxygen atoms and hydrogen bonds with six molecules of water. At −50 °C the NMR spectra display three resonances, two of which are in the area of hexacoordinated tin compounds (−356.4 and −352.3 ppm) while the third signal (−532.9 ppm) indicates the presence of heptacoordinated tin. The 119Sn chemical shift of a ‘regular’ pentacoordinated 1-t-butyliostannatrane 432c is −245.5 ppm. These facts testify that stannatrane 432a retains its trimeric units in solution.

<table>
<thead>
<tr>
<th>TABLE 62. Selected structural parameters of stannatranes XSn(OCH₂CH₂)₃N and their tricyclic analogues</th>
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</thead>
<tbody>
<tr>
<td>Compound</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td><strong>Stannatranes</strong></td>
</tr>
<tr>
<td>432b</td>
</tr>
<tr>
<td>432a</td>
</tr>
<tr>
<td>432c</td>
</tr>
<tr>
<td>450</td>
</tr>
<tr>
<td>422a</td>
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<tr>
<td><strong>Carbastannatranes</strong></td>
</tr>
<tr>
<td>442c</td>
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<tr>
<td>442b</td>
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<tr>
<td>442b</td>
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<tr>
<td>442d</td>
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<tr>
<td>442a</td>
</tr>
<tr>
<td>441a</td>
</tr>
<tr>
<td><strong>Azastannatranes</strong></td>
</tr>
<tr>
<td>449a-C₆H₆</td>
</tr>
<tr>
<td>429</td>
</tr>
<tr>
<td>444c</td>
</tr>
<tr>
<td>444c²</td>
</tr>
</tbody>
</table>

a Deviation of the Sn atom from equatorial plane toward X.
b Trimer.
c Hexagonal.
d Monoclinic.
e Tetrameric.
f Two independent molecules in the unit cell.
X-ray diffraction of the first metal-bound stannatrane 450 shows that the tin atom has a significantly distorted TBP environment with the Os and N atoms in axial positions. The Sn–N bond length is only a little longer than the distance in 1-organostannatranes 432a–c (Table 62). According to the authors, the virtual absence of N–Si interaction in the Si analogue of 450 (N–Si 3.176 Å; typical values for silatranes are in the range of 2.00–2.26 Å) is indicative of the greater ability of tin compared to silicon to form hypervalent compounds.

In the cation of complex 449, the transannular Sn–N bond length (2.29 Å) is shorter than those in 444c and 446 (Table 62). This difference is ascribed to the positive charge in the cation 449. A slight elongation of the Sn–F bond in 449 (by 0.08 Å) in comparison with a ‘standard’ single Sn–F bond (1.96 Å) is also in agreement with this suggestion.

Carbastannatrane 441a is probably the first pentacoordinated tetraorganotin compound whose crystal structure was confirmed by the X-ray method.

1-Fluorocarbastannatrane (442a) is a tetramer held together by intermolecular Sn···F interactions (ca 2.80 Å) and also by F···H and O···H hydrogen bridges. It is the first example of an intermolecular hexacoordinated triorganotin halide. The average lengthening of the Sn–F bonds is about 0.158 Å compared to an Sn–F single bond (1.96 Å) and, according to the authors, this is a result of intramolecular coordination as well as of intermolecular coordination accompanied by hydrogen bridging. In contrast to 442a, 1-halocarbastannatranes 442b–d (Hal = Cl, Br, I) retain a typical atrane structure with pentacoordinate tin atom. The shortest N→Sn distances have close values. It was suggested that the electronegativity and the lone pair interaction of the halogen substituents are counteractive and compensate one another at bromine.

Comparison of 1-chlorocarbastannatrane 442b with its bicyclic ClPhSn(CH2CH2CH2)2NMe and monocyclic ClR2Sn(CH2)3NMe2 (R = Me, Ph) analogues shows that the N→Sn coordination weakens upon transition from tri- to bicyclic and further to monocyclic systems (Scheme 21). In accordance with the theory of hypervalency, this process is accompanied by the gradual shortening of the second axial bond (Cl–Sn).

2. Other tricyclic derivatives

TBP organotin complexes of the type RSn[E(C6H4O-2)3] (E = N, 437, and E = P, 438), where four of the five coordination sites are occupied by the four donor atoms of a tetridentate tripodal trianionic ligand, are well-known. Most recently, their analogous 451a–e were prepared by the reaction of organotrichlorostannanes with the lithium salt of the corresponding ligand, generated in situ from the thiol and BuLi (equation 76). Compound 451e undergoes a metathesis reaction with FeCl3 to give the purple iron complex ClFe[P(3-Me3SiC6H3-2S)3] in one step.

X-ray structure determinations of 451c–e showed a distorted TBP geometry at tin, which is located above the S3 plane. The distortion from the ideal geometry is illustrated by the CSnP angles of 178.5°, 163.3° and 177.1°, as well as by the sum of the SSnS equatorial angles of 354.1°, 352.6° and 350.4°, respectively. The mean length of the equatorial Sn–S bonds is about 2.51 Å, compared to 2.43 Å of a usual Sn–S bond in tetrahedral compounds. The corresponding P→Sn bond lengths in 451c–e of 2.516, 2.513 and 2.613 Å are shorter than that in the related pentacoordinate organotin complexes 268b and 271d (Section VII.A, Tables 45 and 47).
16. Hypervalent compounds of organic germanium, tin and lead derivatives

\[
\begin{align*}
\text{N→Sn (Å)} & \quad 2.38 & 2.43 & 2.58 \\
\text{Sn–Cl (Å)} & \quad 2.554 & 2.550 & 2.498 \\
\Delta \text{Sn (Å)}^a & \quad 0.384 & 0.211 & 0.15 \\
\Delta \Sigma^b & \quad 50 & 70 & 76 \\
\delta^{119}\text{Sn (ppm)} & \quad 19.4 & -54.8 & -138 \\
J^{(119}\text{Sn–}^{13}\text{C} (\text{Hz}) & \quad 477 & 535 & 572 \\
\end{align*}
\]

\(a\) Toward the chlorine. \(b\) The difference of the sums of equatorial and axial angles

SCHEME 21. Comparison of selected X-ray and NMR data for some mono-, bi- and tricyclic compounds

\[
\text{RSnCl}_3 + \left(\begin{array}{c}
\text{SLi}
\end{array}\right) \xrightarrow{\text{THF, °C}} \text{RSnCl}_3 + \left(\begin{array}{c}
\text{SLi}
\end{array}\right)
\]

(451a) R = Me, \(R^1 = R^2 = H\)  
(451b) R = Bu, \(R^1 = R^2 = H\)  
(451c) R = Ph, \(R^1 = R^2 = H\)  
(451d) R = Ph, \(R^1 = H, R^2 = Me\)  
(451e) R = Ph, \(R^1 = \text{SiMe}_3, R^2 = H\)

(76)

VIII. PENTACOORDINATE CATIONIC COMPOUNDS

Intermolecular and intramolecular donor–acceptor interactions are known as a means for stabilization of trivalent germeyl \(^{496}\), stannyl \(^{8,636,885–888}\) and plumbyl \(^{889}\) cations.

A. Germanium Intramolecular Complexes

Synthesis of cation–anion complexes \([L_2\text{Ge}(H)(B)]^{1+}\text{OTf}^-\) (123c-B, L is the potential bidentate 8-methoxynaphthyl ligand, B = \(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2, \text{H}_2\text{O, DMSO}\) containing...
a solvated germyl cation was discussed in Section VI.A.1.a. An X-ray diffraction analysis of $123c \cdot H_2O$ reveals the presence of a dimeric form in which $O-H$ hydrogen bonds between the hydrogen of $H_2O$ and the oxygen atom of the triflate anion connect the two monomers (Scheme 22). The Ge atom shows a slightly distorted TBP geometry with only one methoxy group coordinated to the germanium in each monomer (omitting the rather long $O \cdots Ge$ contact, 2.785 Å, of the second methoxy group). The apical positions are occupied by one methoxy group and an $H_2O$ molecule at a $(Me)OGeO(H_2)$ angle of 168.4°, with $O-Ge$ distances of 2.425 and 1.95 Å, respectively. The deviation of the Ge atom from the equatorial plane defined by the hydrogen and two carbon atoms is 0.27 Å in the direction of the water oxygen. Consequently, water is better leaving from Ge in $S_N-Ge$ reactions as compared to the triflate anion in $123c$, with a coordination site being the same for both compounds. This contrasts drastically with the cation–anion H-associate structure of the hydrochloride PhCONHCH$_2$SiMe$_2$OH $\cdot HCl$ where the central atom has a TBP environment with $O$ atoms in axial positions, but the silicon deviates from the equatorial plane ($\Delta Si$) by 0.024 Å in a direction away from the ‘oxonium’ oxygen atom.

The 1H NMR and IR spectra are consistent with a positively charged germanium center in $123c \cdot H_2O$ showing the low-field chemical shift displacement of the $GeH$ resonance (7.76 ppm) and a very high $v(Ge-H)$ value (2165 cm$^{-1}$).
The reactions of dichlorides \((L^n)_2\text{GeCl}_2\), where \(L\) is the bidentate lactamomethyl C,O-chelating ligand, \(n = 5–7\) (the size of the lactam ring, cf. equation 77), with \(\text{Me}_3\text{SiOTf}, \text{Me}_3\text{SiX}\) \((X = \text{Br, I})\) and lithium or silver salts \((\text{LiBr}, \text{LiI}, \text{LiClO}_4, \text{AgF})\) give rise to two types of compounds, depending on the nature of monodentate ligands in the product\(^{494,496}\). If the nucleofugalities of the entering \((\text{F or Br})\) group is close to that of the leaving \((\text{Cl})\) group, both chlorine atoms are replaced by the nucleophile (Section X.B.2). These reactions proceed with retention of the octahedral configuration of the initial dichlorides, where the carbon atoms are in \textit{trans} positions and the coordinating oxygen and halogen atoms are in \textit{cis} positions with respect to each other. If the nucleofugalities of the entering \((\text{OTf, OCIO}_3, \text{BF}_4, \text{I or I}^3)\) and leaving \((\text{Cl})\) group differ significantly, only one chlorine atom is replaced by the nucleophile regardless of the ratio of reactants \((1 : 1\) or \(1 : 2\)) (equation 77), leading to products \(452–458\) with a change in the coordination of the Ge atom to \((5 + 1)\).

\[
\begin{align*}
(L^n)_2\text{GeX}_2 & \quad \text{MY} = \text{Me}_3\text{SiOTf, Me}_3\text{SiI, LiI, LiClO}_4, \text{AgBF}_4 \\
(\text{X} = \text{Cl, Br}) & \quad (L^n)_2\text{Ge}(\text{X})\text{Y} \\
(452a) & n = 1, \text{X} = \text{Cl, Y} = \text{OTf} \\
(452b) & n = 2, \text{X} = \text{Cl, Y} = \text{OTf} \\
(452c) & n = 3, \text{X} = \text{Cl, Y} = \text{OTf} \\
(453) & n = 3, \text{X} = \text{Br, Y} = \text{OTf} \\
(454a) & n = 1, \text{X} = \text{Cl, Y} = \text{OCIO}_3 \\
(454b) & n = 3, \text{X} = \text{Cl, Y} = \text{OCIO}_3 \\
(455) & n = 3, \text{X} = \text{Cl, Y} = \text{I} \\
(456) & n = 3, \text{X} = \text{Cl, Y} = \text{I}^3 \\
(457) & n = 3, \text{X} = \text{Br, Y} = \text{I} \\
(458) & n = 3, \text{X} = \text{F, Y} = \text{BF}_4 \\
\end{align*}
\]

Analogously, bromide-triflate \(453\) and bromide-iodide \(457\) were synthesized by the reaction of dibromide \((L^7)_2\text{GeBr}_2\) with \(\text{Me}_3\text{SiOTf}\) and \(\text{Me}_3\text{SiI}\), respectively\(^{494}\). Unexpectedly, the fluorotetrafluoroborate \([L^7)_2\text{Ge(}\text{F})_2\text{][BF}_4]\) \(458\) was obtained by replacing one chlorine by fluorine and another one by a \text{BF}_4 group, and treating the corresponding dichloride with \text{AgBF}_4\(^{893}\).

According to X-ray structural determinations (Table 63), the coordination environment at the Ge atom in complexes \(452–458\) is intermediate between an Oh and a TBP with the C and O atoms and the monodentate ligands located in \textit{trans} positions relative to each other. Consequently, in triflates \(452a–c, 453\) and perchlorate \(454b\) the Ge atom has octahedral coordination strongly distorted toward a monocapped TBP, while the iodides \(455, 457\) and the triiodide \(456\) are almost ionic with weak Ge···I coordination \((4.18–4.26\ \text{Å})\). The Ge–Cl bond lengths in \(452a–c, 454a, 455\) and \(456\) \((2.13–2.21\ \text{Å})\), as well as the Ge–Br bond lengths in \(453\) and \(457\) \((2.31\ \text{and} 2.37\ \text{Å})\), respectively) are the shortest such distances.
observed in hypervalent germanium structures\(^2\), whereas the Ge—O(Tf) and Ge—O(ClO\(_3\)) bond lengths (3.02–3.35 Å) are, on the contrary, the longest. Thus, the structures under consideration are more or less close to TBP, where two carbon and halogen atoms are in the equatorial positions and the axial positions are occupied by the two coordinating oxygen atoms, and consequently they may be viewed as doubly-intramolecularly coordinated germacenium ions, or tight ion pairs. Finally, tetafluoroborate \(^458\) has a typical ionic structure, and the array of the Ge atom is a distorted TBP opened, as in iodides \(^455\) and \(^457\), toward the BF\(_4^-\) anion\(^896\).

Note that the electronic system of the Ge atom together with its coordination environment may be regarded as two hypervalent O—Ge—O and X—Ge—Y subsystems which interact only slightly with each other. The Ge—O distances depend only weakly on the size of the lactam ring, whereas a considerable variation (within about 0.30 Å) in the length of the near-ionic sixth Ge···O bond is discernable. For analysis of the extent of the deviation of the geometries of the hypervalent fragments in these complexes from the ideal octahedron by using the parameter \(\Delta\Omega\), see elsewhere\(^478\).

The shortening of one and the significant elongation of another pseudo-axial bond of the X—Ge—Y hypervalent fragment in the mixed bis-chelate complexes \((L^n)_2 Ge(X)Y\) promotes the dissociation of such compounds. As a result, their solutions in CH\(_2 Cl_2\) have a high electroconductivity as compared with \((L^n)_2 GeX_2\) (Table 64), testifying to the existence in solution of germacenium ions \([L^n)_2 Ge(X)]^+\) stabilized by intramolecular (intraionic) coordination.

Preliminary results of \(^1\)H DNMR spectroscopy investigation enable one to estimate the activation free energies for the polytopic rearrangement in \(^452\)a–c, \(^453\), \(^454\)a,b and \(^457\) as >22 kcal mol\(^{-1}\) (the coalescence temperature of the NCH\(_A\)HBGe signals in CDCl\(_3\) is >55°C). These values are significantly higher than those for dichloride \((L^n)_2 GeCl_2\) (10.6–13.6 kcal mol\(^{-1}\))\(^90\).

A series of germanium compounds \(^459\)a–c stabilized by 2,6-bis(dialkyaminomethyl)-4-(\(t\)-butyl)phenyl tridentate ligand was recently obtained (equation 78)\(^897\). Their Si analogues Si-\(^459\)a and Si-\(^459\)d (\(R = H,\ R^1 = Me,\ R^2 = CH=CH_2\)) were analogously prepared.

---

### Table 63. X-ray structural data for cationic pentacoordinated (O—Ge) chelate complexes of the type \((L^5)_2 Ge(X)Y\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>O—Ge (Å)</th>
<th>X—Ge (Å)</th>
<th>Y—Ge (Å)</th>
<th>OGeO (deg)</th>
<th>XGeY (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>((L^5)_2 Ge(Cl)OTf) (452a)</td>
<td>2.047, 2.028</td>
<td>2.159</td>
<td>3.015</td>
<td>167.4</td>
<td>169.1</td>
<td>893, 894</td>
</tr>
<tr>
<td>((L^5)_2 Ge(Cl)OTf) (452b)</td>
<td>2.049, 1.984</td>
<td>2.129</td>
<td>3.355</td>
<td>168.5</td>
<td>165.3</td>
<td>893, 894</td>
</tr>
<tr>
<td>((L^5)_2 Ge(Cl)OTf) (452c)</td>
<td>1.980, 2.012</td>
<td>2.165</td>
<td>3.135</td>
<td>173.8</td>
<td>165.5</td>
<td>893, 894</td>
</tr>
<tr>
<td>((L^5)_2 Ge(Br)OTf) (453)(^a)</td>
<td>1.997, 2.002</td>
<td>2.308</td>
<td>3.270</td>
<td>170.7</td>
<td>168.3</td>
<td>494, 758</td>
</tr>
<tr>
<td>((L^5)_2 Ge(Cl)OClO(_3)) (454a)</td>
<td>1.996, 2.007</td>
<td>2.136</td>
<td>3.170</td>
<td>172.8</td>
<td>162.0</td>
<td>494, 758</td>
</tr>
<tr>
<td>((L^5)_2 Ge(Cl)OClO(_3)) (454b)</td>
<td>1.996, 2.007</td>
<td>2.136</td>
<td>3.170</td>
<td>172.8</td>
<td>162.0</td>
<td>494, 758</td>
</tr>
<tr>
<td>((L^5)_2 Ge(Cl)I) (455)(^b)</td>
<td>2.006, 2.006</td>
<td>2.178</td>
<td>4.215</td>
<td>171.5</td>
<td>180.0</td>
<td>895</td>
</tr>
<tr>
<td>((L^5)_2 Ge(Cl)I) (455)(^b)</td>
<td>2.006, 2.006</td>
<td>2.182</td>
<td>4.219</td>
<td>169.4</td>
<td>180.0</td>
<td>895</td>
</tr>
<tr>
<td>((L^5)_2 Ge(Cl)I) (455)(^b)</td>
<td>2.006, 2.006</td>
<td>2.182</td>
<td>4.219</td>
<td>169.4</td>
<td>180.0</td>
<td>895</td>
</tr>
<tr>
<td>((L^7)_2 Ge(Cl)I) (456)</td>
<td>1.990, 1.991</td>
<td>2.160</td>
<td>4.195</td>
<td>168.7</td>
<td>171.6</td>
<td>895</td>
</tr>
<tr>
<td>((L^7)_2 Ge(Cl)I) (457)</td>
<td>2.02, 2.018</td>
<td>2.372</td>
<td>4.266</td>
<td>170.1</td>
<td>179.3</td>
<td>494, 758</td>
</tr>
<tr>
<td>((L^7)_2 Ge(Cl)I) (458)</td>
<td>2.001, 2.001</td>
<td>1.792</td>
<td>3.434(^c)</td>
<td>175.8</td>
<td>161.8</td>
<td>896</td>
</tr>
</tbody>
</table>

\(^a\)Averaged value for two crystallographically independent molecules.  
\(^b\)Three crystallographically independent molecules.  
\(^c\)The nearest fluorine atom.
TABLE 64. Comparison of molar conductivities (\(\Lambda\)) of solutions of (O–M)-bis-chelate bis(lactamomethyl)silanes, -germanes and-stannanes in CH\(_2\)Cl\(_2\) at 25 °C\(^\text{494,504,893}\)

<table>
<thead>
<tr>
<th>Compound(^a)</th>
<th>Concentration (mmol L(^{-1}))</th>
<th>(\Lambda) (mS cm(^2) mol(^{-1}))</th>
<th>Compound(^a)</th>
<th>Concentration (mmol L(^{-1}))</th>
<th>(\Lambda) (mS cm(^2) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L(^5))(_2)SiCl(_2)</td>
<td>10.4</td>
<td>2500</td>
<td>(L(^7))(_2)Ge(Cl)I(_3) (456)</td>
<td>0.18</td>
<td>6740</td>
</tr>
<tr>
<td>(L(^7))(_2)SiCl(_2)</td>
<td>1.9</td>
<td>4330</td>
<td>(L(^7))(_2)Ge(Br)I (457)</td>
<td>1.0</td>
<td>5500</td>
</tr>
<tr>
<td>(L(^5))(_2)Ge(F)BF(_4) (458)</td>
<td>10.0</td>
<td>3660</td>
<td></td>
<td>0.1</td>
<td>20000</td>
</tr>
<tr>
<td>(L(^5))(_2)Ge(Cl)OTf (452a)</td>
<td>0.9</td>
<td>10900</td>
<td></td>
<td>0.01</td>
<td>80000</td>
</tr>
<tr>
<td>(L(^5))(_2)Ge(Cl)OTf (452b)</td>
<td>1.4</td>
<td>4040</td>
<td>(L(^7))(_2)GeCl(_2)</td>
<td>1.9</td>
<td>1200</td>
</tr>
<tr>
<td>(L(^7))(_2)Ge(Cl)OTf (452c)</td>
<td>5.7</td>
<td>1154</td>
<td>(L(^7))(_2)GeBr(_2)</td>
<td>6.9</td>
<td>39</td>
</tr>
<tr>
<td>(L(^5))(_2)Ge(Cl)OCIO(_3) (454b)</td>
<td>0.14</td>
<td>12500</td>
<td>(L(^7))(_2)SnCl(_2)</td>
<td>0.69</td>
<td>102</td>
</tr>
<tr>
<td>(L(^7))(_2)Ge(Cl)I (457)</td>
<td>7.4</td>
<td>971</td>
<td>(L(^7))(_2)SnCl(_2)</td>
<td>6.7</td>
<td>92.5</td>
</tr>
<tr>
<td>(L(^5))(_2)Ge(Cl)Cl ((\text{459a}))</td>
<td>5.7</td>
<td>5970</td>
<td>(L(^7))(_2)SnBr(_2)</td>
<td>5.1</td>
<td>76</td>
</tr>
<tr>
<td>(L(^5))(_2)Ge(Cl)Cl ((\text{459b}))</td>
<td>0.057</td>
<td>17500</td>
<td>(L(^7))(_2)SnI(_2)</td>
<td>0.5</td>
<td>194</td>
</tr>
<tr>
<td>(L(^7))(_2)Ge(Cl)I (457)</td>
<td>0.8</td>
<td>6700</td>
<td>(L(^5))(_2)SnBr(_2)</td>
<td>5.7</td>
<td>18</td>
</tr>
<tr>
<td>0.08</td>
<td>16500</td>
<td>(L(^5))(_2)SnI(_2)</td>
<td>5.7</td>
<td>33</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)L\(_n\) is the \(n\)-membered bidentate lactamomethyl C,O-chelating ligand.

All the systems were studied by \(^1\)H, \(^{13}\)C, \(^{15}\)N and \(^{29}\)Si NMR spectroscopy in solution and \(\text{459b}\), which was also characterized by an X-ray crystallography, were found to be stable compounds possessing ionic nature. The geometry around the central Ge atom in \(\text{459b}\) is a distorted TBP. The Ge–N distances are essentially equal, with values of 2.31 Å and 2.36 Å indicating a symmetrical structure in the solid state. The NGeN angle is distorted from 180° toward 158.0° in a direction opposite to the Berry pseudorotation coordinate. The overall environment around the Ge atom resembles closely an S\(_N\)2-like transition state with a backside attack of the incoming nucleophile. This symmetrical and hypervalent structure is the prevailing one in CD\(_3\)OD and DMSO-d\(_6\) solution only at low temperatures. At higher temperatures, a complex exchange process takes place.
In conclusion, although the NMR evidence supports the presence of stable pentavalent and symmetrical species in solution of \(459a\) and \(459c\), there is still a probability for intramolecular identity exchange. In contrast, the studies of silicon-containing compounds Si-\(459a\) and Si-\(459d\), have virtually excluded the presence of pentavalent, symmetrical forms as stable species in solution\(^{897}\).

### B. Tin and Lead Complexes

#### 1. Intermolecular complexes

The complex \([\text{Me}_3\text{SnBr}_2][\text{Me}_3\text{Sn(HMPA)}_2]\) (41) in which both the cation and anion contain TBP tin atoms is the first representative of five-coordinated organotin cations, whose structures were proved by X-ray diffraction\(^{227}\). These are numerous examples of cation–anion complexes containing pentacoordinated triorganotin cations stabilized by intermolecular donor–acceptor interaction. Some geometrical parameters for selected cases of cationic species with \([\text{SnC}_3\text{O}_2]^+\) and \([\text{SnC}_3\text{N}_2]^+\) moieties characterized by X-ray data are given in Table 65. The tin atoms in these complexes have a near-TBP geometry with the two electronegative ligands in axial positions with OSnO and NSnN angles close to 180\(^\circ\). For example, in cation \([\text{Me}_3\text{Sn(H}_2\text{O})_2]^+\) (entry 3), the OSnO angle is 177.0\(^\circ\), the mean values of the Sn–O and Sn–C bond lengths are 2.295 and 2.110 Å, respectively, and the sum of the equatorial angles is 359.9\(^\circ\)\(^{899}\). Generally, the O–Sn and N–Sn distances are in the ranges 2.23–2.33 and 2.33–2.38 Å, respectively, significantly longer than the typical bond lengths of 2.12 and 2.15 Å for pentacoordinate organotin compounds\(^8\).

On the basis of NMR data\(^{887}\) an equilibrium including triorganotin cations is suggested between tetravalent and two solvated TBP structures in solution (equation 79).\(^\)\(^9\)

![Image of chemical structure](image)

\(R = \text{Bu, Ph}; X = \text{Cl, ClO}_4, \text{BF}_4; S = \text{CH}_2\text{Cl}_2, \text{Pyr, DMSO, HMPA}\)

The changes in tin coordination are associated with an upfield shift in the tin resonance of the order of 200 ppm and an increase in the Sn–C one-bond coupling of ca 160–200 Hz. Bipyramidal forms are favored if the solvent donicity is increased, including structures in which the solvent molecules occupy the two axial positions of the five-coordinate TBP.

A series of dimeric organotin cations \([\text{R}_2\text{SnOH(H}_2\text{O})_2]^{2+}\) (460) were synthesized from \(\text{R}_2\text{SnO}\) and \(\text{TfOH}\) (equation 80)\(^9\). The reaction proceeds with the participation of 1 equivalent of water, which is present, probably, in a trace amount in the MeCN solvent. The \(\text{H}_2\text{O}\) molecule in 460 can be readily replaced by HMPA to yield \([\text{R}_2\text{SnOH(HMPA)}]^{2+}\) (460d, \(R = n\)-Bu). The structures of 460 were investigated by single-crystal X-ray analysis and solid-state \(^{119}\text{Sn}\) NMR, and by \(^{119}\text{Sn}\) NMR spectra and electrical conductivity measurement in solution.

Compounds 460a and 460b possess cationic structures both in the solid state and in solution. The \(n\)-butyltin derivatives 460c and 460d dissociate also into ionic species in solution but are nonionic in the solid state and involve coordinating triflates, though the...
TABLE 65. Some structural parameters for selected cationic intermolecular pentacoordinate tin complexes containing a [SnC₃X₂]⁺ moiety (X = O, N)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>X–Sn (Å)</th>
<th>XSnX (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Bu₃Sn(H₂O)₂]⁺(L¹)⁻</td>
<td>2.295, 2.326</td>
<td>178.5</td>
<td>898</td>
</tr>
<tr>
<td>2</td>
<td>[Me₃Sn(H₂O)]⁺[Cl(CN)₃]⁻</td>
<td>2.274, 2.364b</td>
<td>176.5</td>
<td>246</td>
</tr>
<tr>
<td>3</td>
<td>[Me₃Sn(H₂O)₂]⁺[(MeSO₂)₂N]⁻</td>
<td>2.255, 2.327</td>
<td>177.0</td>
<td>899</td>
</tr>
<tr>
<td>4</td>
<td>[Me₃Sn(H₂O)₃(L²)]⁺[(MeSO₂)₂N]⁻</td>
<td>2.274, 2.257</td>
<td>171.1</td>
<td>900</td>
</tr>
<tr>
<td>5</td>
<td>[Me₃Sn(Me₃PO)₃]⁺[(MeSO₂)₂N]⁻</td>
<td>2.232, 2.261</td>
<td>177.3</td>
<td>901</td>
</tr>
<tr>
<td>6</td>
<td>[Me₃Sn(Me₃PO)₂]⁺[(MeSO₂)₂N]⁻·Ph₃PO</td>
<td>2.289, 2.226</td>
<td>175.9</td>
<td>901</td>
</tr>
<tr>
<td>7</td>
<td>[Me₃Sn(HMPA)₂]⁺[(Me₃SnBr₂)⁻ (41)]</td>
<td>2.128, 2.128</td>
<td>176.8</td>
<td>227</td>
</tr>
<tr>
<td>8</td>
<td>[Ph₃Sn(HMPA)₂]⁺[(Me₃Sn₂)N]⁻</td>
<td>2.206, 2.213</td>
<td>174.4</td>
<td>900</td>
</tr>
<tr>
<td>9</td>
<td>[(Ph₃Sn(L³)₂]⁺[(MeSO₂)₂N]⁻·MeCN</td>
<td>2.236, 2.247</td>
<td>174.4</td>
<td>902</td>
</tr>
<tr>
<td>10</td>
<td>[Me₃Sn(Me₃PO)₃]⁺[(MeSO₂)₂N]⁻</td>
<td>2.240, 2.204</td>
<td>177.1</td>
<td>900</td>
</tr>
<tr>
<td>11</td>
<td>[Ph₂(p-ClC₆H₄)Sn(Me₃AsO)₂]⁺(BPh₄)⁻</td>
<td>2.219, 2.204</td>
<td>176.6</td>
<td>903</td>
</tr>
<tr>
<td>12</td>
<td>[Me₃Sn(Me₃SO₂)]⁺[(FSO₂)₂N]⁻</td>
<td>2.249, 2.282</td>
<td>172.4</td>
<td>904</td>
</tr>
<tr>
<td>13</td>
<td>[Me₃Sn(Me₃NHCONH₂)]⁺[(MeSO₂)₂N]⁻</td>
<td>2.280, 2.236</td>
<td>176.8</td>
<td>902</td>
</tr>
<tr>
<td>14</td>
<td>[Ph₃Sn(Me₃NHCONH₂)]⁺[(MeSO₂)₂N]⁻</td>
<td>2.227, 2.245</td>
<td>177.8</td>
<td>902</td>
</tr>
<tr>
<td>15</td>
<td>[Me₃Sn(L⁴)₂]⁺[(FSO₂)₂N]⁻</td>
<td>2.286, 2.274</td>
<td>179.2</td>
<td>904</td>
</tr>
<tr>
<td>16</td>
<td>[Ph₃Sn(Me₃N₄H₃CH₂COO⁻)]₂⁺Cl⁻</td>
<td>2.280, 2.280</td>
<td>174.8</td>
<td>905</td>
</tr>
<tr>
<td>17</td>
<td>[Ph₃Sn(Me₃N₄H₃CH₂COO⁻)]₂⁺SCN⁻</td>
<td>2.219, 2.209</td>
<td>177.9</td>
<td>905</td>
</tr>
<tr>
<td>18</td>
<td>[Me₃Sn(Me₃SnOH)₂]⁺⁺⁻</td>
<td>2.253, 2.243</td>
<td>176.6</td>
<td>906</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.258, 2.248</td>
<td>178.5</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>[Me₃Sn(Me₃SnOH)₂]⁺⁻⁻</td>
<td>2.250, 2.250</td>
<td>177.6</td>
<td>907</td>
</tr>
<tr>
<td>20</td>
<td>[Me₃Sn(Me₃SnOH)₂]⁺⁺⁻</td>
<td>2.258, 2.258</td>
<td>179.0</td>
<td>908</td>
</tr>
<tr>
<td>21</td>
<td>[Me₃Sn(NH₃)₂]⁺⁺[(Me₃SO₂)₂N]⁻</td>
<td>2.328, 2.382</td>
<td>179.2</td>
<td>909</td>
</tr>
<tr>
<td>22</td>
<td>[(c-Hex)₃Sn(MeCN)₂]⁺⁺(SbF₆)⁻</td>
<td>2.374, 2.472</td>
<td>177.2</td>
<td>910</td>
</tr>
<tr>
<td>23</td>
<td>[Ph₃Sn(Im)₂]⁺⁺[(MeSO₂)₂N]⁻</td>
<td>2.355, 2.312</td>
<td>170.2</td>
<td>900</td>
</tr>
<tr>
<td>24</td>
<td>[Me₃Sn(L⁵)₂]⁺⁺Cl⁻</td>
<td>2.351, 2.351</td>
<td>176.0</td>
<td>911</td>
</tr>
<tr>
<td>25</td>
<td>[L⁶(Me₃SnL⁷)₂]⁺⁺[(MeSO₂)₂N]₄</td>
<td>2.343, 2.429</td>
<td>177.8</td>
<td>902</td>
</tr>
</tbody>
</table>

**a**Ligands:
L¹ = pentakis(methoxycarbonyl)cyclopentadienide.
L² = pyridine-N-oxide.
L³ = O₂P(Ph)₂(C₂H₅)₂PPh₂O.
L⁴ = N,N'-dimethylethyleneurea-O.
L⁵ = 4-phenylimidazole.
L⁶ = μ₂-4,4'-bipyridine.
L⁷ = 4,4'-bipyridinium.
bSn—N.
cTwo independent molecules in the unit cell.

bonding is very weak (Sn–O(Tf) 2.62 and 2.82 Å, respectively). The corresponding distances in ionic species with bulkier alkyl groups are 4.15–4.82 Å for 460a and 3.86–4.29 Å for 460b while the sums of the covalent radii and the van der Waals radii of Sn and O are 2.12 Å and 3.70 Å, respectively (Table 1). Additionally, the cationic character is reflected in the stronger coordination by H₂O molecules: Sn–O(H₂) 2.29 for 460a, 2.26 for 460b and 2.41 for 460c.

In contrast, the analogous t-butyltin halides, [(t-Bu)₃SnOH](X)₂ (X = Cl, Br)ʰ, and methyltin and t-butyltin nitrates, [Me₂SnOH(NO₃)]²⁻ and [(t-Bu)₂SnOH(NO₃)]²⁻, have a nonionic structure with hydroxyl bridges, and the halogen atoms and nitrate ligands are covalently bonded to tin. It is concluded that both bulky alkyl groups attached
to tin and electronegative ligands such as triflate are crucial for the generation of the cationic species\textsuperscript{912,913}.

The polymeric structure of \([(\text{Me}_2\text{Sn})_2(\text{OH})_3]^+\text{ClO}_4^-\) has been determined by X-ray analysis\textsuperscript{915}. The polymer consists of five-coordinate tin units with di- and mono-hydroxo bridging. The coordination geometry at tin is a distorted TBP with the two methyl groups and one \(\mu\)-hydroxo group in equatorial positions and the other two \(\mu\)-hydroxo groups in axial positions.

![Diagram of the polymeric structure of \([(\text{Me}_2\text{Sn})_2(\text{OH})_3]^+\text{ClO}_4^-\)](image)

\begin{equation}
\text{R}_2\text{SnO} + \text{TiOH} \xrightarrow{\text{H}_2\text{O}} [\begin{array}{c}
\text{H}_2\text{O} \text{Sn} \text{O} \\
\text{R} \\
\text{R} \\
\text{H} \\
\text{Sn} \text{OH}_2
\end{array}]^{2+} 2\text{OTf}^{-}
\end{equation}

\(\text{(460a)} \text{ R = } \text{t-Bu}\\n\text{(460b)} \text{ R = } \text{CH}_2\text{CH(Ph)Et}\\n\text{(460c)} \text{ R = } \text{n-Bu}

2. Intramolecular complexes

The first few pentacoordinate cationic tin complexes 461\textsuperscript{916,917} and 462\textsuperscript{916} were discussed in an earlier review\textsuperscript{636}. Based on \(^1\text{H}, \quad^{13}\text{C}\) and \(^{119}\text{Sn}\) spectroscopic studies\textsuperscript{916} as well as on conductivity measurements\textsuperscript{916}, ionic structures for these complexes were suggested. In the case of bromide 461a\textsuperscript{917} an ionic structure was unambiguously proved by X-ray diffraction. More recently, the structure of the analogous chloride as a 1 : 1 double salt with tetraaqualithium bromide, namely \([\text{Me}_2\text{SnC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6]^+\text{Cl}^- \cdot [\text{Li}(\text{H}_2\text{O})_4]^+\text{Br}^- (463)\), was reported\textsuperscript{918}.

![Diagram of the ionic structure of \([\text{Me}_2\text{SnC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6]^+\text{Cl}^- \cdot [\text{Li}(\text{H}_2\text{O})_4]^+\text{Br}^- (463)\)](image)

\(\text{(461)} \text{ X = Cl, Br, I; R, R}^1 = \text{Me, neopentyl, Ph, p-Tol}\\n\text{(461a)} \text{ X = Br, R = R}^1 = \text{Me}

The five-coordinate triorganotin cation in 463 has a planar SnC\(_3\) girdle (\(\Sigma\text{CSnC} = 360^\circ\)) and a distorted trans-TBP geometry about tin with the nitrogen atoms in the axial positions at the NSnN angle of 152.7\(^\circ\). The N–Sn distances (2.36 and 2.45 Å) are somewhat shorter than those found in halides \(\text{Me}_2\text{PhN}\text{SnCl} (240a)\textsuperscript{656} (2.49 \text{ Å}), \text{MePhPhN}\text{SnBr}\)
16. Hypervalent compounds of organic germanium, tin and lead derivatives

(248a) (2.48 and 2.55 Å) and Ph₂Ph₅SnBr (242) (2.51 Å) (Section VII.A.1.c), which are molecular triorganotin compounds substituted by only one CH₂NMe₂ in the phenyl ring.

The reaction of dinuclear stannane 464 with [PtCl₂(COD)] (COD = cycloocta-1,5-diene) or Me₃SnCl led to methyl group transfer to platinum or tin, respectively, with formation of the cations 465a and 465b, differing in the counter anion (equation 81). These cations interact with the mononuclear hexacoordinate tetraorganotin compound Me₃Sn[C₆H₃(CH₂NMe₂)₂-2,6] to give the pentacoordinate cationic tin complexes {Me₂Sn[C₆H₃(CH₂NMe₂)₂-2,6]}²⁺ + 2X⁻ (X = Cl or Me₃SnCl₂).

An X-ray structure determination of 465b reveals that the central dimetalated aryl ligand system provides tridentate meridional NCN'-coordination to both tin centers. The N–Sn distances (2.392 and 2.395 Å) and the NSnN angles (152.0°) are close to those found for the triorganotin cation in salt 463.

In contrast to equation 81, the neutral five- and six-coordinate organotin derivatives, the heterocyclic compounds 427a, 427b, 428a, 428b and 431, containing the monoanionic O,C,O-coordinating ligand {4-t-Bu-2,6-[PO(OEt)₂]₂C₆H₂}⁻, were only isolated as end products by treatment of six-coordinate precursors {4-t-Bu-2,6-[PO(OEt)₂]₂C₆H₂}SnRR¹ (426a, 426b, 430) with HCl or X₂ (X = Br, I, see Section VII.B.2)¹⁴⁷,⁷⁶²,⁷⁶⁹. However, cationic tin species of type 429 are suggested as intermediates in these reactions. The isolation of the related hexafluorophosphate derivative {4-t-Bu-2,6-[PO(OPr-i)₂]₂C₆H₂}SnPh₂⁺PF₆⁻ supports the intermediacy of 429.
Only recently, an aliphatic analogue of the pentacoordinate cationic tin complexes 461, the triorganotin iodide derivative 466, was obtained (equation 82)\(^9\)\(^{18}\).

\[
\text{Ph}_2\text{Sn}[(\text{CH}_2)_3\text{NMe}_2]_2 + \text{I}_2 \xrightarrow{\text{CH}_2\text{Cl}_2 - \text{PhI}} \begin{array}{c}
\text{Me}_2\text{N} \\
\text{NMe}_2 \\
\text{Ph} \\
\text{Sn} \\
\end{array} \\
\text{I}^- \\
(82)
\]

\[
(466)
\]

According to an X-ray analysis, 466 consists of an intramolecularly coordinated triorganotin cation and iodide anion with the I⋯Sn separation at 4.457 Å, a distance slightly larger than the sum of van der Waals radii of Sn and I (Table 1). The array of the Sn atom is a slightly distorted TBP (the NSnN angle is 174.6°), opened, like in the cation–anion germanium iodide complexes 455, 457, and the tetrafluoroborate 458 (Section VIII.A), toward the anion (the CSnC angle is 131.7°). The N⋯Sn distances (2.392 and 2.401 Å) are close to those found for the triorganotin cation in the salt 465b, differing significantly from those in the closely related intramolecularly hexacoordinated triorganotin iodide [8-Me2N-1-C10H6]2SnIMe (2.53 and 3.10 Å)\(^9\)\(^{19}\).

Wrackmeyer and coworkers described a family of triorganotin and triorganolead cations, namely 467–469 (R, R1, R2 = Alk, Ph; L = 2-Pyr, CH2NMe2, CH=CHOMe, CH2SEt), stabilized by the asymmetric side-on coordination of the C≡C bond to the metal atom in alkynyhydrides. The cationic center in these zwitterionic compounds may be alternatively viewed as containing Sn formally five- or six-coordinate to carbon as shown, for example, in structures 467' and 468'. The nature of the stabilization of triorganotin cations, as well as the competition between intramolecular coordinating O–, S– or N–Sn bonds (functional substituent in L) and side-on π coordination to C≡C bonds in 469 is considered on the basis of comparison of X-ray data for compounds 469a–c and those for complexes 467a and 468a having no functional group.

\[
\begin{align*}
(467) & \quad M = \text{Sn} \\
(467a) & \quad R^1 = \text{i-Pr}, \quad R^2 = \text{Et} \\
(468) & \quad M = \text{Pb} \\
(468a) & \quad R^1 = \text{Me}, \quad R^2 = \text{i-Pr} \\
(467') & \quad M = \text{Sn} \\
(468') & \quad M = \text{Pb} \\
(469) & \quad (a) \quad L = \text{CH}_2\text{NMe}_2, \quad R = \text{Et} \\
& \quad (b) \quad L = \text{CH}_2\text{NMe}_2, \quad R = \text{i-Pr} \\
& \quad (c) \quad L = \text{CH} = \text{CHOMe}, \quad R = \text{i-Pr}
\end{align*}
\]

This topic was discussed in more detail in other reviews\(^9,\)\(^53\).
IX. HEXACOORDINATE ANIONIC COMPOUNDS

A. Intermolecular Complexes

1. Germanium

Complexes of (trifluoromethyl)halogermanes with fluoride ions\textsuperscript{207,208,922–924} are discussed in Section IV.A.1. In the presence of KF the fluorides CF\textsubscript{3}GeF\textsubscript{3} and (CF\textsubscript{3})\textsubscript{2}GeF\textsubscript{2} are capable of forming anions 470 and 471, respectively. Tris- and tetrakis-CF\textsubscript{3} derivatives generally form the (CF\textsubscript{3})\textsubscript{n}GeF\textsubscript{5−n} \textsubscript{n}(n = 3, 4) adducts, although the excess of KF in aprotic solvents may lead to dianions 29 and 28 that are stable only in the total absence of moisture\textsuperscript{207,208}. According to \textsuperscript{19}F NMR spectra, all the dinegatively charged anions have octahedral structures with cis-configuration of CF\textsubscript{3} groups\textsuperscript{208}. The structure of 471 in the salt K\textsubscript{2}[CF\textsubscript{3})\textsubscript{2}GeF\textsubscript{4}] was confirmed by X-ray data\textsuperscript{207}. The Ge\textsuperscript{−}F bond lengths are 1.833 and 1.824 Å for equatorial and axial F atoms, respectively, while the Ge\textsuperscript{−}C distances are 2.041 Å.

The first representative of hexacoordinate germanium compounds with a GeF\textsubscript{5}C framework, the zwitterionic germanate 472, was recently synthesized (equation 83)\textsuperscript{925}.

\[
\begin{align*}
\text{(MeO)}\text{3GeCH}_2\text{N} & \quad \text{HF} \\
\text{NMe} & \\
\end{align*}
\]

(472)

A crystal structure determination of 472 \cdot H\textsubscript{2}O reveals a slightly distorted octahedral geometry about the germanium atom dominated by intermolecular N\textsuperscript{−}H\cdots F and O\textsuperscript{−}H\cdots F hydrogen bonds. The Ge\textsuperscript{−}C distances, 1.977 and 1.978 Å for two independent zwitterions in the unit cell, are similar to those obtained for anion 471\textsuperscript{207}. The Ge\textsuperscript{−}F distances in 472 \cdot H\textsubscript{2}O are 1.788–1.867 Å, longer than those obtained for the GeF\textsubscript{6}\textsuperscript{2−} anion (1.77 Å\textsuperscript{926} and 1.79 Å\textsuperscript{927}) but comparable to those reported for 471.

According to X-ray data, the GeCl\textsubscript{6}\textsuperscript{2−} anion in the salt [GeCl\textsubscript{6}][Ph\textsubscript{4}P]\textsubscript{2} described recently\textsuperscript{928} possesses a centrosymmetric octahedral structure. The Ge\textsuperscript{−}Cl bond lengths, 2.292 Å (average), are similar to those reported for the axial bonds in pentacoordinate GeCl\textsubscript{5}− ions, i.e. 2.25–2.32 Å\textsuperscript{306}, significantly longer than in the simple tetrahedral species GeCl\textsubscript{4} (2.113 Å, electron diffraction)\textsuperscript{9}. Distorted octahedral Ge(N\textsubscript{3})\textsubscript{6}\textsuperscript{2−} ions of C\textsubscript{1} symmetry were found in the complex [Ge(N\textsubscript{3})\textsubscript{6}][Na\textsubscript{2}(THF)\textsubscript{3}(Et\textsubscript{2}O)], including the interionic interactions between the anions and the solvated sodium cations with the average Ge\textsuperscript{−}N distance at 1.981 Å\textsuperscript{929}. However, the crystal structure of the salt [Ge(N\textsubscript{3})\textsubscript{6}][Na(PPh\textsubscript{3})\textsubscript{2}] reveals the presence of separated Ge(N\textsubscript{3})\textsubscript{6}\textsuperscript{2−} ions of S\textsubscript{2} symmetry enclosed by the voluminous counterions (the mean Ge\textsuperscript{−}N bond length is 1.974 Å).
2. Tin and lead

Attempts to prepare stable six-coordinate adducts like \([\text{Ph}_3\text{SnX}_2 \cdot \text{B}]^−\) or \([\text{Ph}_3\text{SnX}_3]^2−\) from the reactions of \(\text{Ph}_3\text{SnF}_2^−\) or \(\text{Ph}_3\text{SnFCl}^−\) with HMPA, DMSO, \(\text{F}^−\) and \(\text{Cl}^−\), as well as from \(\text{Ph}_3\text{SnCl}\) with an excess of \(\text{Cl}^−\) and \(\text{Br}^−\), were unsuccessful, although the presence of such anions in aprotic solution was detected by NMR spectroscopy. In contrast, rather stable mono- and dianions containing two, one or no organic groups at tin are known. NMR data are given elsewhere.

As for monoanions, the crystal structures of the only diorganotin derivative \(\text{MeSnMeClCl}\), two mono-organotin complexes \(\text{MeSnPyrX}^−\) \((\text{X} = \text{Cl}, \text{R} = \text{Et})\) \((\text{474a})\) and \(\text{MeSnPyrX}^−\) \((\text{X} = \text{Br}, \text{R} = \text{Bu})\) \((\text{474b})\), and a number of anions of the type \(\text{DSnCl}^−\) \((\text{D} = \text{MeCN}, \text{H}_2\text{O}, \text{THF})\) \((\text{475})\) have been described. Selected structural parameters for these compounds are given in Table 66.

\[
\begin{align*}
\text{Cl}_2\text{MeSnMeCl} & \quad [\text{HT}]^{2+}, \text{Cl}^− \quad \text{(473)} \\
[\text{X}] & \quad \text{Sn} \quad \text{X} \quad \text{PyrH}^+ \quad \text{(474a)} \text{ X} = \text{Cl}, \text{R} = \text{Et} \\
[\text{X}] & \quad \text{Sn} \quad \text{X} \quad \text{Pyr} \quad \text{(474B)} \text{ X} = \text{Br}, \text{R} = \text{Bu} \\
\text{Cl}_2\text{D} & \quad \text{Sn} \quad \text{Cl} \quad \text{(475)} \text{D} = \text{MeCN}, \text{H}_2\text{O}, \text{THF}
\end{align*}
\]

Aqua-chloro complexes, \(\text{473}\) and \([\text{Ph}_3\text{SnCl}_4][\text{HT}]\text{H}_2\text{O}\) \((\text{476})\) \((\text{T} = \text{thiamine})\), were recently obtained by the reaction of \(\text{TCI} \cdot \text{HCl}\) (vitamin \(\text{B}_1\) hydrochloride, \(\text{HT}^{2+}2\text{Cl}^−\)) with \(\text{Me}_2\text{SnCl}_2\) or \(\text{Ph}_2\text{SnCl}_2\), respectively, in 9 : 1 ethanol—water. In the anion of \(\text{470}\) (Table 66, entry 1), the tin atom coordinates to two trans carbon atoms of the methyl groups, three \(\text{Cl}\) atoms and the \(\text{O}\) atom of a water molecule in a distorted octahedral arrangement (the \(\text{CSnC}\) angle of 165.8° is the most distorted geometrical parameter). The \(\text{O}−\text{Sn}\) bond, 2.418 Å, is longer than in neutral aqua-chloro complexes \(\text{Me}_2\text{Sn}(\text{H}_2\text{O})\text{Cl}_2\) (2.235 Å) and \(\text{Me}_2\text{Sn}(\text{H}_2\text{O})\text{Cl}_2\) (2.407 Å). Comparison of the structural parameters of \(\text{Me}_2\text{Sn}(\text{H}_2\text{O})\text{Cl}_3^−\) with those of \(\text{Me}_2\text{SnCl}_3^−\) shows that coordination to water does not significantly change the \(\text{Sn}−\text{Cl}\) bond distances, but does lengthen the \(\text{Sn}−\text{C}\) bond distances and widen the \(\text{CSnC}\) angle from 140 to 165.8°.

In anions of \(\text{474a}\) and \(\text{474b}\) \((\text{entries 2 and 3})\), the pyridine molecule is trans to the alkyl group, and there is nonequivalence of the \(\text{Sn}−\text{Cl}\) and \(\text{Sn}−\text{Br}\) distances owing to hydrogen bonding with the pyridinium cation. A cis-shortening of the mean values of the \(\text{Sn}−\text{Cl}\) and \(\text{Sn}−\text{Br}\) distances by the influence of the alkyl group was noted, as well as an equal \(\text{Sn}−\text{C}\) and \(\text{Sn}−\text{N}\) bond lengthening on going from chloride \(\text{474a}\) to bromide \(\text{474B}\).

A special feature of anions \(\text{475}\) in complexes with different counterions \((\text{entries 4}−\text{16})\) is a lengthening of the \(\text{N}−\text{Sn}\) or \(\text{O}−\text{Sn}\) coordinative bonds up to 2.28–2.32 and 2.17–2.27 Å, respectively, compared to the mean values for penta- and hexacoordinated tin compounds (2.12 and 2.15 Å). Accordingly, the \(\text{Sn}−\text{Cl}\) bond length trans to \(\text{N}\) or \(\text{O}\), at 2.36–2.42 Å, is somewhat shorter than that in hypervalent compounds (2.45 Å), and is generally shorter in comparison with the other \(\text{Sn}−\text{Cl}\) bonds in these complexes.

The reaction of butyltin trichloride with 1-(2-methyl-2,3-dihydrobenzotriazol-2-yl)-propan-2-one gives an organotin complex that was formulated as containing the \([\text{BuSn(OH)}\text{Cl}_3]^2−\) anion. However, a reinvestigation of the crystal structure of this complex reveals a neutral hydroxyl-bridged aqua-butyldichlorotin hydroxide dimer that is linked to four 2-methylbenzothiazole molecules by short hydrogen bonds.
TABLE 66. X-ray data for anions \( R_2SnDX_3^- \), \( RSn(D)X_4^- \) and \( Sn(D)X_5^- \) in hexacoordinate anionic tin complexes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compounda</th>
<th>D−Sn (Å)</th>
<th>Sn−Yb (Å)</th>
<th>Sn−Xc (Å)</th>
<th>DSnY (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><a href="HT">Me₂Sn(H₂O)Cl₃</a>Cl (473)d</td>
<td>2.418</td>
<td>2.486</td>
<td>2.562, 2.690</td>
<td>176.5</td>
<td>930</td>
</tr>
<tr>
<td>2</td>
<td>[EtSn(Pyr)Cl₄]−(PyrH)+</td>
<td>2.206</td>
<td>2.09</td>
<td>2.514, 2.475</td>
<td>931</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>[BuSn(Pyr)Br₄]−(PyrH)+</td>
<td>2.281</td>
<td>2.170</td>
<td>2.678, 2.636</td>
<td>174.8</td>
<td>931</td>
</tr>
<tr>
<td>4</td>
<td>[Sn(MeCN)Cl₅]−(L1)+</td>
<td>2.323</td>
<td>2.378</td>
<td>2.398, 2.401</td>
<td>177.9</td>
<td>932</td>
</tr>
<tr>
<td>5</td>
<td>[Sn(MeCN)Cl₅]−(L₂)+</td>
<td>2.293</td>
<td>2.416</td>
<td>2.386, 2.408</td>
<td>178.4</td>
<td>933</td>
</tr>
<tr>
<td>6</td>
<td>[Sn(H₂O)Cl₅]−(Ph₄P)+</td>
<td>2.24</td>
<td>2.355</td>
<td>2.386</td>
<td>180.0</td>
<td>298</td>
</tr>
<tr>
<td>7</td>
<td>[Sn(H₂O)Cl₅]−(L₃)+</td>
<td>2.166</td>
<td>2.371</td>
<td>2.375, 2.429</td>
<td>177.2</td>
<td>934</td>
</tr>
<tr>
<td>8</td>
<td>[Sn(H₂O)Cl₅]−(L₄)+</td>
<td>2.188</td>
<td>2.421</td>
<td>2.381, 2.384</td>
<td>179.4</td>
<td>935</td>
</tr>
<tr>
<td>9</td>
<td>[Sn(H₂O)Cl₅]−(L₅)+f</td>
<td>2.234</td>
<td>2.356</td>
<td>2.392, 2.398</td>
<td>174.8</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>[Sn(THF)Cl₅]−(L₆)+</td>
<td>2.244</td>
<td>2.378</td>
<td>2.405, 2.410</td>
<td>177.4</td>
<td>937</td>
</tr>
<tr>
<td>11</td>
<td>[Sn(THF)Cl₅]−(L₇)+</td>
<td>2.247</td>
<td>2.380</td>
<td>2.391, 2.398</td>
<td>178.8</td>
<td>938</td>
</tr>
<tr>
<td>12</td>
<td>[Sn(THF)Cl₅]−(L₈)+</td>
<td>2.265</td>
<td>2.380</td>
<td>2.387, 2.393</td>
<td>178.6</td>
<td>939</td>
</tr>
<tr>
<td>13</td>
<td>[Sn(THF)Cl₅]−(L₉)+</td>
<td>2.271</td>
<td>2.378</td>
<td>2.394, 2.398</td>
<td>178.9</td>
<td>940</td>
</tr>
<tr>
<td>14</td>
<td>[Sn(THF)Cl₅]−(L₁₀)+</td>
<td>2.257</td>
<td>2.368</td>
<td>2.395, 2.397</td>
<td>180.0</td>
<td>940</td>
</tr>
<tr>
<td>15</td>
<td>[Sn(THF)Cl₅]−(L₁₁)+</td>
<td>2.269</td>
<td>2.382</td>
<td>2.396, 2.411</td>
<td>178.5</td>
<td>941</td>
</tr>
<tr>
<td>16</td>
<td>[Sn(THF)Cl₅]−(L₁₂)+</td>
<td>2.245</td>
<td>2.394</td>
<td>2.385, 2.394</td>
<td>176.5</td>
<td>942</td>
</tr>
</tbody>
</table>

aLigands:
T = thiamine.
L¹ = tetrakis(acetonitrile)palladium(II).
L² = cyclopentathiazenium.
L³ = 4,5-dihydro-3,5,5-trimethylpyrazolium.
L⁴ = bis(1,4,7,10,13-pentaaza-16-azoniacyclo-octadecane).
L⁵ = carbonyl-(η⁵-cyclopentadienyl)-nitrosotriphenylphosphinomolybdenum trichlorotin.
L⁶ = dichlorotetraphenylcarbonyl(η⁵-cyclopentadienyl)-nitrosotriphenylphosphinomolybdenum trichlorotin.
L⁷ = dichlorotetraphenylcarbonyl(η⁵-cyclopentadienyl)-nitrosotriphenylphosphinomolybdenum trichlorotin.
L⁸ = hexakis(µ₂-chloro)dodecakis(tetrahydrofuran)tetrarmanganous(II).
L⁹ = tris(µ₂-chloro)bis[tris(tetrahydrofuran)nickel(II)]
L¹₀ = tris(µ₂-chloro)hexakis(tetrahydrofuran)diiron(II).
L¹₁ = dichlorotetraphenylcarbonyl(η⁵-cyclopentadienyl)-nitrosotriphenylphosphinomolybdenum trichlorotin.
L¹₂ = dichlorotetraphenylcarbonyl(η⁵-cyclopentadienyl)-nitrosotriphenylphosphinomolybdenum trichlorotin.
bSn−C or Sn−X bond trans to D.
cAverage value.
dSn−C, 2.088 Å; CSnC, 165.8°; ClSnCl, 177.8°.
eH-bonded.
fTwo independent anions.

The chloro dianion in the complex [Me₆Sn₃Cl₈][L]₂ (477, L = dibenzotetrathiafulvalene) can be also considered as the adduct Me₂SnCl₂·2Me₂SnCl₃−. In this dianion the internal tin atom, Sn², has a near-octahedral configuration with a C−Sn−C angle of 177.9°, while the coordination environment of the two terminal tin atoms, Sn¹ and Sn³, can be described as a distorted octahedron (the C−Sn−C angle is about 160°). Consequently, there are three types of Sn−Cl bonds distinguished by their length. The four terminal Sn¹−Cl and Sn¹−Cl bonds, at 2.42−2.46 Å, are the shortest, while the four bridged Sn²−Cl bonds are longer (2.63−2.68 Å). Finally, the four other bridged Sn¹−Cl and Sn³−Cl bonds of 2.96−3.10 Å are longest among those detected for hypervalent organotin chlorides, but yet significantly shorter than the sum of van der Waals radii of the tin and chlorine atoms.
Reaction of diorganotin dihalides with halide ions, which can lead to the formation of either pentacoordinate trihalodiorganostannates $R_2SnX_3^{2-}$ or hexacoordinate tetrahalodiorganostannates $R_2SnX_4^{2-}$, was discussed in Section IV.A.4. As noted, the $[Ph_2SnCl_4]^{2-}$ anion is formed from the disproportionation reaction of $Ph_2SnCl_3^{2-}$ (equation 10, Section IV.A.4) rather than by addition of chloride ion to the latter281.

Table 67 presents selected X-ray data for anions $R_2SnX_4^{2-}$ (478), $RSnX_5^{2-}$ (479) and $PhPbCl_5^{2-}$ (480) in hexacoordinate anionic tin and lead complexes. Most of the $R_2SnX_4^{2-}$ anions generally have a centrosymmetric trans-octahedral structure and $X = Cl$. For the other halides, only the crystal structures of $[Me_2SnBr_4](Et_4N)^{2-}$, $[Ph_2SnBr_4](NHC_5H_5)^{2-}$ and $[Me_2SnF_4](NH_4)^{2-}$ have been reported. It is significant that the latter crystallizes as an anhydrous salt, probably because all its F atoms are already involved in hydrogen bonds278, while $K_2[Me_2SnF_4]$ crystallizes as a dihydrate from aqueous solutions967.

Among $L_2SnX_4$ complexes, the salts of anions $R_2SnX_4^{2-}$ possess the longest $Sn-X$ distances and the largest Mössbauer quadrupole splitting values and they were used for the correlation between both parameters968,969. The average $Sn-Hal$ distance (2.127 Å in $Me_2SnF_4^{2-}$ (entry 1), 2.600–2.625 Å in $Me_2SnCl_4^{2-}$ (entries 2–8) and 2.768 Å in $Me_2SnBr_4^{2-}$ (entry 17) is significantly longer than for the corresponding octahedral $SnHal_6^{2-}$ (Table 67), consistent with the concept that the strong donor methyl groups weaken the $Sn-Hal$ bonds278. This is also in agreement with the isovalent rehybridization concept970a, since the $Sn$ atom will concentrate larger s character into the hybrid orbitals directed toward the less electronegative methyl groups, and larger p character in the hybrid orbitals directed to Hal.

The $Me_2SnCl_4^{2-}$ anion has generally a centrosymmetric trans-octahedral structure. The observed differences in the $Sn-Cl$ bond lengths (entries 2–8) can be ascribed mainly to hydrogen-bonding effects causing elongation of these bonds. Thus, the shortest $Sn-Cl$ distances are found for the tetraathiafulvalenium compound (entry 2) in which no H-bonds are present288. In the case of 8-methylaminoquinolinium derivative (entry 9), all the $Sn-Cl$ distances are different (2.442, 2.461, 2.894 and 3.098 Å)953. The two long $Sn-Cl$ bonds are trans to the short ones and their Cl atoms are H-bonded to the N−H groups of the cations. The $Sn-C$ bonds are bent away from the short $Sn-Cl$ bonds so that the
TABLE 67. X-ray data for anions $R_2SnX_2^{-}$ and $RSnX_2^{-}$ in hexacoordinate anionic tin complexes and related species$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound$^b$</th>
<th>C–Sn (Å)</th>
<th>Sn–X (Å)</th>
<th>C–Sn–C (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Me$_2$SnF$_4$(NH$_4$)$_2$]$^c$</td>
<td>2.108$^c$</td>
<td>2.127$^c$, 2.126</td>
<td>180.0</td>
<td>278</td>
</tr>
<tr>
<td>2</td>
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<td>2.625; 2.668</td>
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<td>2.407$^h$, 2.519$^j$</td>
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<td>907</td>
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<td>2.19</td>
<td>2.461$^b$, 2.626$^b$</td>
<td>172.8</td>
<td>960</td>
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$^a$Sn–X bond length for anions SnX$_2$$^-$ (Å): 1.955 (X = F)$^{278}$; 2.342, 2.401$^{962}$, 2.402–2.421$^{959}$, 2.420 (av)$^{963}$, 2.422 (av)$^{964}$, 2.426 (av)$^{965}$, 2.438 (av)$^{966}$ (X = Cl); 2.605 (X = Br)$^{959}$; 2.864 (X = I)$^{280}$; the Pb–Cl bond length in PbCl$_6$$^-$ is 2.510 Å$^{437}$.

$^b$Ligands in complexes: L$_1$ = tetraethylfurfuralenium, L$_2$ = H$_2$NOCOC$_2$H$_4$NH$_2$·2, L$_3$ = 2-H$_2$NC$_5$H$_4$NH, L$_4$ = 2,6-diacetylpyridine-bis(2-furoylhydrazone)dimethyltin, L$_5$ =N,N’-dimethyl-5-nitro-2’-bi-imidazol-3’-ium, L$_6$ = cytosinium, L$_7$ = 8-methylaminoquinolinium, L$_8$ = N-(4-hydroxybenzylidene)-4-methoxyaniline, L$_9$ = 8-methoxyquinolinium, L$_{10}$ = (3-MePz)$_3$SnBuCl$_2$, T = thiamine, Pz = Pyrazole.

$^c$Centrosymmetric anion.

$^d$Two crystallographically independent anions in the unit cell.

$^e$Average value.

$^f$ClSnClicis).

$^g$Sn–Cl···H(N).

$^h$Trans to carbon.

$^i$Cis to carbon (average).

$^j$CSnHal(trans).
As the Cl\(^-\) ions are removed, the remaining Sn–Cl bonds get shorter and the CSnC angle becomes narrower\textsuperscript{953}.

The average Sn–Cl distance in anions R\(_2\)SnCl\(_4\)\(^{2-}\) is correlated with the Lewis acidity of the diorganothiotin moiety. The average Sn–Cl bond distances in the Vin\(_2\)Sn (2.593 Å) complexes and Pb\(_2\)Sn (2.583 Å) (entries 11 and 13) are practically equivalent, as both involve C\(_{sp2}\) atoms, and are shorter than the distance found in the Me\(_2\)Sn compounds (e.g. 2.628, entry 5).

There are two kinds of Pb\(_2\)SnCl\(_4\)\(^{2-}\) anions in 476, one placed between two cations with its phenyl groups stacking over their pyrimidine rings, and the other without a close relationship to any cation. The two Sn atoms lie on a crystallographic inversion center\textsuperscript{930}.

A comparison of the six-coordinate and five-coordinate anions, Me\(_2\)SnBr\(_4\)\(^{2-}\) and Me\(_2\)SnBr\(_3\)\(^-\), demonstrates Sn–Br distances in the order Sn–Br (oct) (2.768 Å) > Sn–Br (ax) (2.734 Å) > Sn–Br (eq) (2.498 Å)\textsuperscript{270}. The latter distance is of the same order of magnitude as that in tetracoordinate compounds (2.49 Å)\textsuperscript{9}.

High level \textit{ab initio} SCF MO calculations showed that trans-[R\(_2\)SnX\(_4\)]\(^{2-}\) anions are stable with respect to their cis-isomers by ca 19 kcal mol\(^{-1}\) (R = Me, Et; X = Cl)\textsuperscript{270}. While the gas-phase formation of pentacoordinate [R\(_2\)SnX\(_3\)]\(^-\) anions from R\(_2\)SnX\(_2\) and X\(^-\) is an exothermic process, hexacoordinate [R\(_2\)SnX\(_4\)]\(^{2-}\) anions are unstable in the gas phase toward dissociation into [R\(_2\)SnX\(_3\)]\(^-\) and X\(^-\) (R = Me, Et; X = Hal). For octahedral trans-[R\(_2\)SnX\(_4\)]\(^{2-}\) anions, the Sn–X bonds are even longer (by ca 3%) than the axial Sn–X bond in the TBP [R\(_2\)SnX\(_3\)]\(^-\) anions. Moreover, for cis-[R\(_2\)SnCl\(_4\)]\(^{2-}\) anions (R = Me, Et), the Sn–Cl bonds cis to the R groups are longer than the trans bonds, in line with the \textit{cis} weakening effect of the R groups previously found experimentally\textsuperscript{25,970b}.

Reaction of KF with RSnCl\(_3\) in water leads to the formation of water-soluble complexes of the type K\(_2\)[RSnF\(_5\)]\textsuperscript{296,971a}. Similarly, and in contrast to the reaction between halide ions and X\(_3\)Sn(CH\(_2\))\(_n\)SnX\(_3\) (X = Cl, Br; n = 1, 3, 4, 8), which yield five-coordinate dinuclear 1:2 adducts (equation 13, Section IV.A.5), the hexachloride Cl\(_3\)Sn(CH\(_2\))\(_3\)SnCl\(_3\) reacts with an excess of KF in water to give the dianionic species K\(_2\)[F\(_3\)Sn(CH\(_2\))\(_3\)SnF\(_5\)] (481) in solution. The \(^{119}\)Sn and \(^{19}\)F NMR data indicate that the tin atoms in both K\(_2\)[BuSnF\(_5\)] and 481 are six-coordinate (\(\delta^{119}\)Sn = 625.1 and = 615.7 ppm, respectively)\textsuperscript{296}.

X-ray studies of hexacoordinate RSnX\(_5\)\(^{2-}\) anions of the type 479 (entries 21–26)\textsuperscript{295,907,950–961} showed octahedral geometry for all the tin atoms with the shorter Sn–X distances (2.42–2.47 Å for X = Cl, 2.56 Å for X = Br) for those trans to the Sn–C bond. The mean values of the remaining four Sn–X distances are in the range of 2.48–2.52 Å (X = Cl) and 2.70 Å (X = Br). These data were used as evidence of \textit{trans}-strengthening in octahedral tin chlorine- and bromine-containing complexes\textsuperscript{959}. A similar geometry is found for the hexacoordinate PhPbCl\(_5\)\(^{2-}\) (480, entry 27)\textsuperscript{960} with a Pb–Cl distance \textit{trans} to the phenyl ligand of 2.46 Å, which is significantly shorter than the other four Pb–Cl distances (2.60–2.68 Å). Earlier examples of complexes with this anion can be found elsewhere\textsuperscript{305}.

The reaction of the difluoride [Me\(_2\)N(CH\(_2\))\(_3\)]\(_2\)SnF\(_2\) with an excess of Bu\(_4\)NF · 3H\(_2\)O in CH\(_2\)Cl\(_2\) solution lead to the zwitterionic compounds 482 and 483, depending on the concentration of reactants\textsuperscript{971b}. It is suggested that attack of fluoride ions at tin which intramolecularly coordinated in the precursor difluoride [Me\(_2\)N(CH\(_2\))\(_3\)]\(_2\)SnF\(_2\) results in Sn–bond dissociation and enhancement of the nucleophilicity of the 3-dimethylaminopropyl nitrogens by the hypercoordinate C\(_2\)SnF\(_3\)\(^-\) and C\(_2\)SnF\(_4\)\(^{2-}\) configurated tin centers. Consequently, the reaction of tertiary amino groups with dichloromethane is facilitated.
An X-ray diffraction of 483, which is formed in more concentrated solutions, reveals a near-ideal octahedral structure with FSnF\(\text{trans}\) and CSnC angles of 180° and Sn–F bond lengths in the range 2.06–2.11 Å, which is above the standard value for tetracoordinate compounds (1.96 Å)\(^9\) and Sn\(\text{F}_6\)^2– anion (1.955 Å)\(^{278}\), and is very close to those in Me\(_2\)Sn\(\text{F}_4\)^2– (ca 2.13 Å)\(^{278}\).

**B. Intramolecular Complexes**

A number of anionic hexacoordinate O,O- and S,S-chelates have been reported. Among them, the acetylacetonate \([\text{Cl}_4\text{Sn(MeCOCHCOMe)}][\text{Et}_3\text{NH}]\) (484)\(^{972}\) and oxalato ditin species \([\text{Cl}_4\text{Sn(OOCCOO)}\text{SnCl}_4][\text{Et}_4\text{N}]\)\(^{2973}\) are rare examples of mono-chelate anionic complexes. A crystallographic study of 484 showed a near-octahedral geometry at tin with two axial (ClSnCl 172.3°, Sn–Cl 2.400 and 2.445 Å) and equatorial (ClSnCl 97.1°, Sn–Cl 2.370 Å) chlorine atoms, as well as two equatorial oxygen atoms (OSnO 87.5°, Sn–O 2.093 Å).

Another example for mono-chelate complexes investigated for their antitumour activity\(^{857}\) consists of tetraethylammonium halide adducts 485 (X = Hal, R = Alk, Ar) containing O,N,O-tridentate dianionic ligand.

Rare representatives of anionic hexacoordinate organotin chelates are the bisoxalato complexes 486a\(^{974}\) and 486b\(^{975}\). According to an X-ray study, the anion in 486a adopts
a skew-trapezoidal geometry owing to anisobidentate chelation by the oxalato groups (Sn–O = 2.110, 2.112, 2.363 and 2.348 Å; CSnC 146.7°). In the diphenyl analogue \( \text{Sn} \) which was unexpectedly isolated from the disproportionation of the precursor oxalato-riphenylstannate, the tin atom exists in a distorted octahedral environment with somewhat different but closer O–Sn distances (2.121 and 2.184 Å) than in the anion of \( \text{Sn} \), and two cis-phenyl groups (CSnC 106.0°).

In the related dimethyl analogue, the aqua complex \( [\text{Me}_2\text{Sn}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})][(c-\text{C}_6\text{H}_{11})_2\text{NH}_2]_2 \)\(^{976}\), the coordination number of tin is expanded from six to seven due to the coordinated water molecule (Sn–O(\( \text{H}_2 \)) = 2.428 Å). The Sn atom is chelated by two isobidentate oxalato groups (O–Sn = 2.24–2.32 Å) and exists in a \( \text{trans} - \text{C}_2\text{SnO}_5 \) pentagonal–bipyramidal environment (CSnC 173.5°). A similar structure was earlier found for \( [\text{Me}_2\text{Sn}(\text{OAc})_3][\text{NMe}_4], \) in which the tin atom is chelated by two anisobidentate acetato groups (O–Sn 2.270, 2.271 Å and 2.524, 2.520 Å) and one monodentate acetato group (O–Sn 2.113 Å, the second O···Sn separation is 3.334 Å)\(^{29}\).

Unlike organogermanium and organotin derivatives, bis- and tris-chelates without M–C bonds have been known for a long time. Tris(2,3-butanediolato) dianionic germanium complexes were used in reactions with organometallic reagents for the preparation of organogermanes\(^{977,978}\). X-ray studies of the hexacoordinate anions, trisoxalate \( \text{Ge(OCCOO)}_3 \)\(^{2−} \)\(^{979,980}\) and trisoxalate \( \text{Ge}(1,2-\text{OC}_6\text{H}_4\text{O})_3 \)\(^{2−} \)\(^{981,982}\), reveal the germanium center to be octahedrally coordinated by three 1,2-diolato ligands with OGeO angles in the ranges of 84°–86° and 173.0–175.4°, and the Ge–O bond lengths in the range 1.84–1.90 Å. A similar geometry is found for their tin analogues, tris(1,2-OC\(_6\)H\(_4\)O\(_3\))\(^{2−} \), (Sn4(NO\(_2\)-1,2-OC\(_6\)H\(_4\)O)\(_3\))\(^{2−} \), Sn(1,2-OC\(_6\)Cl\(_2\)O)\(_3\))\(^{2−} \) and the catecholthiolate Sn(1,2-OC\(_6\)H\(_4\)S)\(_3\))\(^{2−} \). The structure of the bis-chelate bis(tetramethylammonium) bis(citrato)tin containing O,O,O-dianionic tridentate ligand was also established\(^{985}\).

Hexacoordinate 1,2-dithiolato complexes, the bis-MN derivatives, e.g. \([\text{MNT})_2 \)\( \text{Sn(OH)}_2[\text{Et}_4\text{N}]_2 \)\(^{986}\), and bis-DMIT compounds, \( \text{Sn(OH)}_2[\text{Et}_4\text{N}]_2 \)\(^{987}\), as well as tris-chelates containing DMIT, \( \text{Sn(OH)}_2[\text{Et}_4\text{N}]_2 \)\(^{987}\), and DSIT, \( [\text{Sn(DSIT)}_3][\text{R}_4\text{N}]_2 \)\(^{987}\), \( [\text{Sn(DSIT)}_3][\text{R}_4\text{N}]_2 \)\(^{987}\), \( [\text{Sn(DSIT)}_3][\text{R}_4\text{N}]_2 \)\(^{987}\), \( [\text{Sn(DSIT)}_3][\text{R}_4\text{N}]_2 \)\(^{987}\), \( [\text{Sn(DSIT)}_3][\text{R}_4\text{N}]_2 \)\(^{987}\), \( [\text{Sn(DSIT)}_3][\text{R}_4\text{N}]_2 \)\(^{987}\), were reported. Dihalides \( \text{Sn}(1,2-\text{OC}_6\text{H}_4\text{O})_3 \)\(^{2−} \), \( \text{Sn}(4-\text{NO}_2-1,2-\text{OC}_6\text{H}_4\text{O})_3 \)\(^{2−} \), \( \text{Sn}(1,2-\text{OC}_6\text{Cl}_2\text{O})_3 \)\(^{2−} \) and the catecholthiolate \( \text{Sn}(1,2-\text{OC}_6\text{H}_4\text{S})_3 \)\(^{2−} \) were prepared from \( [\text{Zn(DMIT)}_2][\text{Bu}_4\text{N}]_2 \), SnX\(_4\) in the presence of Bu\(_4\)Nb. Note that while the bis-chelate dianions, \( [\text{Sn(DMIT)}_2\text{X}_2]^{-} \) (X = Br, I), were synthesized\(^{987}\), the corresponding fluoride and chloride compounds were yet to be isolated\(^{988}\). Isolation of the tris(DMIT)stannate salts was achieved from reactions of SnCl\(_4\) with \([\text{Zn(DMIT)}_2][\text{M}]_2 \), from reaction mixtures containing \( [\text{Sn(DMIT)}_2\text{X}_2][\text{M}]_2 \) (X = Br, I) and fluoride ion and from the reactions of SnCl\(_2\) with Sn(OAc)\(_4\) in the presence of MX (X = F, Br or I). The related DMIO and DSIT derivatives \( \text{Sn(OH)}_2[\text{Et}_4\text{N}]_2 \)\(^{987}\), and \( \text{Sn(OH)}_2[\text{Et}_4\text{N}]_2 \)\(^{987}\), were obtained by the reaction of tin(IV) compounds with dithiolato and dielenolate precursors\(^{988}\).

Crystal structure determinations of the bis- and tris-(dithiolato)stannate salts \( \text{Sn(OH)}_2[\text{Et}_4\text{N}]_2 \)\(^{987}\), \( \text{Sn(OH)}_2[\text{Et}_4\text{N}]_2 \)\(^{987}\), \( \text{Sn(OH)}_2[\text{Et}_4\text{N}]_2 \)\(^{987}\), and \( \text{Sn(OH)}_2[\text{Et}_4\text{N}]_2 \)\(^{987}\), revealed an essentially octahedral geometry about tin with chelate bite angles of 80.7–87.4°, Sn–S distances of 2.52–2.57 Å and \( \text{trans} \) SSnS angles from 162.3 to 174.6°. For \( \text{Sn} \) containing cis-iiodide ligands, the Sn–I bond lengths are 2.724 and 2.727 Å with an ISnI angle of 90.1°. The Sn–I values compare with those found for tetracoordinate, tetrahedral R\(_3\)SnI compounds. The differences between the values of the Sn–S bond lengths \( \text{trans} \) to sulfur (2.520 and 2.539 Å) and \( \text{trans} \) to iodine (2.554 and 2.566 Å) are relatively small.

A statistical analysis, carried out on the crystal structure data for the tris-chelates \( \text{Sn(OH)}_2[\text{Et}_4\text{N}]_2 \)\(^{987}\), indicated that the most critical factors in controlling the overall shape of the dianion were the distances of the Sn atom from the dithiolate ligand planes.
The $^{119}$Sn NMR spectra of the 1,2-dithiolato complexes discussed above in various solvents indicate ionized species with anions containing six-coordinate tin atoms. The $\delta^{119}$Sn NMR values are about $-248$ ppm for $[\text{Sn(DMIT)}_2\text{X}_2]^{2-}$, $-249 \pm 2$ ppm for $[\text{Sn(DMIT)}_3]^{2-}$, $278 \pm 5$ for $[\text{Sn(DMIO)}_3]^{2-}$ and $-237$ for a single $[\text{Sn(DSIT)}_3]^{2-}$ complex$^{987,988}$; these values are in the region for six-coordinate tin species.

X. HEXACOORDINATE NEUTRAL COMPOUNDS

Some neutral complexes, in which the central atom is hexacoordinate due to intermolecular or/and intramolecular coordination, have been described. The presence of the electronegative substituents is essential for the formation of such complexes, and their stability generally increases in the sequence: Ge < Sn < Pb.

A. Complexes with Intermolecular Coordination

Hexacoordinate neutral complexes can include either two monodentate or one bidentate donor ligand. Formally, the latter is a chelate complex; however, the presence of two intermolecular coordinate bonds enables one to consider such a ligand in this section.

1. Germanium

A clearly pronounced acceptor ability of the tetravalent organogermanes $R_n\text{GeCl}_{4-n}$ ($n = 1, 3, R = \text{Ph}; n = 2, R = \text{Me}$) toward N-, P- and O-donor molecules was deduced from calorimetric titration. $\text{Me}_2\text{GeCl}_2$ forms $1:2$ complexes with $\text{Bu}_3\text{N}^{54}$, but, as well as
Ph$_2$GeCl$_2$\textsuperscript{53}, it does not react with 2,2$'$-bipyridine, 2-methylpyridine and with O- and P-donors. The reaction of diorganodichlorogermanes with 1,10-phenanthroline (Phen) results in hexacoordinate adducts R$_2$GeCl$_2$·Phen (R = n-Bu, Ph), but their physical-chemical characteristics were not reported, with the exception of their melting points\textsuperscript{58}. Phenyltrichlorogermane forms 1 : 2 adducts with all the monodentate ligands investigated and 1 : 1 complexes with bidentate ligands. Several adducts were isolated, but their structures were not studied in detail.

The composition and structure of the adducts of trifluoromethylhalogermanes and (CF$_3$)$_4$Ge with N- and O-donating ligands have been studied\textsuperscript{922,989}. Trifluoromethylhalogermanes easily form 1 : 1 and 1 : 2 complexes with amines and ammonia. (CF$_3$)$_4$Ge gives adducts\textsuperscript{491} with ammonia and primary amines (equation 84).

\[
(CF_3)_4Ge + nNH_2R \rightarrow (CF_3)_4(\text{GeNH}_2R)_n
\]

\((491)\ R = \text{H}, \ n = 2, 3\)

\((491)\ R = \text{Me}, \ n = 1, 2\)

Secondary and tertiary amines, pyridine, aniline and 1,2-diaminobenzene do not react with (CF$_3$)$_4$Ge due to steric factors. Complexes of the type\textsuperscript{491} slowly decompose on storage to afford cyclic oligomers such as [(CF$_3$)$_2$GeNR]$_3$\textsuperscript{989}. Hexacoordination of the germanium in\textsuperscript{491} and analogous complexes with N- and O-donors (CF$_3$)$_4$GeL$_2$ (L = NH$_3$, MeNH$_2$, DMSO, Me$_2$P(O)H was established by $^1$H NMR, IR and Raman spectroscopy\textsuperscript{989}.

Structurally characterized GeX$_4$D$_2$ systems possess cis-isomers in the case of bidentate ligands as for\textsuperscript{492} and trans-isomers for monodentate bis-ligands (Table 68). The structure of the tetrachlorobis(4-methylpyridine)germanium\textsuperscript{993}, tetrabromobis(4-methylpyridine)germanium, tetrabromobis(3,4-dimethylpyridine)germanium\textsuperscript{994} and\textsuperscript{493} is octahedron with two aromatic nitrogen- and arsenic-donor ligands in trans-axial positions.

The structures of germanium complexes\textsuperscript{494a,995,494b,996,495a,997 and 495b,998} show that the central Ge atom has an octahedral structure with two bidentate deprotonated catechol moiety in equatorial positions.

Complex\textsuperscript{494a} has an ideal octahedral structure (O $\rightarrow$ Ge $\leftarrow$ O 180°), and the distance between the Ge and the equatorial plane is 0.0 Å. Among the three types of Ge–O bonds,

| TABLE 68. Selected structural data for GeX$_4$-D$_2$ complexes |
|------------------|--------|--------|--------|--------|--------|
|                  | X      | D      | D → Ge | Ge–X  | D → Sn ← D | Reference |
| ![Diagram](image) | ![Diagram](image) | 2.023  | 1.756(eq) | 79.3  | 990       |
| ![Diagram](image) | ![Diagram](image) | 2.029  | 1.777(ax) |        |           |
| ![Diagram](image) | ![Diagram](image) | 2.472  | 2.341    | 180.0 | 991       |
| ![Diagram](image) | ![Diagram](image) | 2.307  |          |        |           |
| ![Diagram](image) | ![Diagram](image) | 2.112  | 2.446    | 180.0 | 992       |
| ![Diagram](image) | ![Diagram](image) | 2.307  |          |        |           |
the bond lengths for the aqua oxygens (O → Ge 1.949 Å) are larger than those for the carboxylate oxygens (1.817 and 1.866 Å). The methanol adduct 495a has a slightly distorted octahedral structure with two molecules of methanol in axial positions. The O → Ge bond lengths (1.994 Å) for the methanol oxygens are longer than those for the catechol oxygens (1.823 and 1.850 Å) resulting from the stronger bonding to the aryloxide ligands.

73Ge chemical shifts for a series of hexacoordinated organogermanium GeX4D2 complexes (X = Cl, NCS, D2 = Bipy, Phen), as well as for GeBr4 · Bipy or GeI4 · Bipy complexes, were observed. A dramatic upfield 73Ge NMR shift for hexacoordinated organogermanium complexes GeCl₄(NCS)₄−n · D₂ (D₂ = Bipy and Phen) is associated with a change from tetracoordinated Ge to the hexacoordinated state (Table 69). The difference in the 73Ge chemical shifts, for example, for D₂ = Bipy (∆δ = −334.6 ppm) and for D₂ = Phen (−351.3 ppm) suggests the formation of a stronger complex. A large (50–57 ppm) upfield shift of the 15N resonances of Bipy in the complexes with respect to the free ligand (δ¹⁵N = −73.1 ppm in DMSO-d₆) is consistent with the involvement of the nitrogen lone pair in the N → Ge bond formation.

### Table 69. δ⁷³Ge value (in ppm) for hexacoordinated organogermanium compounds in acetone-d₆

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ⁷³Ge</th>
<th>Compound</th>
<th>δ⁷³Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeCl₄</td>
<td>30.9</td>
<td>GeCl₂(NCS)₂ · Bipy</td>
<td>−327.1</td>
</tr>
<tr>
<td>GeCl₄ · Phen</td>
<td>−319.4</td>
<td>GeCl(NCS)₃ · Bipy</td>
<td>−340.2</td>
</tr>
<tr>
<td>GeCl₄ · Bipy</td>
<td>−313.7</td>
<td>Ge(NCS)₄ · Bipy</td>
<td>−351.8</td>
</tr>
<tr>
<td>GeCl₃(NCS) · Bipy</td>
<td>−319.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2. Tin

a. $XR_3Sn \cdot D_2$ systems. For this type of triorganotin complexes a second electronegative substituent $X$ for hypervalent bonding is absent and this does not promote formation of the hexacoordinate state. A rare example is the triphenyltin derivative $496^{1000}$, where the coordinate $N^1 \rightarrow Sn$ bond trans to oxygen (2.395 Å) is shorter than that trans to Ph (2.602 Å). The deviation from linearity in the former hypervalent bonding, ($N^1 \rightarrow Sn–O 158.8^\circ$), as compared to the latter, ($N^2 \rightarrow Sn–C 176.4^\circ$), is due to the additional intramolecular $O \cdot \cdot \cdot Sn$ (3.401 Å) contact$^{1000}$.

b. $X_2R_2Sn \cdot D_2$ systems. In recent years there has been increasing interest in the synthesis and structural study of octahedral diorganotin dihalide complexes, $R_2SnHal_2 \cdot D_2$, owing to their antitumour activity$^{280}$. Attempts to correlate structural data and antitumour activity have concluded that biologically active complexes have Sn–N bond lengths of $\geq 2.4$ Å, suggesting that dissociation of ligands is an important step in their mechanism of action. In principle, these types of diorganotin complexes can exist in five forms of geometrical isomers as shown below. The most widespread and representative from X-ray data are two isomers: (cis-D, trans-R) and all-trans.

```
cis-D trans-R
```

```
cis-D, trans-X
```

```
cis-D, trans-X
```

```
cis-D, trans-X
```

```
cis-D, trans-X
```

The most electronegative substituent $X$ should be placed, as a rule, in a trans-position to the coordination bond according to a linear hypervalent $D \rightarrow M–X$ bonding, i.e. the structure of octahedral $MR_2X_2 \cdot D_2$-type complexes assumes two linear $D \rightarrow M–X$ fragments with a cis-arrangement for $D$ and $X$ (cis-D, trans-R). Two linear fragments with organic substituents $D \rightarrow M–C$ (cis-D, trans-X), as well as less symmetrical structures (all-cis) were not observed experimentally. In some cases the donor fragments $D$ are in a trans-arrangement (trans-D), for which (all-trans) octahedral structures are mainly found, while a configuration with two linear $X–M–C$ fragments (trans-D, cis-X, R) is rare.

The difference in energies of cis- and trans-D isomers seems to be insignificant, in accordance with the simultaneous presence of both isomers in $Et_2SnCl_2(Ph_3PO)_2^{1001}$. In solution, the establishment of cis/trans-D equilibria in hexacoordinate tin complexes is generally fast on the $^1H$ NMR time scale. A rare observation of different isomers of neutral octahedral diorganotin compounds in solution was described$^{1002}$. This is somewhat surprising, but may be traced to the usually poor solubility of hexacoordinate organotin compounds, making low-temperature NMR studies difficult if not impossible.
16. Hypervalent compounds of organic germanium, tin and lead derivatives

i. Octahedral complexes with cis-D (trans-R) structure. The most important structural data of cis-SnR2X2 · D2 complexes with N,N-coordinating ligands are collected in Tables 70 and 71.

The adduct Me2SnBr2 · (MeCONMe2)_2 exists in a variety of structural types, in which the Sn atom can be, in particular, hexacoordinated. In this case, the preferred solid-state molecular structure of the central tin atom is cis-dibromo-trans-dimethyl. The structures of hexacoordinate ditin adducts 497, 498, 355 and 499 have also been reported.

The dihalide cis-SnR2X2 · D2 complexes with monodentate O- and S-donor ligands (e.g. DMSO, DMF) have been studied extensively (Table 72). In all cases, the tin atoms exhibit a distorted octahedral geometry. The degree of distortion becomes obvious when the angles C−Sn−Ca and O→Sn−halogen are compared. The Sn−halogen bonds are longer than in the precursor uncomplexed compounds.

An X-ray structure determination of cis-Me2SnHal2 · 2D (500) (D = N-methyl-pyrrolidin-2-one) shows that the coordination of the lactam ligand to Sn is realized via oxygen (Table 72). A comparative study of the bond lengths leads to the unexpected observation that the O→Sn bonds in 500a (Hal = Cl) are the longest in the series (2.446 and 2.460 Å). The O→Sn bond lengths are almost identical in 500b (Hal = Br), 2.323 and 2.345 Å, and in 500c (Hal = I), 2.294 and 2.326 Å. This effect might be even greater on going from Br to I, but the size of the ligand seems to become predominant.

The six-coordinate phosphine oxide complexes of diorganotins 501, 502a, 502b and 503 adopt the common cis-geometry at the Sn atom.
TABLE 70. Selected structural data for \textit{cis}-SnR$_2$Cl$_2$·D$_2$ complexes (one bidentate N,N-coordinating ligand)

<table>
<thead>
<tr>
<th>R</th>
<th>D$_2$</th>
<th>R$\rightarrow$ Sn (Å)</th>
<th>Sn–Cl (Å)</th>
<th>R-Sn-R (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>N$_2$-Aminoquinoline</td>
<td>2.322, 2.357</td>
<td>2.547, 2.620</td>
<td>176.9</td>
<td>1003</td>
</tr>
<tr>
<td>Me</td>
<td>Phen</td>
<td>2.385</td>
<td>2.521</td>
<td>178.0</td>
<td>809</td>
</tr>
<tr>
<td>Me</td>
<td>Bipy</td>
<td>2.395</td>
<td>2.351</td>
<td>175.9</td>
<td>1004</td>
</tr>
<tr>
<td>Me</td>
<td>2-(2-Pyridyl)benzimidazole</td>
<td>2.422, 2.447</td>
<td>2.483, 2.550</td>
<td>171.9</td>
<td>1005</td>
</tr>
<tr>
<td>Me</td>
<td>(2-Pyridylmethylene)-2-toluidine</td>
<td>2.427, 2.444</td>
<td>2.485, 2.507</td>
<td>171.5</td>
<td>1006</td>
</tr>
<tr>
<td>Me</td>
<td>Bis(4-methylpiperazinyl)methane</td>
<td>2.438</td>
<td>2.499</td>
<td>173.9</td>
<td>1007</td>
</tr>
<tr>
<td>Me</td>
<td>N'-Phenylpyridine-2-carbaldehyde</td>
<td>2.439, 2.539</td>
<td>2.462, 2.541</td>
<td>167.3</td>
<td>1008</td>
</tr>
<tr>
<td>Me</td>
<td>N-(2-Pyridylmethylene)-4-toluidine</td>
<td>2.443, 2.485</td>
<td>2.494, 2.503</td>
<td>171.6</td>
<td>1009</td>
</tr>
<tr>
<td>Me</td>
<td>2-Methoxyphenyl(2-pyridylmethylidene)amine</td>
<td>2.456, 2.460</td>
<td>2.496, 2.520</td>
<td>172.8</td>
<td>1010</td>
</tr>
<tr>
<td>Et</td>
<td>3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine</td>
<td>2.448, 2.549</td>
<td>2.450, 2.508</td>
<td>164.6</td>
<td>1011</td>
</tr>
<tr>
<td>i-Pr</td>
<td>Bipy</td>
<td>2.377, 2.400</td>
<td>2.546, 2.569</td>
<td>177.3</td>
<td>1004</td>
</tr>
<tr>
<td>i-Pr</td>
<td>Phen</td>
<td>2.396, 2.400</td>
<td>2.537, 2.568</td>
<td>178.5</td>
<td>1012</td>
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<tr>
<td>Bu</td>
<td>Phen</td>
<td>2.352, 2.432</td>
<td>2.550, 2.552</td>
<td>177.0</td>
<td>1013</td>
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<tr>
<td>Bu</td>
<td>4,7-Diphenylphenanthroline</td>
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<td>1014</td>
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<td>2.490, 2.573</td>
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<td>1004</td>
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<tr>
<td>Bu</td>
<td>Bipy</td>
<td>2.405, 2.412</td>
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<td>169.3</td>
<td>1015</td>
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<tr>
<td>Bu</td>
<td>Bis(1-methyl-2-imidazolylthio)methane</td>
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<td>2.507</td>
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<td>471</td>
</tr>
<tr>
<td>c-C$_5$H$_9$</td>
<td>4,4'-Me$_2$ bipy$^b$</td>
<td>2.435, 2.436</td>
<td>2.507, 2.508</td>
<td>174.5</td>
<td>1016</td>
</tr>
<tr>
<td>c-C$<em>6$H$</em>{11}$</td>
<td>Phen</td>
<td>2.394, 2.408</td>
<td>2.539, 2.548</td>
<td>176.8</td>
<td>1012</td>
</tr>
<tr>
<td>C$<em>5$H$</em>{11}$</td>
<td>4,4'-Me$_2$ bipy$^b$</td>
<td>2.439</td>
<td>2.508</td>
<td>174.4</td>
<td>1017</td>
</tr>
<tr>
<td>CH$_2$Ph</td>
<td>Phen</td>
<td>2.356, 2.365</td>
<td>2.511, 2.511</td>
<td>178.5</td>
<td>1012</td>
</tr>
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<td>CH$_2$Ph</td>
<td>Bipy</td>
<td>2.372, 2.383</td>
<td>2.504, 2.525</td>
<td>178.4</td>
<td>1004</td>
</tr>
<tr>
<td>(CH$_2$)$_2$CN</td>
<td>Bipy</td>
<td>2.338, 2.346</td>
<td>2.505, 2.530</td>
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<td>1018</td>
</tr>
<tr>
<td>(CH$_2$)$_2$CN</td>
<td>Phen</td>
<td>2.353, 2.355</td>
<td>2.509, 2.549</td>
<td>177.3</td>
<td>1019</td>
</tr>
<tr>
<td>Me, Ph</td>
<td>Bipy</td>
<td>2.389, 2.402</td>
<td>2.489, 2.490</td>
<td>171.7</td>
<td>809</td>
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<tr>
<td>Me, Ph</td>
<td>Phen</td>
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<td>1012</td>
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<tr>
<td>Me, Ph</td>
<td>Bipy</td>
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<td>2.488, 2.492</td>
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<td>809</td>
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<tr>
<td>Vin</td>
<td>Bipy</td>
<td>2.388, 2.391</td>
<td>2.500, 2.481</td>
<td>173.3</td>
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</tr>
<tr>
<td>Vin</td>
<td>Bipy</td>
<td>2.359, 2.395</td>
<td>2.463, 2.529</td>
<td>171.4</td>
<td>809</td>
</tr>
<tr>
<td>Ph</td>
<td>8-Aminoquinoline</td>
<td>2.305, 2.321</td>
<td>2.502, 2.518</td>
<td>106.9</td>
<td>1020</td>
</tr>
<tr>
<td>R</td>
<td>D₂</td>
<td>N → Sn (Å)</td>
<td>Sn–Cl (Å)</td>
<td>R-Sn-R (deg)</td>
<td>Reference</td>
</tr>
<tr>
<td>-----------------------</td>
<td>-------------</td>
<td>------------------</td>
<td>-----------------</td>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Ph</td>
<td>Bipy</td>
<td>2.325, 2.333</td>
<td>2.468, 2.478</td>
<td>177.6</td>
<td>1021</td>
</tr>
<tr>
<td>Ph</td>
<td>Phen</td>
<td>2.341, 2.379</td>
<td>2.449, 2.456</td>
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<td>1022</td>
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<tr>
<td>Ph</td>
<td>Bipy</td>
<td>2.345, 2.376</td>
<td>2.507, 2.511</td>
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<td>1023</td>
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<tr>
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<td>5-Methylphenanthroline</td>
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<td>2.438, 2.460</td>
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<td>1024</td>
</tr>
<tr>
<td>Ph</td>
<td>4,7-Dimethylphenanthroline</td>
<td>2.363, 2.371</td>
<td>2.486, 2.488</td>
<td>171.5</td>
<td>1024</td>
</tr>
<tr>
<td>Ph</td>
<td>Bipy</td>
<td>2.398, 2.413</td>
<td>2.451, 2.466</td>
<td>169.3</td>
<td>1025</td>
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<tr>
<td>Ph</td>
<td>Bis(3,5-dimethylpyrazolyl)methane</td>
<td>2.448, 2.526</td>
<td>2.414, 2.493</td>
<td>166.9</td>
<td>1026</td>
</tr>
<tr>
<td>Ph</td>
<td>4,5-Diazafluorene-9-one</td>
<td>2.499, 2.614</td>
<td>2.427, 2.443</td>
<td>162.3</td>
<td>1024</td>
</tr>
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<td>p-Tol</td>
<td>Bipy</td>
<td>2.306, 2.374</td>
<td>2.493, 2.507</td>
<td>108.7</td>
<td>1027</td>
</tr>
<tr>
<td>4-ClC₆H₄(β)ᵃ</td>
<td>4,4’-Me₂bipyᵇ</td>
<td>2.294, 2.322</td>
<td>2.475, 2.510</td>
<td>106.3</td>
<td>1028</td>
</tr>
<tr>
<td>4-ClC₆H₄(α)ᵇ</td>
<td>4,4’-Me₂bipyᵇ</td>
<td>2.311, 2.327</td>
<td>2.459, 2.491</td>
<td>163.5</td>
<td>1030</td>
</tr>
<tr>
<td>4-ClC₆H₄(α)ᵇ</td>
<td>4,4’-Me₂bipyᵇ</td>
<td>2.322, 2.294</td>
<td>2.509, 2.475</td>
<td>163.0</td>
<td>1028</td>
</tr>
<tr>
<td>4-ClC₆H₄(β)ᵃ</td>
<td>4,4’-Me₂bipyᵇ</td>
<td>2.317, 2.343</td>
<td>2.475, 2.478</td>
<td>106.8</td>
<td>1028</td>
</tr>
<tr>
<td>3, 4-Cl₂C₆H₃</td>
<td>4,4’-Me₂bipyᵇ</td>
<td>2.313, 2.335</td>
<td>2.463, 2.466</td>
<td>174.3</td>
<td>1031</td>
</tr>
<tr>
<td>NCS</td>
<td>Bipy</td>
<td>2.328</td>
<td>2.140(Sn-N),</td>
<td>106.3</td>
<td>1032</td>
</tr>
<tr>
<td>Me, Rᶜ (497)</td>
<td>Pyridazine</td>
<td>2.608 (Sn¹),</td>
<td>2.434 (Sn¹)</td>
<td>153.7 (Sn¹)</td>
<td>355</td>
</tr>
<tr>
<td>Me, Rᶜ (498)</td>
<td>Bipy</td>
<td>2.270</td>
<td>2.577</td>
<td>171.1</td>
<td>355</td>
</tr>
</tbody>
</table>

ᵃToluene solvate.
b(4,4’-dimethyl-2,2’-bipyridyl-N,N’).
cCH₂SnMeCl₂.
TABLE 71. Selected structural data for cis-SnR₂X₂ · D₂ complexes (one bidentate N,N-coordinating ligand)

<table>
<thead>
<tr>
<th>X</th>
<th>R</th>
<th>D₂</th>
<th>N → Sn (Å)</th>
<th>Sn–Cl (Å)</th>
<th>R–Sn–R (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br</td>
<td>Me</td>
<td>(N,N′-dimethyl-2,2′-imidazole)</td>
<td>2.292, 2.314</td>
<td>2.719, 2.768</td>
<td>177.68</td>
<td>1033</td>
</tr>
<tr>
<td>Br</td>
<td>Et</td>
<td>bis(1-methyl-2-imidazolylthio)methane</td>
<td>2.418, 2.499</td>
<td>2.686, 2.713</td>
<td>168.27</td>
<td>471</td>
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<tr>
<td>OCOCF₃</td>
<td>Vin</td>
<td>Bipy</td>
<td>2.339, 2.341</td>
<td>2.177, 2.251</td>
<td>174.32</td>
<td>1034</td>
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<tr>
<td>X¹</td>
<td>Me</td>
<td>1,10-phenanthroline</td>
<td>2.463, 2.497</td>
<td>2.235, 2.358</td>
<td>156.96</td>
<td>1035</td>
</tr>
</tbody>
</table>

X¹ = 1-Phenyl-5-thione-1,2,3,4-tetrazole.

TABLE 72. Selected structural data for cis-SnR₂X₂ · D₂ complexes (two monodentate O- or S-donor ligands)

<table>
<thead>
<tr>
<th>R</th>
<th>X</th>
<th>D²</th>
<th>O → Sn (Å)</th>
<th>Sn–X (Å)</th>
<th>R-Sn-R (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>Cl</td>
<td>DMSO</td>
<td>2.35, 2.36</td>
<td>2.49, 2.53</td>
<td>172.4</td>
<td>1038</td>
</tr>
<tr>
<td>Me</td>
<td>Cl</td>
<td>DMSO</td>
<td>2.273, 2.310</td>
<td>2.486, 2.524</td>
<td>170.28</td>
<td>1039</td>
</tr>
<tr>
<td>Me</td>
<td>Cl</td>
<td>DMSO</td>
<td>2.317, 2.368</td>
<td>2.486, 2.527</td>
<td>169.97</td>
<td>1040</td>
</tr>
<tr>
<td>Me</td>
<td>Cl</td>
<td>DMF</td>
<td>2.394</td>
<td>2.474</td>
<td>164.82</td>
<td>1039</td>
</tr>
<tr>
<td>Me</td>
<td>Cl</td>
<td>D₁</td>
<td>2.434, 2.401</td>
<td>2.485, 2.496</td>
<td>166.6</td>
<td>1027</td>
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<tr>
<td>Me (500a)</td>
<td>Cl</td>
<td>D₂</td>
<td>2.4464, 2.4598</td>
<td>2.474, 2.477</td>
<td>159.56</td>
<td>1041</td>
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<tr>
<td>Me</td>
<td>Cl</td>
<td>D₁</td>
<td>2.316, 2.320</td>
<td>2.515, 2.520</td>
<td>172.31</td>
<td>1042</td>
</tr>
<tr>
<td>Me</td>
<td>Cl</td>
<td>D₄</td>
<td>2.397, 2.404</td>
<td>2.483, 2.486</td>
<td>165.27</td>
<td>1043</td>
</tr>
<tr>
<td>Et</td>
<td>Cl</td>
<td>Ph₃PO</td>
<td>2.408, 2.449</td>
<td>2.485, 2.453</td>
<td>156.3</td>
<td>1001</td>
</tr>
<tr>
<td>Bu</td>
<td>Cl</td>
<td>D₁</td>
<td>2.497, 2.527</td>
<td>2.460, 2.466</td>
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<td>1044</td>
</tr>
<tr>
<td>Ph</td>
<td>Cl</td>
<td>DMSO</td>
<td>2.279, 2.355</td>
<td>2.474, 2.513</td>
<td>167.17</td>
<td>1045</td>
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<tr>
<td>4F-C₆H₄</td>
<td>Cl</td>
<td>D₁</td>
<td>2.308, 2.328</td>
<td>2.468, 2.473</td>
<td>168.30</td>
<td>1046</td>
</tr>
<tr>
<td>Me</td>
<td>Br</td>
<td>DMSO</td>
<td>2.223</td>
<td>2.747</td>
<td>179.97</td>
<td>1047</td>
</tr>
<tr>
<td>Me</td>
<td>Br</td>
<td>HMPA</td>
<td>2.230</td>
<td>2.735</td>
<td>179.98</td>
<td>627</td>
</tr>
<tr>
<td>Me</td>
<td>Br</td>
<td>D₁</td>
<td>2.348, 2.399</td>
<td>2.659, 2.638</td>
<td>164.1</td>
<td>1036</td>
</tr>
<tr>
<td>Me (500b)</td>
<td>Br</td>
<td>D₂</td>
<td>2.323, 2.345</td>
<td>2.674, 2.676</td>
<td>169.66</td>
<td>1041</td>
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<tr>
<td>Et</td>
<td>Br</td>
<td>Ph₃PO</td>
<td>2.230, 2.264</td>
<td>2.716, 2.800</td>
<td>178.01</td>
<td>1048</td>
</tr>
<tr>
<td>Et</td>
<td>Br</td>
<td>HMPA</td>
<td>2.209</td>
<td>2.752</td>
<td>180.00</td>
<td>1049</td>
</tr>
<tr>
<td>Et</td>
<td>Br</td>
<td>HMPA</td>
<td>2.227</td>
<td>2.756</td>
<td>180.00</td>
<td>1049</td>
</tr>
<tr>
<td>Me (500c)</td>
<td>I</td>
<td>D₂</td>
<td>2.294, 2.326</td>
<td>2.913, 2.930</td>
<td>170.27</td>
<td>1041</td>
</tr>
<tr>
<td>Et</td>
<td>I</td>
<td>Ph₃PO</td>
<td>2.265, 2.256</td>
<td>2.936, 3.101</td>
<td>173.58</td>
<td>1050</td>
</tr>
<tr>
<td>Et</td>
<td>I</td>
<td>HMPA</td>
<td>2.244</td>
<td>3.016</td>
<td>179.97</td>
<td>1050</td>
</tr>
<tr>
<td>Et</td>
<td>Br</td>
<td>D₁</td>
<td>2.771</td>
<td>2.759</td>
<td>180.00</td>
<td>1051</td>
</tr>
<tr>
<td>Vin</td>
<td>Cl</td>
<td>D₄</td>
<td>2.733</td>
<td>2.575</td>
<td>179.98</td>
<td>1052</td>
</tr>
</tbody>
</table>

D₁ = 2-imidazolidino,
D₂ = N-methylpyrrolidin-2-one-O,
D₃ = catena-(μ²-meso-1,2-bis(n-propylsulfinyl)ethane),
D₄ = catena-(μ²-meso-1,2-bis(phenylsulfinyl)ethane),
D₅ = thirane-1-oxide-O,
D₆ = dimethylacetamide,
D₇ = 3H-imidazole-2-thione,
D₈ = 3H-imidazoline-2-thione.
The spectroscopic and X-ray studies of diphosphoryl adducts of diorganotin(IV) halides revealed that they possess different structures depending on the nature of organotin halide and the diphosphoryl ligand \(^{127,1056,1057}\). Thus, methylene-diphosphonates and -diphosphinates usually serve as bidentate chelating ligands, providing monomeric octahedral complexes preferably with the trans-R configuration for diorganotin adducts \(^{127,1056}\). Bridging by methylenediphosphoryl ligands appears to be rare \(^{1056,1057}\).

It has been established for methylenediphosphonate complexes that substitution of a halogen atom by a more electropositive organic group in the trans-position relative to phosphoryl leads to strengthening of the Sn–O bond together with a significant lowering of the \(^2J^{(119)Sn−31P}\) magnitude \(^{1057,1058}\). This influence also exists in ethylenediphosphonate adducts \(^{125}\).

**ii. Octahedral complexes with all-trans structure.** These diorganotin species are represented in Table 73 for N-donor ligands and in Table 74 for O-donor ligands, respectively. The tin atom exhibits slightly distorted octahedral coordination geometry with two X atoms, two methyl C atoms and the N atoms of two ligands in an all-trans configuration. The D → Sn, Sn–X and Sn–C bond distances are identical in the pairs. The bond angles around the six-coordinated tin do not deviate more than 2° from ideal.

The azole ligands are always bonded to the organotin(IV) moiety through their pyridine-like nitrogen atom (Table 73). In 1-methylimidazole (NMI) complexes of the type \(\text{R}_2\text{SnX}_2 \cdot \text{D}_2\) (504), the N → Sn bond distance in the iodide 504c \((\text{R}=\text{Et})\) \(^{356}\), 2.366 Å, is slightly longer than that in chloride 504b \((\text{R}=\text{Me})\) \(^{1060}\), 2.329 Å, and bromide 504c
TABLE 73. Selected bond lengths in \textit{all-trans} SnR₂X₂ · D₂ complexes (two monodentate N-donor ligands)

<table>
<thead>
<tr>
<th>R</th>
<th>D (compound)</th>
<th>N → Sn (Å)</th>
<th>Sn–Cl (Å)</th>
<th>Sn–C (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>Im</td>
<td>2.312</td>
<td>2.5955</td>
<td>2.110</td>
<td>1059</td>
</tr>
<tr>
<td></td>
<td>NMI (504a)</td>
<td>2.329</td>
<td>2.571</td>
<td>2.118</td>
<td>1060</td>
</tr>
<tr>
<td></td>
<td>Pz</td>
<td>2.338</td>
<td>2.570</td>
<td>2.114</td>
<td>1061</td>
</tr>
<tr>
<td></td>
<td>4-Me-Pz</td>
<td>2.351</td>
<td>2.572</td>
<td>2.128</td>
<td>1062</td>
</tr>
<tr>
<td></td>
<td>4-Br-Pz</td>
<td>2.359</td>
<td>2.563</td>
<td>2.129</td>
<td>1063</td>
</tr>
<tr>
<td></td>
<td>3,4,5-Me₃-Pz</td>
<td>2.37, 2.38</td>
<td>2.563, 2.596</td>
<td>2.125, 2.128</td>
<td>1064</td>
</tr>
<tr>
<td></td>
<td>Ind (505a)</td>
<td>2.377</td>
<td>2.590</td>
<td>2.12</td>
<td>1065,1066</td>
</tr>
<tr>
<td></td>
<td>3,5-Me₂-Pz</td>
<td>2.379</td>
<td>2.581</td>
<td>2.11</td>
<td>1067</td>
</tr>
<tr>
<td></td>
<td>2-Cl-Im</td>
<td>2.380</td>
<td>2.591</td>
<td>2.134</td>
<td>1068</td>
</tr>
<tr>
<td></td>
<td>3-Me-adenine</td>
<td>2.384</td>
<td>2.596</td>
<td>2.121</td>
<td>1069</td>
</tr>
<tr>
<td></td>
<td>Pyridine</td>
<td>2.39</td>
<td>2.570</td>
<td>2.15</td>
<td>1070</td>
</tr>
<tr>
<td>Et</td>
<td>Pyridine</td>
<td>2.410, 2.411</td>
<td>2.591</td>
<td>2.151</td>
<td>1071</td>
</tr>
<tr>
<td>Bu</td>
<td>Pz</td>
<td>2.329, 2.388</td>
<td>2.587, 2.592</td>
<td>2.131, 2.149</td>
<td>1072</td>
</tr>
<tr>
<td>Bu</td>
<td>D¹</td>
<td>2.236</td>
<td>2.634</td>
<td>—</td>
<td>1073</td>
</tr>
<tr>
<td>Ph</td>
<td>Pz</td>
<td>2.315, 2.341</td>
<td>2.526, 2.536</td>
<td>2.140, 2.146</td>
<td>1074</td>
</tr>
<tr>
<td></td>
<td>Thiazole</td>
<td>2.368, 2.369</td>
<td>2.508, 2.569</td>
<td>2.153, 2.160</td>
<td>1075</td>
</tr>
</tbody>
</table>

| Et | NMI (504b)   | 2.336      | 2.738    | 2.125    | 356       |
| Me | NMI (504b)   | 2.340, 2.360 | 2.703, 2.766 | 2.125, 2.135 | 1076 |
| Me | Ind (505b)   | 2.368, 2.370 | 2.508, 2.569 | 2.154, 2.158 | 1077 |
| Me | Ind (505b)   | 2.370      | 2.733    | —        | 1065      |
| Et | Dipyrazole   | 2.356      | 2.746    | 2.093    | 1078      |
| Et | Thiazole     | 2.398      | 2.744    | 2.129    | 1079      |
| c-Hex | Pz        | 2.376      | 2.748    | 2.118    | 1080      |
| c-Hex | Im          | 2.393      | 2.759    | 2.176    | 1080      |

| X = I |
| Et   | NMI (504c)   | 2.366      | 2.990    | 2.148    | 356       |

\(^{a}\)Im = imidazole, NMI = 1-methylimidazole, Pz = pyrazole, Ind = indazole, D¹ = 2-[(phenylethylimino)methyl] phenol-O.

(R = Me)\(^{356}\), 2.336 Å, in agreement with the lower Lewis acidity of diodo with respect to dichloro and dibromo diorganotin species.

The structures of indazole (Ind) complexes Me₂SnX₂ · 2Ind (505a (X=Cl) and 505b (X = Cl)) are very similar, with practically undistorted \textit{trans}-octahedral coordination\(^{1065}\). In spite of the different acceptor capacities of these two species, the N → Sn bond length in 505a is practically the same length as that in 505b, probably because of the hydrogen bond.

In the crystal phase, the molecule of the adduct is always stabilized by a complex network of intermolecular hydrogen bonds between the coordinated halide atoms and the N-H groups of the organic ligands of the neighboring units.

The bond angles around the six-coordinated tin in spirocyclic 506 and 507 do not deviate from the ideal \textit{all-trans} configuration\(^{1081,1082}\).

There is a comprehensive review of tin adducts with nitrogen heterocycles\(^{362}\).

For a long time all efforts at isolating both a five- and six-coordinated diorganotin dihalide adduct containing the same donor ligand had failed. The authors\(^{424}\) were successful in obtaining the precise conditions necessary to isolate 1 : 1 (Table 28) and 1 : 2
16. Hypervalent compounds of organic germanium, tin and lead derivatives

(Table 74) adducts of Ph₂SnCl₂ with Ph₃PO. The O → Sn bond length decreases from a value of 2.278 Å in the 1 : 1 adduct to a value of 2.214 Å in the 1 : 2 adduct (Table 74). The decrease in the O → Sn donor bond length was attributed to increased Snδ+–Clδ− character on formation of the 1 : 2 adduct. Despite this decrease, the P–O bond length remains unchanged and hence the ν(P=O) stretching frequency also remains essentially unchanged on addition of the second mole of Ph₃PO to Ph₂SnCl₂ (ν(P=O) = 1140 cm⁻¹) 424.

For dichloro 1092 and diiodo 356 diorganotin adducts, considerable evidence exists for Sn–halogen bond length differences between the cis and trans arrangements, the former having shorter distances.

c. X₃RM · D₂ systems. These complexes are generally more stable than those of R₂SnX₂ having the same ligand. In neutral octahedral 1 : 2 adducts RSnX₃ · 2D the monodentate

<table>
<thead>
<tr>
<th>R</th>
<th>X</th>
<th>D¹</th>
<th>O → Sn</th>
<th>Sn–X (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
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<td>OPPH₃</td>
<td>2.214</td>
<td>2.554</td>
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<td>Cl</td>
<td>D¹</td>
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<td>Cl</td>
<td>HMPA</td>
<td>2.232</td>
<td>2.575</td>
<td>1084</td>
</tr>
<tr>
<td>Me</td>
<td>Cl</td>
<td>OH₂</td>
<td>2.234</td>
<td>2.112</td>
<td>943</td>
</tr>
<tr>
<td>Me</td>
<td>Cl</td>
<td>OH₂</td>
<td>2.406, 2.422</td>
<td>2.100, 2.113</td>
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<tr>
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<td>Cl</td>
<td>OH₂</td>
<td>2.456</td>
<td>2.120</td>
<td>1087</td>
</tr>
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<td>Ph, Bu</td>
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<td>D²</td>
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<td>2.06</td>
<td>1088</td>
</tr>
<tr>
<td>Me</td>
<td>Cl</td>
<td>C₅H₅NO</td>
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<td>2.58</td>
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<td>Cl</td>
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<td>2.570</td>
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<tr>
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<td>Cl</td>
<td>Ph₂PO</td>
<td>2.237, 2.258</td>
<td>2.601, 2.605</td>
<td>1001</td>
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<td>Br</td>
<td>HMPA</td>
<td>2.230</td>
<td>2.735</td>
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<td>Ph</td>
<td>SCN</td>
<td>HMPA</td>
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<td>2.128</td>
<td>1089</td>
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<tr>
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<td>SCN</td>
<td>OSO₂F</td>
<td>2.359</td>
<td>2.092</td>
<td>1090</td>
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<tr>
<td>Me</td>
<td>Cl</td>
<td>D³</td>
<td>2.730</td>
<td>2.615</td>
<td>391</td>
</tr>
<tr>
<td>Me</td>
<td>Cl</td>
<td>D⁴</td>
<td>2.734</td>
<td>2.623</td>
<td>1091</td>
</tr>
</tbody>
</table>

¹D¹ = quinoline N-oxide, D² = Ph₂P(O)CH₂CH₂P(O)Ph₂, D³ = 1,3-dimethylthiourea, D⁴ = 2(1H)-pyridinedithione-S.
²tetakis(purine) solvate.
³15-crown-5 solvate.
donor ligands D can be in a cis (508) or a trans (509) configuration. In the cis-isomer, the halide atoms can be arranged in two ways: fac- (at the corners of an octahedral face, 508a) and mer-arrangements (the tin atom is placed in the plane of the halide atoms, 508b).

Numerous compounds with a trans structure have been synthesized: EtSnCl\(_3\) · 2Ph\(_3\)PO\(^{1093}\), EtSnCl\(_3\) · 2(Me\(_2\)N)\(_3\)PO\(^{1094}\), EtSnCl\(_3\) · 2(Me\(_2\)N)\(_2\)CO\(^{1095}\), PhSnCl\(_3\) · 2(Me\(_2\)N)\(_3\)PO\(^{1095}\), EtSn\(_3\) · 2Ph\(_3\)PO\(^{1096}\) and EtSnBr\(_3\) · 2Ph\(_3\)PO\(^{1097}\), as well as the cis-fac compounds EtSn\(_3\) · 2(Me\(_2\)N)\(_3\)PO\(^{1098}\), n-BuSnCl\(_3\) · 2(Me\(_2\)N)\(_3\)PO\(^{1099}\) and the cis-mer compounds EtSn\(_3\) · 2Ph\(_3\)SO\(^{1100}\), n-BuSnBr\(_3\) · 2Ph\(_3\)SO\(^{1101}\).

In the octahedral Sn atom in BnSnCl\(_3\)(Phen) · C\(_6\)H\(_6\) (510) the two N atoms occupy positions trans to two of the Cl\(^1\) atoms, leaving one Cl\(^2\) atom trans to the C atom (Table 75)\(^{1102}\). As a result there are two classes of Sn–Cl interaction. The Cl atoms trans to the N atoms form longer Sn–Cl bonds (2.428 and 2.430 Å) than the Cl atom trans to the C atom (2.400 Å). However, in the crystal structure of the related n-butyl compound BnSnCl\(_3\)(Phen) (511)\(^{1103}\) one N-donor atom is trans to the organic substituent (cis-mer isomers), leading to disparate Sn–N bond distances\(^{1102}\).

\(i\)-PrSnCl\(_3\) · 2DMF (512)\(^{1104}\) and \(i\)-PrSnCl\(_3\) · 2DMSO (513)\(^{1105}\) are the only examples of 1 : 2 adducts of organotin trihalides with monodentate ligands containing oxygen as donor atoms which could be isolated as both fac and mer isomers. Both 512 and 513 showed a significant lengthening of the covalent Sn–Cl bonds in the hypervalent O → Sn–Cl fragments compared to bonds that lie cis to the O → Sn bond. In particular, for 513 the Sn–Cl bond lengths in the cis-fac isomers are 2.468 and 2.480 Å as compared with 2.398 Å (2.445, 2.463 and 2.410 Å, respectively, for another asymmetric unit) while in the cis-mer isomers the corresponding distance is 2.497 Å as compared with those of 2.440 and 2.468 Å (2.491, 2.455 and 2.470 Å, respectively, for the other asymmetric unit)\(^{1105}\).

The \(^{119}\)Sn NMR spectrum of the adduct PhSnCl\(_3\) · (EtO)\(_2\)POCH\(_2\)CH\(_2\)PO(OEt)\(_2\) at \(-90^\circ\)C consists of a triplet at \(-557\) ppm and a doublet of doublets at \(-551\) ppm with approximately 5 : 1 relative intensities. These resonances were attributed to isomers of the hexacoordinate complex\(^{301,1056}\). The first isomer has two equivalent phosphorus atoms in the tin coordination sphere and consists of cis-fac octahedra in accordance with the preferred cis-bridging behavior of the ethylene-diphosphonate ligand. The second isomer with nonequivalent phosphorus atoms consists of cis-mer octahedra\(^{125}\).

### TABLE 75. Selected bond lengths for SnRCl\(_3\) · Phen\(^a\) complexes (cis-fac isomer)

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>N → Sn (Å)</th>
<th>Sn–Cl(^1) (Å)</th>
<th>Sn–Cl(^2) (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>510</td>
<td>Bn</td>
<td>2.281, 2.283</td>
<td>2.428, 2.430</td>
<td>2.400</td>
<td>1102</td>
</tr>
<tr>
<td>511</td>
<td>n-Bu</td>
<td>2.243, 2.322</td>
<td>2.423, 2.456</td>
<td>2.399</td>
<td>1103</td>
</tr>
</tbody>
</table>

\(^a\)Phen = 1,10-phenanthroline.
16. Hypervalent compounds of organic germanium, tin and lead derivatives

**d. $X_4M\cdot D_2$ systems.** Organotin tetrahalide adducts of this type, where $X = \text{Cl, Br and I}$, $D = \text{monodentate ligand involving oxygen}$, $\text{nitrogen}$, $\text{phosphorus}$, and, to a lesser extent, $\text{sulfur}$ and $\text{selenium}$ as coordinating atom, are known. Perhaps the major point of interest in these bis adducts is the cis/trans isomerism around the metal atom. A search of the Cambridge Crystallographic Database reveals about 40 examples divided almost fifty-fifty between cis and trans isomers.

Studies of the SnX$_4$–THF reaction system ($X = F, \text{Cl, Br, I}$) have established an adduct SnX$_4$(THF)$_2$ formation only for $X = \text{Cl and Br}$, but not for $X = F$ and I. The metal–ligand (THF) bond distances in the trans-O–Sn–O linkage reflect the relative acceptor order: SnCl$_4 >$ SnBr$_4$.

There are no literature reports of structurally characterized SnF$_4\cdot D_2$ systems, and only one of a cis-bidentate ligand, i.e. SnF$_4(2,2'$-bipyridyl)$^{990}$. Some reports described SnF$_4$(MeCN)$_2$ as trans-adduct based on infrared and Mössbauer spectroscopic data$^{1113}$. Table 76 and 77 provide prominent structurally characterized examples of cis- and trans-SnX$_4D_2$ systems.

Comparisons of Sn–Cl bond distances for similar systems show little variation (Tables 76 and 77). Table 76 and 77 provide prominent structurally characterized examples of cis- and trans-SnX$_4D_2$ systems.

**TABLE 76. Selected bond lengths for cis-SnX$_4$·2D complexes**

<table>
<thead>
<tr>
<th>Compound</th>
<th>D → Sn (Å)</th>
<th>Sn–X (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[SnCl$_4$(H$_2$O)$_2$]·18-crown-6-2H$_2$O$^a$</td>
<td>2.16</td>
<td>2.37, 2.38</td>
<td>1114</td>
</tr>
<tr>
<td></td>
<td>2.10</td>
<td>2.379, 2.40</td>
<td></td>
</tr>
<tr>
<td>[SnCl$_4$(H$_2$O)$_2$]·18-crown-6-2H$_2$O-CHCl$_3$</td>
<td>2.113</td>
<td>2.392, 2.400</td>
<td>1115</td>
</tr>
<tr>
<td></td>
<td>2.115</td>
<td>2.391, 2.393</td>
<td></td>
</tr>
<tr>
<td>SnCl$_4$·2Me$_2$SO$^a$</td>
<td>2.110</td>
<td>2.369, 2.406</td>
<td>1106</td>
</tr>
<tr>
<td></td>
<td>2.110</td>
<td>2.377, 2.396</td>
<td></td>
</tr>
<tr>
<td>SnBr$_4$·2Ph$_3$PO</td>
<td>2.080</td>
<td>2.537, 2.557</td>
<td>969</td>
</tr>
<tr>
<td>SnBr$_4$·2Me$_2$SO$^a$</td>
<td>2.205</td>
<td>2.535, 2.549</td>
<td>1116</td>
</tr>
<tr>
<td></td>
<td>2.153</td>
<td>2.531, 2.549</td>
<td></td>
</tr>
<tr>
<td>SnBr$_4$·2Me$_2$S</td>
<td>2.65</td>
<td>2.554, 2.554</td>
<td>1110</td>
</tr>
<tr>
<td>SnI$_4$·2Ph$_2$SO$^a$</td>
<td>2.249</td>
<td>2.776, 2.781</td>
<td>1100</td>
</tr>
<tr>
<td></td>
<td>2.189</td>
<td>2.773, 2.806</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Two crystallographically independent molecules.

**TABLE 77. Selected bond lengths for trans-SnX$_4$·2D complexes**

<table>
<thead>
<tr>
<th>Compound</th>
<th>D → Sn (Å)</th>
<th>Sn–X (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnCl$_4$·(c-C$<em>6$H$</em>{11}$OH)$_2$·2c-C$<em>6$H$</em>{11}$OH</td>
<td>2.137</td>
<td>2.367, 2.387</td>
<td>1117</td>
</tr>
<tr>
<td>[SnCl$_4$(H$_2$O)$_2$]·15-crown-5</td>
<td>2.107, 2.125</td>
<td>2.364, 2.379</td>
<td>1118</td>
</tr>
<tr>
<td>SnCl$_4$·(1,5-dithiacyclooctane)$_2$</td>
<td>2.602</td>
<td>2.414, 2.428</td>
<td>1119</td>
</tr>
<tr>
<td>SnCl$_4$·2Me$_2$Se</td>
<td>2.700</td>
<td>2.413, 2.427</td>
<td>1111</td>
</tr>
<tr>
<td>SnBr$_4$·2Me$_2$Se</td>
<td>2.731</td>
<td>2.576, 2.587</td>
<td>1111</td>
</tr>
<tr>
<td>SnBr$_4$·2Ph$_3$PO</td>
<td>2.101</td>
<td>2.557 (mean)</td>
<td>1120</td>
</tr>
<tr>
<td>SnBr$_4$·2Me$_2$S</td>
<td>2.692, 2.692</td>
<td>2.532, 2.554</td>
<td>1110</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.539, 2.557</td>
<td></td>
</tr>
<tr>
<td>SnI$_4$·2Et$_3$P</td>
<td>2.69</td>
<td>2.863, 2.872</td>
<td>1110</td>
</tr>
<tr>
<td>SnCl$_4$·2THF</td>
<td>2.166</td>
<td>2.373, 2.383</td>
<td>1112</td>
</tr>
<tr>
<td>SnBr$_4$·2THF</td>
<td>2.220</td>
<td>2.383, 2.531</td>
<td>1112</td>
</tr>
</tbody>
</table>
2H2O1114, 2.37–2.40 Å, are a little longer compared with 2.364–2.391 Å in trans-SnCl4( H2O)2·15-crown-51118.

There are several examples where both arrangements have been crystallographically characterized, e.g. in cis-SnBr4·2Ph3PO1120 and trans-SnBr4·2Ph3PO969, and there is one example where the two isomers have been found in the same crystal domain, e.g. in SnBr4·2Me2SS1110 there are two cis-SnBr4·2Me2S molecules and one trans-SnBr4·2Me2S molecule located in the unit cell.

Arguments used to explain the isolation of one isomer over the other have typically been based upon the solid adducts, but this is unsatisfactory since many systems show the coexistence of both forms in the solid state. It has been shown that adducts can undergo isomerization in the solid state, e.g. SnX4D2 with X = Cl, D = DMF, DMA or DMSO and for X = Br, D = DMF or DMA were obtained from solution as the cis isomers, and converted to the trans form by heating1121.

Solvent effects have been shown to be important in the isolation of particular adducts; both cis and trans forms of SnCl4·2THF have been crystallized, the cis from dichloromethane and the trans from n-pentane. Therefore, trans isomers are preferred in weakly polar solvents while cis isomers are favored in more polar media1112.

The reaction between Ph2SnCl2 and thiosemicarbazide using acetone–ethanol as a solvent mixture resulted in the formation of bis(acetone thiosemicarbazone-S)dichlorodiphenyltin. In the monomeric hexacoordinate complex, each of the two monodentate ligands coordinate to the tin atom through the sulfur atom to form a distorted-octahedral geometry (the S→Sn bond length is 2.712 Å)1122.

Complexation of SnHal4 (Hal = Cl, Br) with monodentate tertiary phosphines (Ph3P, Ph2MeP, PhMe2P and Bu3P) has been studied by 119Sn and 31P NMR spectroscopies in CH2Cl2 solutions at various donor/acceptor (D/A) ratios and depend on the temperature (−90 °C and +3 °C). Selected NMR parameters for the complexes are given in Table 78.

Analysis of the SnBr4−Bu3P system shows that only AD2 complexes exist in solutions at −90 °C independent of the D/A ratio. The values of δ(119Sn) and (31P) for the products isolated at D/A <0.5 at room temperature evidently show that formation of AD complexes takes place before the oxidation of phosphines occurs (oxidation of tertiary phosphines with excess of SnHal4 leads to an alternative mechanism for the formation of R3PHal+SnHal5−)26. In the SnCl4−Me2PhP system, in which only weakly dissociated AD2 complex exists at room temperature independent of the D/A ratios, oxidation of the phosphate proceeds extremely slowly26.

<table>
<thead>
<tr>
<th>Complex</th>
<th>δ31P (ppm)</th>
<th>Δδ31P (ppm)</th>
<th>δ119Sn (ppm)</th>
<th>J(31P−119Sn) (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnCl4·2Bu3P</td>
<td>18.6</td>
<td>51.1</td>
<td>−567</td>
<td>2550</td>
</tr>
<tr>
<td>SnCl4·2Me2PhP</td>
<td>5.2</td>
<td>45.2</td>
<td>—</td>
<td>2600</td>
</tr>
<tr>
<td>SnCl4·2MePh2P</td>
<td>1.8</td>
<td>29.8</td>
<td>—</td>
<td>2260</td>
</tr>
<tr>
<td>SnCl4·2Bu3P</td>
<td>5.1</td>
<td>13.5</td>
<td>—</td>
<td>1850</td>
</tr>
<tr>
<td>SnCl4·Ph3P</td>
<td>19.0</td>
<td>27.4</td>
<td>−593</td>
<td>1960</td>
</tr>
<tr>
<td>SnCl4·Me2PhP</td>
<td>14.4</td>
<td>54.4</td>
<td>—</td>
<td>2600</td>
</tr>
<tr>
<td>SnCl4·MePh2P</td>
<td>8.4</td>
<td>36.4</td>
<td>−390</td>
<td>2060</td>
</tr>
<tr>
<td>SnCl4·Bu3P</td>
<td>36.0</td>
<td>68.5</td>
<td>−455</td>
<td>2200</td>
</tr>
<tr>
<td>SnBr4·Bu3P</td>
<td>19.3</td>
<td>51.8</td>
<td>—</td>
<td>1290</td>
</tr>
</tbody>
</table>

\[ Δδ = δ(\text{complex}) − δ(\text{phosphine}). \]
3. Lead

The differences between lead and tin bond lengths in mixed-ligand complexes are not equal for all bonds. The replacement of tin by lead leads to the lengthening of $N \rightarrow M$, $O \rightarrow M$ and $M \rightarrow Cl$ bonds by 0.11–0.20 Å (Table 79)\textsuperscript{437}.

Contrary to $Ph_2PbCl_2 \cdot 2Im$\textsuperscript{1124} and to $Ph_2Pb(NCS)_2 \cdot 2HMPA$\textsuperscript{1089,1125} with an all-\textit{trans} arrangement of ligands around the lead atom, in $Ph_3PbCl_2 \cdot 2DMSO$ and $Ph_2PbCl_2 \cdot 2HMPA$, the donor molecules and chlorine atoms are placed \textit{cis} to each other, with \textit{trans}-positioned phenyl groups\textsuperscript{437}. However, the bond lengths in polyhedra with \textit{cis} and \textit{trans} coordination are markedly different.

The rehybridization of the valence orbitals in lead complexes is more effective, i.e. the concentration of s-electrons in the Pb–C bonds is larger and/or the gap between the s- and p-levels of the lead atom is larger in comparison with tin\textsuperscript{437}. The high oxidation capacity of Pb$^{4+}$ and the high stability of Pb$^{2+}$ favor the last assertion. The more effective rehybridization leads to decreased electron-withdrawing capacity of the Pb$^2_2$ and Pb$^+_3$ groups, i.e. to increase in the Pb–X bond ionicity in phenyl halides and pseudohalides and to a greater redistribution of electron density in the hypervalent fragments. In \textit{cis} complexes of Pb$\text{MC}_2 \cdot 2D$ the difference between lead and tin for coordinate bonds $\Delta(D \rightarrow M) = 0.20$ Å (DMSO) and 0.16 (Bipy) are more than for the covalent bonds $\Delta(Pb–Cl) = 0.12$ Å, whereas in \textit{all-trans} $Ph_2M(NCS)_2 \cdot 2$HMPPT the corresponding values $\Delta(O \rightarrow M) = 0.18$ Å and $\Delta(N \rightarrow M) = 0.16$ Å are fairly close (Table 79).

The relative weakening of $D \rightarrow Pb$ bonds is not accompanied by an increased tetrahedralization of the residual moiety (the C–Pb–C and C–Sn–C angles are almost equal) as found in similar cases, since a concentration of s-electrons in the Pb–C bonds occurs simultaneously\textsuperscript{437}.

B. Chelate Complexes

Hexacoordinate neutral complexes of group 14 elements with only one multidentate ligand are much less known than those with two multidentate ligands.

### TABLE 79. Bond lengths (Å) and angles (deg) (averaged) in comparable lead and tin $D \rightarrow M$ complexes of the type $R_2MCl_2 \cdot 2D$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$D \rightarrow Sn$ (D)</th>
<th>$\Delta^a$</th>
<th>Sn–Cl (D)</th>
<th>$\Delta$</th>
<th>Sn–C</th>
<th>$\Delta^a$</th>
<th>RSnR</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$cis$-$Ph_2SnCl_2 \cdot 2DMSO$</td>
<td>2.318(O)</td>
<td>—</td>
<td>2.494</td>
<td>—</td>
<td>2.117</td>
<td>—</td>
<td>167.2</td>
<td>1046</td>
</tr>
<tr>
<td>$cis$-$Ph_2PbCl_2 \cdot 2DMSO$</td>
<td>2.513(O)</td>
<td>0.20</td>
<td>2.609</td>
<td>0.12</td>
<td>2.165</td>
<td>0.05</td>
<td>165.2</td>
<td>437</td>
</tr>
<tr>
<td>$cis$-$Ph_2PbCl_2 \cdot 2HMPA$</td>
<td>2.506(O)</td>
<td>—</td>
<td>2.603</td>
<td>—</td>
<td>2.134</td>
<td>—</td>
<td>170.12</td>
<td>437</td>
</tr>
<tr>
<td>$cis$-$Ph_2SnCl_2 \cdot Bipy$</td>
<td>2.360(N)</td>
<td>—</td>
<td>2.510</td>
<td>—</td>
<td>2.152</td>
<td>—</td>
<td>173.5</td>
<td>1023</td>
</tr>
<tr>
<td>$cis$-$Ph_2PbCl_2 \cdot Bipy$</td>
<td>2.521(N)</td>
<td>0.16</td>
<td>2.632</td>
<td>0.12</td>
<td>2.167</td>
<td>0.02</td>
<td>177.3</td>
<td>282</td>
</tr>
<tr>
<td>(4-ClC$_6$H$_4$)$_2$SnCl$_2 \cdot 4,4'$-Me$_2$Bipy</td>
<td>2.314(N)</td>
<td>—</td>
<td>2.484</td>
<td>—</td>
<td>2.163</td>
<td>—</td>
<td>177.4</td>
<td>1030</td>
</tr>
<tr>
<td>$trans$-$Ph_2PbCl_2 \cdot 2Im^b$</td>
<td>2.45(N)</td>
<td>0.14</td>
<td>2.700</td>
<td>0.22</td>
<td>2.18</td>
<td>0.02</td>
<td>179.07</td>
<td>1123,1124</td>
</tr>
<tr>
<td>$cis$-$Ph_2PbCl_2 \cdot 2Im^b$</td>
<td>2.426(N)</td>
<td>—</td>
<td>2.692</td>
<td>—</td>
<td>2.164</td>
<td>—</td>
<td>129.17</td>
<td>1124</td>
</tr>
<tr>
<td>$trans$-$Ph_2Sn(NCS)$_2 \cdot 2HMPA$</td>
<td>2.184(O)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>2.138</td>
<td>—</td>
<td>1089</td>
<td></td>
</tr>
<tr>
<td>$trans$-$Ph_2Pb(NCS)$_2 \cdot 2HMPA$</td>
<td>2.345(O)</td>
<td>0.18</td>
<td>2.43(N)</td>
<td>0.16</td>
<td>2.155</td>
<td>0.02</td>
<td>180.00</td>
<td>1089</td>
</tr>
</tbody>
</table>

\textsuperscript{4}$^a$\textit{\Delta} is the difference between values for lead and tin.  
\textsuperscript{b}Im = imidazole.
1. One multidentate ligand

Complexes 514, 516 and 517a–f (for substituents, see Table 80) are representatives of compounds containing tridentate coordinating ligands. In the solid state, hexacoordination of the tin atom in 514 results from two ether O → Sn interactions with bond distances of 2.553 (O1) and 2.540 Å (O2). The trans angles, i.e. O2 → Sn–Cl1, O1 → Sn–Cl2 and C–Sn–C, of 171.6, 154.2 and 155.5°, respectively, indicate significant deviations from the ideal geometry. In solution, a dynamic equilibrium including intramolecular O → Sn interactions is observed. The concentration-independent 117Sn chemical shift of compound 514 at −73.6 ppm (CDCl3) is different from that of a reference compound without a Lewis donor, i.e. n-BuPhSnCl2 (+45 ppm), but is fairly typical for a hypervalent diorganotin dichloride. Its alkyl 1J(119Sn–13C) coupling constants of 629 Hz also reflect a stronger coordination at tin as compared to n-BuPhSnCl2 (503 Hz).

X-ray data for tridentate complexes 515–517 were reported (Table 80). In 517a–c, the Sn atom has a distorted octahedral coordination geometry, with the halo ligand and the thiosemicarbazone moiety in the equatorial plane and the methyl groups in the axial positions. The two chlorines in 517d–f occupy the apical positions, while the ligand and the organic group are in the equatorial plane.

Synthesis and some properties of six-coordinate organotin compounds 426a, 426b, 428a, 428b and 430, containing the monoanionic O,C,O-coordinating ligand \{4-\text{t}-\text{Bu}-2,6-[PO(OEt)2]2C6H2\}−, were discussed in Section VII.B.2. Structures and X-ray data are presented in Table 81. X-ray investigations reveal weak intramolecular O → Sn interactions for 426a (2.865–3.063 Å) and 426b (2.939–3.108 Å) but strong O → Sn coordination for 428a (2.203/2.278 Å) and 430 (2.221–2.225 Å) (Table 81).
TABLE 80. Selected bond distances and angles for complexes 515–517

<table>
<thead>
<tr>
<th>Compound</th>
<th>X</th>
<th>R</th>
<th>R1</th>
<th>N → Sn (Å)</th>
<th>N → Sn (deg)</th>
<th>Other angles (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>515</td>
<td></td>
<td></td>
<td></td>
<td>2.501, 2.427</td>
<td>150.7</td>
<td>177.3(ISnI)</td>
<td>1128</td>
</tr>
<tr>
<td>516</td>
<td>Cl</td>
<td>Me</td>
<td></td>
<td>2.857, 2.998</td>
<td>107.1</td>
<td>178.5(RSnR)</td>
<td>37</td>
</tr>
<tr>
<td>517a</td>
<td>Br</td>
<td>Me</td>
<td>Me</td>
<td>2.351(N1)</td>
<td>65.3</td>
<td>145.1(CSnC)</td>
<td>1129</td>
</tr>
<tr>
<td>517b</td>
<td>Cl</td>
<td>Ph</td>
<td>R2</td>
<td>2.523(N1)</td>
<td>66.1</td>
<td>144.2(CSnC)</td>
<td>1129</td>
</tr>
<tr>
<td>517c</td>
<td>Cl</td>
<td>Ph</td>
<td>R2</td>
<td>2.510(N1)</td>
<td>67.1</td>
<td>156.9(CSnC)</td>
<td>1130</td>
</tr>
<tr>
<td>517d</td>
<td>n-Bu</td>
<td>Cl</td>
<td>R2</td>
<td>2.29(N1)</td>
<td>71.1</td>
<td>168.3(ClSnCl)</td>
<td>1131</td>
</tr>
<tr>
<td>517e</td>
<td>Ph</td>
<td>Cl</td>
<td>R2</td>
<td>2.226(N1)</td>
<td>72.0</td>
<td>166.0(ClSnCl)</td>
<td>1131</td>
</tr>
<tr>
<td>517f</td>
<td>Ph</td>
<td>Cl</td>
<td>NMe2</td>
<td>2.181(N1)</td>
<td>73.2</td>
<td>169.5(ClSnCl)</td>
<td>1131</td>
</tr>
</tbody>
</table>

*R2 = HNN=C(Me)Pyr-2.

The existence of two independent molecules in the crystal unit of 426a is also reflected by the observation of two equally intense 119Sn MAS NMR resonances at −181.7 and −227.7 ppm. The NMR spectra show (Table 81) that strong O–Sn contacts are present in halides 428a and 430, whereas weak intramolecular coordination is observed in 426a and 426b. Moreover, in comparison with tetracoordinate Ph3SnCH2SiMe3 (Δ119Sn = −88.6 ppm), the 119Sn NMR data of 425b [δ(119Sn) = −127.5, J(119Sn−31P) = 38 Hz] indicate a coordination number greater than four at the tin atom in both solution and the solid state.

Other representatives of compounds with tridentate O,C,O-chelating ligand are complexes 518769, 519772 and 520773. The structural data for 519 and 520 are given in Table 81.

Complexes 521865, 5221132 and 5231132 are examples of hexacoordinate diorganotin compounds bearing dianionic tridentate O,N,O-chelating ligands.

Of special interest are coordination compounds formed by the interaction of the metal with potentially tetratedentate ligands. Among them are complexes 5241133 and 5251134 with...
16. Hypervalent compounds of organic germanium, tin and lead derivatives

O,N,O,O- and C,N,N,C-chelating ligands, as well as complexes containing tetraanionic, 526\textsuperscript{1135} and diatomic, 527\textsuperscript{1136}, 528a–c\textsuperscript{241,243} and 529\textsuperscript{1137}, O,N,N,O-chelating ligands. Selected X-ray data for these compounds are presented in Tables 82 and 83.

We exemplify selected structural parameters for some tetradeionate porphyrins (530), phthalocyanines (531a) and porphyrazines (531b) (M = Ge, Sn) in Table 84 but detailed discussion is beyond the scope of this review.

A germanium complex with ethylenediaminetetraacetic acid (Hedta) 532 has a pentadentate edta ligand with one protonated acetate group which does not coordinate, forming a six-coordinate complex 1150.

TABLE 82. Selected bond distances and angles for complexes 524–526

<table>
<thead>
<tr>
<th>Compound</th>
<th>D → Sn (Å)</th>
<th>D → Sn–X(R)(deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>524</td>
<td>2.155(OH), 2.316(N)</td>
<td>150.50(N–Sn–C), 95.5(O–Sn–O)</td>
<td>1133</td>
</tr>
<tr>
<td>525</td>
<td>2.765(N\textsuperscript{1}), 2.850(N\textsuperscript{2})</td>
<td>70.8(N\textsuperscript{1}–Sn–C\textsuperscript{1}), 165.6(N\textsuperscript{2}–Sn–S\textsuperscript{1})</td>
<td>1134</td>
</tr>
<tr>
<td>526</td>
<td>2.345(N\textsuperscript{1}), 2.341(N\textsuperscript{2})</td>
<td>162.6(N\textsuperscript{1}–Sn–C\textsuperscript{1}), 160.4(N\textsuperscript{2}–Sn–C\textsuperscript{2})</td>
<td>1135</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Bite angle.

TABLE 83. Selected bond distances and angles for complexes 527, 528a–c and 529

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>N → Sn (Å)</th>
<th>NSnN (deg)</th>
<th>RSnR (deg)</th>
<th>OSnO (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>527</td>
<td>Me</td>
<td>2.250, 2.265</td>
<td>72.9</td>
<td>159.8</td>
<td>127.8</td>
<td>1136</td>
</tr>
<tr>
<td>528a</td>
<td>Bu</td>
<td>2.266, 2.280</td>
<td>72.0</td>
<td>156.8</td>
<td>128.8</td>
<td>1139</td>
</tr>
<tr>
<td>528b</td>
<td>Ph</td>
<td>2.260, 2.290</td>
<td>73.2</td>
<td>165.9</td>
<td>124.2</td>
<td>1138</td>
</tr>
<tr>
<td>529</td>
<td>Ph</td>
<td>2.195, 2.216</td>
<td>75.4</td>
<td>168.5</td>
<td>124.8</td>
<td>1137</td>
</tr>
</tbody>
</table>

TABLE 84. Selected bond distances and angles for some porphyrin, phthalocyanine and porphyrazine complexes of germanium and tin

<table>
<thead>
<tr>
<th>Type of compound</th>
<th>M</th>
<th>X</th>
<th>R</th>
<th>R\textsuperscript{1}</th>
<th>N → M (Å)</th>
<th>N–M (Å)</th>
<th>M–X</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>530</td>
<td>Ge</td>
<td>N\textsubscript{3}</td>
<td>p-Tol</td>
<td>H</td>
<td>1.983</td>
<td>1.983</td>
<td>1.964</td>
<td>1141</td>
</tr>
<tr>
<td></td>
<td>Ge</td>
<td>OH</td>
<td>Ph</td>
<td>H</td>
<td>2.027</td>
<td>2.027</td>
<td>1.809</td>
<td>1144</td>
</tr>
<tr>
<td></td>
<td>Ge</td>
<td>OMe</td>
<td>H</td>
<td>H</td>
<td>2.020\textsuperscript{a}</td>
<td>2.011\textsuperscript{a}</td>
<td>1.821\textsuperscript{a}</td>
<td>1143</td>
</tr>
<tr>
<td></td>
<td>Ge</td>
<td>OMe</td>
<td>Ph</td>
<td>H</td>
<td>2.041</td>
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<td>1144</td>
</tr>
<tr>
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<td>Ge</td>
<td>OEt</td>
<td>Ph</td>
<td>H</td>
<td>2.032</td>
<td>2.024</td>
<td>1.822</td>
<td>1145</td>
</tr>
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<td>2.182\textsuperscript{a}</td>
<td>2.200\textsuperscript{a}</td>
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<td>C≡CBu-\text{t}</td>
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<td>531b</td>
<td>Ge</td>
<td>OCH\textsubscript{2}CH\textsubscript{2}OEt</td>
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<td>1.934</td>
<td>1.805</td>
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</table>

\textsuperscript{a}Average value.

\textsuperscript{b}Two molecules in the unit cell.

\textsuperscript{c}The angle CSnC is 134.0°.
(524)

(525)

(526)

(527)

(528) (a) R = Me  
     (b) R = Bu  
     (c) R = Ph  

(529)
2. Two multidentate ligands

a. Four-membered chelate rings. The most favored and stable chelate ring is the five-membered ring; four- and six-membered chelate rings are also obtained. Four-membered
chelate rings are particularly strained and seldom formed. A very weak intramolecular O → Sn interaction in o-anisylstannanes (o-An)2SnPh2 (290), (o-An)2SnBr2 (292a), (o-An)2SnI2 (292b) and related compounds239,686,690 was discussed in Section VII.A.2.a (cf. Table 50). Other potential representatives of hexacoordinate four-membered chelates are carboxylates R2M(O2CR1)2 (533), dithiocarbamates [R2M(S2CNR1)2] (534) and xanthates [R2M(S2COR1)2] (535) (M = Ge, Sn, Pb). Selected structural data for some carboxylates 533 (M = Sn, Pb), dithiocarbamates 534 (M = Sn) and xanthates 535 (M = Sn) are given in Tables 85 and 86.

Crystallographic studies of organotin and organolead carboxylates revealed that their structures are dependent on both the nature of the substituent bound to the tin atom and the type of carboxylate ligand. The C–Sn–C angles of 122.2–154.6° found in R2Sn(O2CR1)2 (Table 85) are close to the average value of the two extremes (90° for the cis-isomers and 180° for the trans-isomers). This coordination geometry is best described as skew-trapezoidal bipyramidal. The skew-trapezoidal bipyramid can be envisaged as a distortion of a regular trans octahedron and it is especially favored if the chelate bite angle is small1151.

A secondary interaction with the nonbonding sulfur atoms is observed for dithiocarbamates Me2Ge(S2CNMe2)2 522 (2.685 Å) and Ph2Ge(S2CNEt2)2 1174 (3.183 Å). For the xanthate Ph2Ge(S2COMe)2, the O–Ge–S bite angle of 57.8° is much smaller than the C–Ge–C angles of 111.1° to 117.5°. The decrease allows the oxygen atoms to take up a distance of 2.920 Å from germanium, which is less than the sum of the van der Waals radii. On a relative scale, the S → Ge secondary interactions for the dithiocarbamates are 20–40% longer than the sum of the covalent radii, whereas the O → Ge distance in the xanthate is approximately 50% longer.

Crystallographic studies revealed three distinct structural motifs for diorganotin dithiocarbamates R2Sn(S2CNR1)2 534 (Table 86)126. For the predominant motif, the geometry about the Sn atom is skew-trapezoidal bipyramidal with the basal plane defined by the four S atoms derived from two asymmetrically chelating dithiolate ligands, i.e. the shorter and longer Sn–S bond distances are approximately 2.5 and 3.0 Å, respectively. For the dithiocarbamates that adopt this motif, the Sn-bound substituents represented include R = Me, n-Bu and c-Hex. Similar geometry was found in the related xanthate derivatives R2Sn(S2COR1)2 (535, R = Me, Ph).

In the second motif, the chlorine substituents in 534, R = Cl are sufficiently electronegative to increase the Lewis acidity of the tin atom that is most favorable for hypervalent S → Sn–Hal interactions. The result is that coordinate interactions are arranged in a trans fashion with almost symmetric chelation by the dithiocarbamate ligands in a distorted octahedral geometry 535. The related compounds X2Sn(S2CNEt2)2, where X = Cl, Br and I1197,1198, also feature cis-octahedral structures. A similar structure is found for four monodentate ligands, i.e. in [Sn(S2CNEt2)4]1199. The different configurations are shown nearby.

When one chlorine of [Cl2Sn(S2CNEt2)2] is replaced by a vinyl1200 or phenyl243,1192, the cis-octahedral geometry remains. Moreover, a six-coordinate, distorted octahedral geometry is found in the structure of Ph2Sn(S2CNEt2)21188,1189. The phenyl groups occupy approximate cis positions, i.e. the C–Sn–C angle is approximately 102° compared with the C–Sn–C angles of 125–150° found in the predominant motif described above. Symmetrical Sn–S distances are also found for Ph2Sn(S2P(OPr-i)2)2 1196. This structure is situated about a crystallographic center of inversion, which constrains the C–Sn–C angle to 180°. In contrast, in vin2Sn(S2CNN2)2 (R12, c-Hex) with lower Lewis acidity, the geometry about the tin atom is best described as being distorted octahedral (a skew-trapezoidal bipyramidal), with a trans disposition of the vinyl groups126.
TABLE 85. Selected structural parameters for compounds R₂M(O₂CR¹)₂ of the type 533
(M = Sn, Pb)

<table>
<thead>
<tr>
<th>R</th>
<th>R¹</th>
<th>O → M (Å)</th>
<th>M−O (Å)</th>
<th>R−Sn−R (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>Ph</td>
<td>2.505, 2.510</td>
<td>2.128, 2.156</td>
<td>147.1</td>
<td>1151</td>
</tr>
<tr>
<td>Me</td>
<td>2-HOC₆H₄</td>
<td>2.502, 2.577</td>
<td>2.111, 2.112</td>
<td>138.2</td>
<td>1152</td>
</tr>
<tr>
<td>Me</td>
<td>4-H₂NC₆H₄</td>
<td>2.544, 2.577</td>
<td>2.077, 2.096</td>
<td>134.7</td>
<td>1153</td>
</tr>
<tr>
<td>Me</td>
<td>Re(CO)(NO)MCp</td>
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<td>2.078</td>
<td>132.6</td>
<td>1154</td>
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<tr>
<td>Et</td>
<td>2-Thi</td>
<td>2.474, 2.556</td>
<td>2.129, 2.143</td>
<td>151.7</td>
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<tr>
<td>Et</td>
<td>2-Thi-CH=CH</td>
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<td>2.106</td>
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<td>1156</td>
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<tr>
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<td>143.5</td>
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<tr>
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<td>2.107, 2.127</td>
<td>139.1</td>
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<tr>
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<td>1166</td>
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a(2E)-2-(2-hydroxy-5-methylphenyl)diazenylphenyl.

bRR.

R¹

![skew-trapezoidal bipyramidal](533)

![cis-octahedral](534)
TABLE 86. Selected structural parameters for dithiocarbamates \( \text{R}_2\text{Sn(S}_2\text{CNR}_1^2 \) 534 (M = Sn) and xanthates \( \text{R}_2\text{Sn(S}_2\text{COR}_1^2 \) 535

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<tr>
<th>R</th>
<th>NR(_1^2)</th>
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<th>R−Sn−R</th>
<th>Ref.</th>
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<td>Ph</td>
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<td>2.558, 2.607</td>
<td>101.7</td>
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<tr>
<td>Cl</td>
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<td>2.535, 2.540</td>
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<td>Cl</td>
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<td>2.528, 2.553</td>
<td>94.1(^b)</td>
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<tr>
<td>Cl</td>
<td>NE(_2)</td>
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<td>2.502, 2.512</td>
<td>91.8(^c)</td>
<td>1193</td>
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</table>

The third structural type is found in the structure of \( t\text{-Bu}_2\text{Sn(S}_2\text{CNMe}_2^2 \) with bulky ligands where a five-coordinate Sn atom is present\(^815\). The second dithiocarbamate ligand coordinate is a monodentate mode, there being neither intra- nor intermolecular significant S → Sn interaction.

Table 87 lists the average disparity in the Sn−S distances between the Sn ← S and Sn−S bond lengths, \( \Delta(\text{Sn−S}) \), for a series of \( \text{R}_2\text{Sn(S}_2\text{CNR}_1^2 \) structures\(^12\). As the
TABLE 87. Average Δ(Sn−S) values and average R−Sn−R angles for tin compounds R₂Sn(S₂CNR₁)₂ of the type 534

<table>
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<tr>
<th>R²</th>
<th>R¹</th>
<th>Geometry²</th>
<th>Δ(Sn−S)</th>
<th>R−Sn−R</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
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<td>Cl, n-Bu</td>
<td>Et</td>
<td>cis</td>
<td>0.05</td>
<td>89.9</td>
<td>170</td>
</tr>
<tr>
<td>Cl, Cl</td>
<td>Et</td>
<td>cis</td>
<td>0.07</td>
<td>91.8</td>
<td>1193</td>
</tr>
<tr>
<td>Cl, CH₂CO₂Me</td>
<td>Et</td>
<td>cis</td>
<td>0.12</td>
<td>93.6</td>
<td>739</td>
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<tr>
<td>Cl, Ph</td>
<td>Et</td>
<td>cis</td>
<td>0.09</td>
<td>94.0</td>
<td>1192</td>
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<td>Cl, Vin</td>
<td>Et</td>
<td>cis</td>
<td>0.06</td>
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<td>Ph, Ph²</td>
<td>Et</td>
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<td>0.10</td>
<td>101.1</td>
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<tr>
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<td>Et</td>
<td>cis</td>
<td>0.12</td>
<td>101.8</td>
<td>1189</td>
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<tr>
<td>Vin, Vin</td>
<td>Et, c-Hex⁴</td>
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<td>133.3</td>
<td>126</td>
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<tr>
<td>Vin, Vin</td>
<td>Et</td>
<td>trans</td>
<td>0.47</td>
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<td>0.39</td>
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<td>Me, Me</td>
<td>CH₂CH₂OH</td>
<td>tetragonal</td>
<td>—</td>
<td>139.3</td>
<td>1201</td>
</tr>
</tbody>
</table>

² cis, cis-octahedral; trans, skew-trapezoidal bipyramidal.
³ Polymorph.
⁴ Monoclinic polymorph.
⁵ Two different R¹ groups.

Lewis acidity of the tin atom in R₂Sn is reduced, e.g. by substituting chloride for phenyl, the degree of symmetry in the Sn−S distances increases and the R−Sn−R angle deviates from 90°.

It has been found that in the absence of crystal packing effects, the solid-state geometries converged uniformly to more symmetric structures. For the dithiocarbamate ligands in the more symmetric tetragonal form Ph₂Sn(S₂CNEt₂)₂, the average Sn−S bond distance is 2.608 Å¹¹⁹⁰ with slightly asymmetric Sn−S distances (Δ(Sn−S) = 0.103 Å). In contrast, in the monoclinic form the average Sn−S distance is 2.644 Å with Δ(Sn−S) = 0.219 Å¹¹⁸⁹.

In Table 88 are collected selected structural parameters for some hexacoordinate complexes with potential bidentate S,N-coordinating ligands of the type 536. According to X-ray data, the tin atom in these compounds has a highly distorted octahedral geometry with the two S atoms in cis-position and the two nitrogen and two carbon atoms at angles between 90° and 180° (CSnC about 130° and NSnN about 150°).

In the (2-chlorobenzyl)tris(pyridine-2-thiolato)tin, two of the three pyridine-2-thiolato ligands (SPyr) are bidentate and one is monodentate¹²⁰⁷. The axial bond angles N−Sn−C (157.9°), N−Sn−S (154.3°) and S−Sn−S (144.6°) demonstrate the heavy distortion of the octahedron. The N → Sn distances of two of the SPyr ligands (2.303 and 2.324 Å) are shorter than in p-TolSn(SPy)₃ (2.466 Å)¹²⁰⁸, MeSn(SPy)₃ (2.483 Å), PhSn(SPy)₃ (2.432 Å)¹²⁰⁹ and Ph₂Sn(SPy)₂ (2.667 Å)¹²¹⁰, also with a N → Sn coordination. In contrast to the former, in these complexes as well as in Ph₂SnCl(SPy)¹²¹⁰, the SPyr fragment acts as a bidentate ligand and thus the Sn atom achieves coordination numbers of 7, 6 and 5, respectively. However, in Sn(SPy)₄ · HSPyr, the Sn atom was found not to be eight-coordinate, as might have been expected, but only six-coordinate, with two SPyr ligands being bidentate and the other two monodentate¹²¹¹.

The tendency toward hexacoordination in diphosphanylmethanide cis-octahedral complexes 537–539 follows the sequence: Ge < Si < Sn, quite different from the usually accepted order: Si < Ge < Sn¹²¹². The authors attributed this discrepancy to the low polarity of the M−P bonds and, in particular, to the especially nonpolar nature of the
Ge–P bond. For hypervalent bonds, it is the first structurally characterized example of a series ranging from silicon to tin with an identical set of ligands and with a low sum of electronegativities.

Complexes 540–543 are representatives of compounds containing two four-membered bidentate N,N-, O,O- and S,S-coordinating ligands. Selected structural parameters for these compounds, which point to their distorted octahedral structures, are collected in Table 89.

b. Five-membered chelate rings (N → M). The reaction of (ClCH₂)₂GeCl₂ with N-TMS thiolactams in a 1 : 2 ratio proceeds under mild conditions (mixing at −196°C and room temperature allowed to be reached under a vacuum to remove the evolving Me₃SiCl) and leads to bis-chelates 544a–c (equation 85)¹²¹⁹. In the case of the caprolactam derivative a very small yield of the reaction product in a 1 : 1 ratio, i.e. thiolactim ether 156b, was isolated (Section VI.A.2).

According to X-ray structural data (Table 90), the Ge atom in thiolactim ethers 544a–c have a slightly distorted octahedral coordination by virtue of the two intramolecular N → Ge coordinated bonds with the all-trans arrangement around the central atom¹²¹⁹. The N → Ge distances (2.03–2.12 Å) are rather close and the Ge–Cl distances (2.40–2.42 Å) are somewhat shorter than those in (N–Ge) monochelate thioethers 156a and 156b (Section VI.A.2 and Table 36), but both distances are still essentially longer than in tetrahedral germanium compounds.

The tin atom in dichlorides [Me₂N(CH₂)₃]₂SnCl₂ (N → Sn distance of 2.403 Å¹²²⁰), (Me₂NCH₂CH₂CMé₂)₂SnCl₂ (2.448 Å¹²²⁰) and difluoride [Me₂N(CH₂)₃]₂SnF₂ · 2H₂O (545) (2.366 Å¹²²¹) shows slightly distorted all-trans octahedral configuration. The only
distortion from the ideal geometry can be attributed to some strain in the five-membered NSnC₃ ring. Below −50°C, ¹¹⁹Sn and ¹⁹F NMR coupling data indicate the existence of two isomers for 545, the major species having an all-trans structure as in the crystal state, while the minor species has a cis arrangement for the fluorine and for the nitrogen atoms and trans arrangement for the carbon atoms (equation 86). The ³J(¹¹⁹Sn−¹H) coupling through the Me₂N→Sn bond exists in both the slow- and fast-exchange ranges. Together with the loss of the ¹J(¹¹⁹Sn−¹⁹F) coupling at high temperature, this serves as evidence that the Me₂N→Sn coordination is maintained during the cis-trans isomerization which occurs through a dissociative mechanism involving tin–fluorine bond rupture₁²²¹.

Density functional B3LYP calculation performed on [H₂N(CH₂)₃]₂SnF₂ isomers of the model compound showed that the all-trans isomer is energetically preferred. However, the LUMO of the cis isomer is of lower energy than the LUMO of the former, which suggests that the fluoride attack at tin in solution leading to hexacoordinate anionic species (Section IX.B) can take place at the cis isomer⁹⁷¹b.

The cyclo-stannasiloxanes M(OSiPh₂)₂O, M = Sn[(CH₂)₃NMe₂]₂ (546)₁²²², Sn[(CH₂)₃N(Me)CH₂]₂ (547) and cyclo-M(OSiPh₂O)₂M, M = Sn[(CH₂)₃NMe₂]₂ (548)⁷₁⁶ exhibit reduced ring strain as a result of intramolecular coordination. The tin atoms adopt a distorted-octahedral configuration with the two carbon atoms and the two hypervalent N→Sn−O bonds in mutually trans configuration. The distortions from the ideal configuration are illustrated by the deviation from 180° of the trans angles C−Sn−C (546, 154.3°; 547, 167.4°; 548, 151.5°). The N→Sn distances increase from 2.621,
### TABLE 88. Selected structural parameters for compounds $R_2SnD_2$ of the type 536 (D is a bidentate ligand containing SCN fragment)

<table>
<thead>
<tr>
<th>R</th>
<th>D</th>
<th>$N \rightarrow Sn$ (Å)</th>
<th>$N \rightarrow Sn-R$ (deg)</th>
<th>$R-Sn-R$ (deg)</th>
<th>$S-Sn-S$ (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>![Me]</td>
<td>2.702</td>
<td>83.22</td>
<td>125.02</td>
<td>86.9</td>
<td>1202</td>
</tr>
<tr>
<td></td>
<td>![Et]</td>
<td>2.750</td>
<td>82.76</td>
<td>127.29</td>
<td>86.5</td>
<td>1203</td>
</tr>
<tr>
<td>Bu</td>
<td>![Bu]</td>
<td>2.648</td>
<td>84.43</td>
<td>136.86</td>
<td>91.9</td>
<td>1204</td>
</tr>
<tr>
<td>Bu</td>
<td>![Bu]</td>
<td>2.805</td>
<td>84.18</td>
<td>133.62</td>
<td>88.7</td>
<td>759</td>
</tr>
<tr>
<td>Bu</td>
<td>![Bu]</td>
<td>2.812</td>
<td>83.37</td>
<td>133.24</td>
<td>91.2</td>
<td>759</td>
</tr>
<tr>
<td>c-Hex</td>
<td>![c-Hex]</td>
<td>2.720</td>
<td>79.46</td>
<td>126.86</td>
<td>91.4</td>
<td>1205</td>
</tr>
<tr>
<td>Ph</td>
<td>![Ph]</td>
<td>2.635</td>
<td>81.62</td>
<td>125.49</td>
<td>87.1</td>
<td>1206</td>
</tr>
</tbody>
</table>

### TABLE 89. Selected structural parameters for compounds $R_2M(X_2)_2$ 540–543

<table>
<thead>
<tr>
<th>Compound</th>
<th>X $\rightarrow$ M Å</th>
<th>X $\rightarrow$ M $\leftarrow$ X (deg)</th>
<th>X–M–X (deg)</th>
<th>R–M–R (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>540</td>
<td>2.061, 2.105(N)</td>
<td>89.9</td>
<td>154.9</td>
<td>93.7(SeGeSe)</td>
<td>1213</td>
</tr>
<tr>
<td>541</td>
<td>2.422, 2.703(O)</td>
<td>175.7</td>
<td>74.7</td>
<td>143.6(CSnC)</td>
<td>1214</td>
</tr>
<tr>
<td>542</td>
<td>3.228, 3.244(S)</td>
<td>137.4</td>
<td>83.9</td>
<td>128.5(CSnC)</td>
<td>1215</td>
</tr>
<tr>
<td>543a (all-trans)</td>
<td>2.688(S)</td>
<td>180.0</td>
<td>180.0</td>
<td>180.0(CSnC)</td>
<td>1216</td>
</tr>
<tr>
<td>543b (cis)</td>
<td>3.017(S)</td>
<td>134.4</td>
<td>81.4</td>
<td>153.5(CPbC)</td>
<td>1217</td>
</tr>
<tr>
<td>543c (cis)</td>
<td>2.941, 2.958(S)</td>
<td>132.0</td>
<td>86.3</td>
<td>166.2(CPbC)</td>
<td>1218</td>
</tr>
</tbody>
</table>

*aThe coordinating atom X.
TABLE 90. Selected bond distances and angles for (N → Ge) bis-chelates $^{544a-c}$$^{1219}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>N → Ge (Å)</th>
<th>Cl–Ge (Å)</th>
<th>N → Ge ← N (deg)</th>
<th>Cl–Ge–Cl (deg)</th>
<th>C–Ge–C (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>544a</td>
<td>2.032, 2.091</td>
<td>2.402, 2.416</td>
<td>179.0</td>
<td>179.2</td>
<td>179.3</td>
</tr>
<tr>
<td>544b</td>
<td>2.074, 2.109</td>
<td>2.402, 2.411</td>
<td>178.2</td>
<td>178.8</td>
<td>177.6</td>
</tr>
<tr>
<td>544c</td>
<td>2.119, 2.119</td>
<td>2.404, 2.406</td>
<td>180.0</td>
<td>180.0</td>
<td>180.0</td>
</tr>
</tbody>
</table>

2.638 Å and 2.508, 2.518 Å for the six-membered $^{546}$ and $^{547}$ to 2.721, 2.811 Å for the eight-membered $^{548}$.

The intramolecular N → Sn distances in stannasiloxane $[\text{Me}_2\text{N}(\text{CH}_2)^2\text{CMe}_2]_2\text{Sn}(\text{OSiMe}_2)_2\text{O}$ ($^{549}$) of 2.879 and 2.957 Å$^{1222}$ are rather long. They are comparable with those found in $[(\text{CH}_2\text{N(Et)})\text{CH}_2\text{CH}_2\text{CH}_2]_2\text{SnS}_2$ (N → Sn 2.766 and 2.859 Å$^{1134}$) and $[(\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2)_2\text{SnS}]_2$ (N → Sn 2.810 and 3.158 Å$^{1223}$). It seems that the intramolecular N → Sn interactions in $^{549}$ prevent its polymerization in the solid state. For the related stannasiloxane $(t$-Bu)$_2\text{Sn}(\text{OSiPh}_2)_2\text{O}$, with no intramolecular donor function, a polymeric structure was observed in the solid state$^{1224}$.

The Sn atoms in organoelement oxides $^{550}$ exhibit distorted octahedral configurations with the carbon atoms in mutual trans and the oxygen and nitrogen atoms in cis positions$^{1225}$.

The diorganotin derivatives $^{551a-d}$, $^{552}$ and $^{553}$ reveal distorted-octahedral geometries for the tin atoms with cis donor (trans-R) configuration$^{1226}$. In contrast, the tin center in $^{554}$ exhibits a distorted-octahedral trans donor (cis-R) configuration, where the N → Sn distances of 2.362 and 2.377 Å are shorter than those in $^{551-553}$ (Table 91). These results
are in line with the observation made in Section X.A 2.a that octahedral cis- and trans-SnR₂ isomeric intermolecular adducts also exhibit rather different N→Sn distances (the cis arrangements having shorter distances).

Unlike 551a–d, for 552 no decoalescence of the N-Me resonances upon temperature lowering was observed and they remained equivalent on the NMR time scale of the measurement, indicating a very low activation barrier for enantiomerization. This indicates that the two N→Sn bonds are very weak. The different behavior observed for the diphenolate and dithiophenolate can be traced to the higher ionic character of the Sn–O versus the Sn–S bond, which makes the former kinetically more labile 1203. In contrast to the methoxy-substituted stannaindane 551a–d and 552, the chiral spiro-catecholate ($\sigma$-O₂C₆H₃OMe-3) 553 enabled observation of the two diastereomers as a 1 : 1 553-A and 553-B mixture 1226. The existence of the diastereomers is also reflected by the observation of two equally intense $^{119}$Sn CP-MAS resonances at $-193.0$ and $-199.8$ ppm. The
NMR spectral behavior of compounds 553 and 554 at low and room temperature means that, with kinetically more stable chelate catecholate ligands, the Sn−O bonds do not rupture. A mechanism which accounts for the coalescence of hexacoordinated stannaindane derivatives 553 and 554 (as well as the thiophenolate derivative 552) involves intramolecular N→Sn dissociation with a following enantiomerization by a Berry pseudorotation for pentacoordinated species\textsuperscript{1226} (equation 87).

In the crystal structure of triorganotin halide 555a, the two C(Ar) atoms are in trans position. For hypervalent bonds, the length of the N→Sn trans to the iodine atom is considerably longer (2.53 Å) than that trans to the methyl group (3.10 Å). The \textsuperscript{1}H, \textsuperscript{13}C
and $^{119}$Sn NMR spectra show that, at low temperature in solution, the compound exists in two geometrically different forms, one as found in the solid state and one with the all-cis configuration (555b). The assignment to isomers was based on the larger low-temperature $^2J(119\text{Sn}-1\text{H})$ and $^1J(119\text{Sn}-13\text{C})$ couplings for the two trans groups than for the third organic group in cis position. At higher temperatures a process involving interconversion between these two isomers becomes fast on the NMR time scale.

Both trans-C(Ar)-556a and all-cis-556b configurations exist as two crystallographically different molecules in crystalline (2-Me$_2$NCH$_2$C$_6$H$_4$)$_4$Sn with weak N $\rightarrow$ Sn interactions of both amino groups. The more symmetric isomer 556a has shorter coordinative bond lengths (3.16, 3.28 Å) than all-cis-556b (3.46, 3.68 Å).

The structure of diorganotin compounds with the general formula [R$_2$Sn(O$_2$CC$_5$H$_4$N-2)$_2$] (557, (a) R = Ph$^{1227}$, (b) R = t-Bu$^{1228}$ and (c) R = Me$^{1229}$ bearing five-membered N,O-coordinating ligand depends largely on the substituents. For monomeric structure 557a the phenyl groups are cis and the oxygen atoms are trans. In 557b the $t$-butyl groups are trans and one of the picolinate ligands chelate the tin atom via one oxygen atom and the nitrogen atom (the second oxygen does not coordinate to tin). For polymeric 557c the picolinate ligands chelate the tin atom via one oxygen atom and the nitrogen atom, but one picolinate coordinates intermolecularly to the tin atom leading to a polymeric structure making each tin atom seven-coordinate. The N $\rightarrow$ Sn distances of 2.393 and 2.507 Å in 557c are intermediate between those found in 557a for both N $\rightarrow$ Sn interactions (2.284 Å$^{1227}$) and 557b (>2.50 Å). The three different molecular geometries for compounds 557 may be explained in terms of electronic or steric factors associated with the Sn-bound R groups, but there are no consistent correlations between them and the structure found in the solid state.
Accumulated X-ray results on neutral (N → Sn) bis-chelate diorganotin structures indicate that the stereochemistry of the SnR₂ skeleton in the octahedral geometries is generally trans or distorted trans for dialkyltin complexes. The trans-SnR₂ geometries were exclusively obtained with monodentate ligands when X = halide or pseudohalide, but not so with bidentate ligands. If the cis–trans energy differences were small in these systems, it might be conceivable, by a suitable choice of the aryl substituents and/or the chelating ligand, to favor one geometrical isomer over the other and, perhaps, even to allow the isolation of both forms.

c. Five-membered chelate rings (O → M). The reaction of (ClCH₂)₂GeCl₂ with N-TMS lactams in a 1 : 2 ratio leads to relatively stable products of two types. Under kinetic control (an inert solvent, 80–100 °C), (N-Ge) bis-chelate 558a is not found when 558b and 558c are detected (equation 88, a), while under more drastic conditions, the reaction yields the thermodynamically more stable (O–Ge) bis-chelates 559a–c (equation 88, a,
The (N–Ge) bis-chelates 558b and 558c, isolated on a preparative scale, isomerize to the corresponding (O–Ge) bis-chelates 559b and 559c when boiled in p-xylene for 0.5–1.5 h (equation 88, b).

By this method, but using (BrCH2)2GeBr2, the (O → Ge) bis-chelates 560a–c were obtained under conditions of thermodynamic control1232. Furthermore, the acyclic amide dichloride [MeCON(Me)CH2]2GeCl2 (561) was prepared analogously1233.

The syntheses of mixed bis-chelates (Ln)2Ge(Cl)Y, where Ln is the bidentate n-membered lactamomethyl C,O-chelating ligand, obtained by replacing one chlorine atom in (Ln)2GeCl2 by a much better leaving group Y (Y = OTf, OClO3, BF4, I or I3), were described in Section VIII.A. In contrast, the replacement of both chlorine atoms of (Ln)2GeCl2 takes place if the nucleofugality of entering and leaving groups are nearly similar (Cl and Br, or Cl and F). Consequently, dibromide 560c was prepared by the reaction of dichloride 559c with both LiBr and Me3SiBr in a 1 : 2 ratio of reactants893. Analogously, difluorides 562a–c were synthesized by treatment of dichlorides 559a–c with an excess of AgF (equation 89)893.

The hexacoordinated state of the central atom in products 558–562 was established using IR spectroscopy and, in the case of (O–Ge) bis-chelates 559–562, also by X-ray
diffraction\textsuperscript{1231–1233}. The Ge atoms in these compounds have an octahedral coordination owing to the two intramolecular O→Ge coordinated bonds. However, unlike in thiolactim ethers \textsuperscript{554a–c}, both the chelate rings and the chlorine atoms have a \textit{cis}-orientation relative to each other.

The parameters of the Ge atom coordination in dichlorides 559\textsubscript{a–c}, 561, dibromides 560\textsubscript{a–c} and difluorides 562\textsubscript{a–c} (Table 92) are close to those in chlorides 142\textsubscript{b}, 1441\textsubscript{a–d} and bromide 149 containing the pentacoordinated Ge atom (Table 33). Nevertheless, the O–Ge and Ge–Hal bonds in the hexacoordinated dihalides under discussion are somewhat shorter than those in the corresponding monohalides. However, these distances are still significantly longer than those in tetracoordinated germanium compounds. Thus, these dihalides have two OGeHal hypervalent fragments. The use of six-coordinate germanium compounds with lactamomethyl C,O-chelating ligands as models of transition states in S\textsubscript{N} reactions involving the five-coordinate Ge atom was discussed\textsuperscript{478}.

The geometrical parameters of the valence environment about the Ge atom in dihalides 559–562 reflect pronounced regularities associated with the change in the size of the lactam ring and the replacement of the halogen ligands. On increasing the size of the lactam ring and on going from fluorides to chlorides and then to bromides, the coordination environment about the germanium atom approximates an octahedron, as is evident, for example, from the increase in the CGeC angles. The extent of the deviation of the geometry of two OGeX hypervalent fragments from the ideal octahedron is characterized by the deviation $\Delta \Omega$ (see above) from the ideal value ($2\pi$) corresponding to the symmetrical O–Ge–Hal hypervalent bond. For dihalides (L\textsuperscript{5})\textsubscript{2}GeX\textsubscript{2} with a five-membered lactam ring, compounds 559\textsubscript{a}, 560\textsubscript{a} and 562\textsubscript{a}, the $\Delta \Omega$ values for the fluoride, chloride and bromide are 52°, 43° and 38°, respectively.

Finally, the hypervalent bonds in structures with five-coordinate (a TBP environment) and six-coordinate (an Oh environment) atoms can be considered by taking into account the difference in the ranges in which the $\Delta \Omega$ values vary, viz $\pi$ and $2/3\pi$ for a TBP and an Oh, respectively\textsuperscript{478}.

Based on the $^1$H DNMR data\textsuperscript{1232}, it is suggested that both diastereomers with either a \textit{cis} or \textit{trans} arrangement of the Br atoms are present in solution of dibromides 560\textsubscript{a–b}. The polytopic rearrangement in dihalides (L\textsubscript{n})\textsubscript{2}GeX\textsubscript{2} is discussed below.

| TABLE 92. Selected structural parameters for neutral (O→Ge) bis-chelates (L\textsubscript{n})\textsubscript{2}GeX\textsubscript{2} |
|------------------|---|---|---|---|---|---|
| Compound | n | X | O→Ge (\textdegree) | X→Ge (\textdegree) | O–Ge–X (deg) | C–Ge–C (deg) | $\Delta \Omega$ (deg)$^a$ | Reference |
| 562\textsubscript{a} | 1 | F | 2.265, 2.265 | 1.754, 1.754 | 171.3, 171.3 | 155.6 | 52 | 1232 |
| 562\textsubscript{b} | 2 | F | 2.232, 2.187 | 1.798, 1.790 | 174.3, 171.5 | 157.4 | 42 | 1232 |
| 562\textsubscript{c} | 3 | F | 2.185, 2.185 | 1.799, 1.799 | 172.2, 171.7 | 161.7 | 37 | 1232 |
| 559\textsubscript{a} | 1 | Cl | 2.183, 2.239 | 2.274, 2.284 | 172.0, 171.6 | 160.3 | 43 | 1231 |
| 559\textsubscript{b} | 2 | Cl | 2.093, 2.220 | 2.280, 2.313 | 173.2, 170.6 | 159.8 | 42$^b$ | 1231 |
| 559\textsubscript{c} | 3 | Cl | 2.113, 2.137 | 2.314, 2.312 | 174.5, 174.1 | 165.0 | 30 | 1231 |
| 561 | $^c$ | Cl | 2.104, 2.116 | 2.325, 2.323 | 172.3, 171.7 | 167.1 | 35 | 1233 |
| 560\textsubscript{a} | 1 | Br | 2.203, 2.139 | 2.458, 2.472 | 172.1, 172.3 | 162.7 | 38 | 1232 |
| 560\textsubscript{b} | 2 | Br | 2.090, 2.111 | 2.520, 2.461 | 173.4, 173.1 | 163.8 | 30 | 1232 |
| 560\textsubscript{c} | 3 | Br | 2.089, 2.087 | 2.506, 2.483 | 174.1, 173.4 | 168.0 | 26 | 1232 |

$^a$ $\Delta \Omega = 2\pi - \Omega$, where $\Omega$ is the solid angle determined by the directions of four pseudo-equatorial bonds and containing an axial ligand ($\Delta \Omega = 0^\circ$ for ideal octahedron); the averaged values for two virtually identical hypervalent bonds in each molecule are given.

$^b$ The point drops out of the common series, likely because the unit cell of 559\textsubscript{b} contains a p-xylene molecule solvate.

$^c$ [MeC(O)N(Me)CH\textsubscript{2}]\textsubscript{2}GeCl\textsubscript{2}.
The general synthetic route to six-coordinate \((O-Sn)\) bis-chelates involves the reaction of a functionalized halide with metallic tin. In earlier papers the numerous examples of synthesis of estertins \(X_2Sn[CHCHR'COOR'']\)\(_2\) \((X = Br, I; R, R' = H, Me, CH_2COOR''; R'' = Alk)\)\(^{1234-1236}\), the amide derivatives \(X_2Sn[CHCHR'CONR''R''']\)\(_2\) \((X = Br, I; R, R' = H, Me, Et, Ar)\)\(^{1237,1238}\) and the ketone derivatives \(X_2Sn[CR_2CH_2COR']\)\(_2\) \((X = Cl, Br, I; R = H, Me; R' = Alk, Ph)\)\(^{1239}\) involved the use of the corresponding halo-esters, -amides and -ketones as precursors. The first hypervalent tin species containing a C,Y-chelating ligand, the dibromide \(Br_2Sn[CH(COOEt)CH_2COOEt]\) \((563)\), whose structure was established by X-ray analysis, has been prepared by the reaction of metallic tin with diethyl bromosuccinate\(^{1240,1241}\). On the other hand, the structure of the first representative of analogous ketone derivatives, diiodide \(564\), was established only recently\(^{1242}\).

The reaction of \(CH_2=CHCOOR\) with Sn/HX \((X = Cl, Br, I)\) can be considered as a convenient preparative variant of the direct method discussed above. A number of \((O-Sn)\) bis-chelate estertins \(X_2Sn[(CH_2)_2COOMe]\)\(_2\) \((338)\) were obtained by this way\(^{720,753}\), as well as by halide exchange reactions\(^{347}\) of dichloride \(338a\), including compounds \(338a-c\) characterized by X-ray crystallography (see Table 93 for structures). The mixed halide species, \(ClBrSn[(CH_2)CH_2COOMe]\)\(_2\) \((339)\)\(^{347}\), and the amide derivative, \(Cl_2Sn[CH_2CH_2CONH_2]\) \((565)\)\(^{722,907}\), were also described.

Syntheses of various hypervalent estertins produced from trichlorides \(329\) and \(335\) were discussed in Section VII.A.2.b. They include compounds whose structures were established by X-ray diffraction, in particular, dimeric hydroxide \(336\)\(^{182}\), sulfides \(351\) and \(352\)\(^{749}\), imine \(349\)\(^{741}\), as well as the DMTC derivatives \(337a\) and \(337b\)\(^{731,182}\).

Structures of hexacoordinate estertin compounds, i.e. species containing the ROOCCH_2-CH_2Sn moiety were partly discussed earlier (Section VII.A.2.b and Table 53). In the estertins \((R^1O_2CCH_2CHR^2)SnX_2\) \(338a-c\), ketone \(564\) and amide \(565\), the tin atom

<table>
<thead>
<tr>
<th>Compound</th>
<th>X</th>
<th>R(^1)</th>
<th>R(^2)</th>
<th>O → Sn (Å)</th>
<th>O → Sn ← O (deg)</th>
<th>X-Sn-X (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>564(^a)</td>
<td></td>
<td></td>
<td></td>
<td>2.427, 2.438</td>
<td>75.7</td>
<td>105.0</td>
<td>1242</td>
</tr>
<tr>
<td>338a</td>
<td>Cl</td>
<td>OMe</td>
<td>H</td>
<td>2.436, 2.438</td>
<td>75.3</td>
<td>105.7</td>
<td></td>
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<tr>
<td>338b</td>
<td>I</td>
<td>OMe</td>
<td>H</td>
<td>2.520, 2.523</td>
<td>88.7</td>
<td>96.3</td>
<td>722</td>
</tr>
<tr>
<td>338c</td>
<td>NCS</td>
<td>OMe</td>
<td>H</td>
<td>2.519, 2.535</td>
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<td>96.9</td>
<td>732</td>
</tr>
<tr>
<td>339</td>
<td>Cl, Br</td>
<td>OMe</td>
<td>H</td>
<td>2.523, 2.527</td>
<td>86.6</td>
<td>98.6</td>
<td>347</td>
</tr>
<tr>
<td>338d</td>
<td>Br</td>
<td>OEt</td>
<td>COOEt</td>
<td>2.432, 2.459</td>
<td>77.4</td>
<td>98.8</td>
<td>1240</td>
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<tr>
<td>565</td>
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<td>81.4</td>
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<td>907</td>
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<td>357</td>
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<td>OMe</td>
<td>H</td>
<td>2.324, 2.327</td>
<td>81.6</td>
<td>95.5</td>
<td>722</td>
</tr>
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<td>303</td>
<td>Cl</td>
<td>CH_2CH_2OMe</td>
<td>H</td>
<td>2.628</td>
<td>123.8</td>
<td>88.4</td>
<td>349</td>
</tr>
<tr>
<td>566</td>
<td>Me</td>
<td>H</td>
<td>Me</td>
<td>2.281</td>
<td>75.8</td>
<td>109.1</td>
<td>1243</td>
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<td>567</td>
<td>Me</td>
<td>H</td>
<td>Me</td>
<td>2.206</td>
<td>76.7</td>
<td>107.7</td>
<td>1244</td>
</tr>
<tr>
<td>567</td>
<td>Et</td>
<td>Me</td>
<td>4-BrC_6H_4</td>
<td>2.373, 2.449</td>
<td>146.6</td>
<td>156.6</td>
<td>1243</td>
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<tr>
<td>567</td>
<td>Bu</td>
<td>Ph</td>
<td>Ph</td>
<td>2.416, 2.425</td>
<td>145.9</td>
<td>133.9</td>
<td>1246</td>
</tr>
<tr>
<td>567</td>
<td>Bu</td>
<td>Me</td>
<td>4-BrC_6H_4</td>
<td>2.364, 2.393</td>
<td>143.4</td>
<td>145.1</td>
<td>1246</td>
</tr>
</tbody>
</table>

\(^a\)Two independent molecules in the unit cell.
possesses a distorted octahedral geometry. The $\text{R}^1\text{O}_2\text{CCH}_2\text{CH}_2$ ligands are bidentate, with the carbonyl oxygen atoms $\text{trans}$ to the $\text{cis}$-halides or pseudohalides. Selected bond angles and lengths for estertins, ketone, amide, and the related compounds $303, 357, 566$ and $567$ are displayed in Table 93.

The $\text{cis}$ Sn–I bond lengths in the ketone $564^{1242}$ and ester $338b^{347}$ are 2.835–2.857 and 2.777–2.780 Å, respectively, longer, as expected, than the tin–iodide bond lengths in tetrahedral four-coordinate diorganotin diiodides (2.67–2.72 Å)$^{172,1247,1248}$.

The NMR spectra of $(\text{MeO}_2\text{CCH}_2\text{CH}_2)_2\text{SnX}_2$ show the following trends: (i) both $\delta^1\text{H}_\alpha$ and $\delta^{13}\text{C}_\alpha$ increase and (ii) both $2J(\text{Sn}–\text{H})$ and $1J(\text{Sn}–\text{C})$ decrease in the sequence $\text{X}_2 = (\text{NCS})_2, \text{Cl}_2, \text{ClBr}, \text{Br}_2, \text{I}_2$, which is the sequence of decreasing electronegativity of $\text{X}_2$ and decreasing mean Sn–X bond energies$^{347}$.

By applying the direct method, $(\text{O–Sn})$-bis-chelate dihalostannanes $(\text{L}^n)_2\text{SnX}_2$ $(568–570)$ were recently synthesized (equation 90)$^{1249,504}$. Analogously, the acyclic amide, dichloride $[\text{MeCON(Me)}\text{CH}_2]_2\text{SnCl}_2$ $(571)$, was obtained$^{1233}$.

The reactions of dichlorides $568a–c$ with lithium salts LiX ($X = \text{Br, I}$), unlike those of germanium derivatives (see equations 77 and 88), result in both cases in the replacement of the two monodentate ligands by nucleophiles to give dibromides $569a–c$ and diiodides $570a–c$ with retention of the configuration of the initial dichloride and with higher yields than in reaction $90^{504}$. The formation of a cation–anion complex $\{[(\text{L}^5)_2\text{Sn}($OH$)]^+\text{BF}_4^-\}_2$ by the reaction of $(\text{L}^5)_2\text{SnCl}_2$ with AgBF$_4$ is discussed in Section XI.B.

The reaction of the N-TMS caprolactam with $(\text{CICH}_2)_2\text{SnCl}_2$, unlike that of the germanium derivative (equation 88), proceeds under more drastic conditions and gives only a poor yield of dichloride $568c$ (18%), i.e. this synthetic route to six-coordinate (O–Sn) bis-chelates has no preparative importance$^{494}$.
The significant upfield chemical shifts of dihalides 568–570 in the $^{119}$Sn NMR spectra in CDCl$_3$ (about $-195$ to $-336$ ppm), and IR data in CHCl$_3$ are indicative of hexacoordination of the tin atom, i.e. of the presence of the two bidentate chelate ligands and two monodentate ligands.$^{504,1249}$

The conductivities of solutions of the tin dihalides under consideration are substantially lower than those of their Si analogues (only data for dichlorides are available), are slightly lower (in particular, as compared to dibromide $^{(560c)}$) than those of their germanium analogues (Table 64) and are close to the intrinsic conductivity of the CH$_2$Cl$_2$ solvent. This is indicative of an increased covalent character of the M–Hal bonds in dihalides $(L^n)_2$MX$_2$, (M = Si, Ge, or Sn) on going from silicon to germanium and then to tin compounds.

According to X-ray structural data, the configuration of the valence environment about the Sn atoms in dihalides $^{568a–c,1249,569a–c,570a,570b,504}$ and $^{571}$ (a cis arrangement of the Hal and O atoms) is identical to that discussed previously in six-coordinate germanium dihalides (Section X.B.2a) containing the MC$_2$O$_2$Hal$_2$ coordination unit (M = Ge or Sn) with an intramolecular O $\rightarrow$ M coordination and a six-coordinate M atom involved in two hypervalent O $\rightarrow$ M–Hal bonds. It is particularly remarkable that replacement of the O atom by the N atom (the MC$_2$N$_2$Hal$_2$ coordination unit) leads to a change of the configuration to transoid.$^{636,1221}$ Apparently, this is a manifestation of the difference in the donor properties of the O and N atoms.

A comparison of the parameters of the Sn atom coordination in the dihalides (Table 94) with the structures of analogous lactamomethyl halide derivatives of five- and six-coordinate Si and Ge derivatives (Tables 33, 34 and 90) demonstrates that the spatial array of the hypervalent fragments containing six-coordinate atoms is less sensitive to the replacement of the halide ligands and the central atoms.$^{504}$ The covalency of the M–Hal bond increases and that of the M–O bond decreases in the series M = Si, Ge and Sn.$^{494}$

When using the parameter $\Delta\Omega$ (see above) for comparison, it is evident that the replacement of a Ge by Sn leads to a decrease in the range over which the $\Delta\Omega$ value varies (from 12–15° to 8–10°) as the size of the lactam rings changes, as well as to some increase in the distortion from ideal octahedral coordination (on the average by 8°). The hypervalent units in dihalides 338a and 563 are more substantially distorted (Table 33) than those in dichlorides 568a–c, 565 and 571. It is reasonable to attribute the noticeable difference in the distortion of the octahedral coordination in 338a and 563 as compared with 565 to the higher donor ability of the O atom of the aminocarbonyl group than that in the alkoxycarbonyl group. The $\Delta\Omega$ value also decreases from 55° for the five-coordinate to 40° in the six-coordinate state in the case of monochloride $^{L^6}$SnMe$_2$Cl (361b)$^{494,758}$ and dichloride $(L^6)_2$SnCl$_2$ (568b).
16. Hypervalent compounds of organic germanium, tin and lead derivatives

TABLE 94. Comparison of selected structural parameters for neutral (O\rightarrow Sn) bis-chelates (L\textsuperscript{n})\textsubscript{2}SnX\textsubscript{2} and related compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>n</th>
<th>X</th>
<th>O\rightarrow Sn (Å)</th>
<th>X–Sn (Å)</th>
<th>O\rightarrow Sn–X (deg)</th>
<th>C–Sn–C (deg)</th>
<th>\Delta\Omega (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>568a</td>
<td>1</td>
<td>Cl</td>
<td>2.271, 2.311</td>
<td>2.432, 2.445</td>
<td>170.3, 171.3</td>
<td>156.7</td>
<td>49</td>
<td>1249</td>
</tr>
<tr>
<td>568b</td>
<td>2</td>
<td>Cl</td>
<td>2.256, 2.265</td>
<td>2.442, 2.461</td>
<td>168.9, 171.1</td>
<td>158.0</td>
<td>40</td>
<td>1249</td>
</tr>
<tr>
<td>568c</td>
<td>3</td>
<td>Cl</td>
<td>2.251, 2.274</td>
<td>2.448, 2.460</td>
<td>172.4, 172.8</td>
<td>160.2</td>
<td>39</td>
<td>1249</td>
</tr>
<tr>
<td>571\textsuperscript{b}</td>
<td>Cl</td>
<td>2.22, 2.294</td>
<td>2.447, 2.459</td>
<td>168.5, 171.4</td>
<td>167.1</td>
<td>44</td>
<td>1249</td>
<td></td>
</tr>
<tr>
<td>2.249, 2.27</td>
<td>2.454, 2.457</td>
<td>169.9, 170.0</td>
<td>157.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>569a</td>
<td>1</td>
<td>Br</td>
<td>2.26, 2.231</td>
<td>2.595, 2.606</td>
<td>170.9, 172.0</td>
<td>157.6</td>
<td>46</td>
<td>504</td>
</tr>
<tr>
<td>569b</td>
<td>2</td>
<td>Br</td>
<td>2.250, 2.272</td>
<td>2.579, 2.613</td>
<td>169.2, 170.4</td>
<td>157.2</td>
<td>42</td>
<td>504</td>
</tr>
<tr>
<td>569c</td>
<td>3</td>
<td>Br</td>
<td>2.255, 2.266</td>
<td>2.591, 2.613</td>
<td>170.9, 172.8</td>
<td>160.8</td>
<td>38</td>
<td>504</td>
</tr>
<tr>
<td>570a</td>
<td>1</td>
<td>I</td>
<td>2.24, 2.27</td>
<td>2.744, 2.798</td>
<td>172.0, 173.2</td>
<td>157.5</td>
<td>45</td>
<td>504</td>
</tr>
<tr>
<td>570b</td>
<td>2</td>
<td>I</td>
<td>2.26, 2.28</td>
<td>2.752, 2.815</td>
<td>170.5, 169.5</td>
<td>156.4</td>
<td>44</td>
<td>504</td>
</tr>
<tr>
<td>338a\textsuperscript{c}</td>
<td>Cl</td>
<td>2.53</td>
<td>2.41</td>
<td>175.5</td>
<td>144.1</td>
<td>60</td>
<td>722</td>
<td></td>
</tr>
<tr>
<td>565\textsuperscript{c}</td>
<td>Cl</td>
<td>2.33</td>
<td>2.46</td>
<td>171.8</td>
<td>160.8</td>
<td>41</td>
<td>722</td>
<td></td>
</tr>
<tr>
<td>563\textsuperscript{c}</td>
<td>Br</td>
<td>2.49</td>
<td>2.51</td>
<td>165.7</td>
<td>148.5</td>
<td>68</td>
<td>1241</td>
<td></td>
</tr>
<tr>
<td>Me\textsubscript{2}SnCl\textsubscript{2} \cdot 2DMSO\textsuperscript{c}</td>
<td>2.29</td>
<td>2.51</td>
<td>173.6</td>
<td>170.3</td>
<td>22</td>
<td>1039</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Me\textsubscript{2}SnCl\textsubscript{2} \cdot 2DMF\textsuperscript{c}</td>
<td>2.39</td>
<td>2.47</td>
<td>175.6</td>
<td>164.8</td>
<td>31</td>
<td>1039</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} \Delta\Omega = 2\pi – \Omega, where \Omega is the solid angle determined by the directions of four pseudo-equatorial bonds and containing an axial ligand (\Delta\Omega = 0° for ideal octahedron); the average values for two virtually identical hypervalent bonds in each molecule are given.

\textsuperscript{b} Two crystallographically independent molecules.

\textsuperscript{c} Average values over two hypervalent O\rightarrow Sn–Hal bonds are given.

Note that in the complex with monodentate ligands, Me\textsubscript{2}SnCl\textsubscript{2} \cdot 2DMF\textsuperscript{1039}, which has a similar environment about the Sn atom to that in dichlorides 568a–c and 571, the average lengths of the hypervalent O\rightarrow Sn and Sn–Cl bonds and the \Delta\Omega value (Table 94) are 2.39 Å, 2.47 Å and 31°, respectively, i.e. the O\rightarrow Sn bond is ca. 0.1 Å longer than the corresponding bonds in 568a–c and 571, indicating that chelation plays an important role in this case.

For each of the dihalides (L\textsuperscript{n})\textsubscript{2}MX\textsubscript{2} the methylene NCH\textsubscript{2}M protons displayed an AB spin system in the \textsuperscript{1}H NMR spectrum, but no splitting of the signals of the methylene \textsuperscript{13}C resonances occurs, indicating a nonequivalence of protons within each methylene group but no loss of its \textit{C\textsubscript{2}} symmetry on the NMR time scale. The free activation energies (\Delta\textit{G}\textsuperscript{#}) of the rearrangement of the hexacoordinated species 559–561 and 568–571 as well as [MeC(O)N(Me)CH\textsubscript{2}]\textsubscript{2}MCl\textsubscript{2} (M = Ge, Sn) found by dynamic \textsuperscript{1}H NMR spectroscopy are listed in Table 95. The values of the barriers for the polytopic rearrangement for Sn derivatives are normally 1–3 kcal mol\textsuperscript{−1} higher than those for their Ge analogues. An increase in the size of the lactam ring in the bidentate ligand is accompanied by an increase in \Delta\textit{G}\textsuperscript{#}. This change is more pronounced for the Ge derivatives. As in the above-considered halides of pentacoordinated silicon and germanium (Table 34), an increased nucleofugality of the substituent X in the series Cl, Br, I results in a decrease in the \Delta\textit{G}\textsuperscript{#} value. In the case of tin dihalides, this tendency is observed only for derivatives with five-membered lactam rings, i.e. for compounds with weaker O \rightarrow Sn coordinated bonds.

d. Six-membered chelate rings. Six-coordinate \textit{\beta}-diketonate diorganotin complexes with two identical symmetrical chelate ligands, such as acetylacentonate (572a and 572b\textsuperscript{501,1251}), generally adopt \textit{trans}-octahedral configuration\textsuperscript{1252}. In contrast, with asymmetric donors, in particular 4-acyl-5-pyrazolones (QH) and \textit{\beta}-diketonate complexes of the type 573 show X-ray crystal structures with strongly distorted octahedral geometry around tin, two different
TABLE 95. Comparison of the barriers for ligand exchange ($\Delta G^\#$) in neutral (O → Ge) and (O → Sn) bis-chelates ($L^n$)$_2$MX$_2$ and related compounds (CDCl$_3$)

<table>
<thead>
<tr>
<th>Type of compound$^a$</th>
<th>Compound</th>
<th>$\Delta G^# \pm 0.2$ Reference</th>
<th>Compound</th>
<th>$\Delta G^# \pm 0.2$ Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(kcal mol$^{-1}$)</td>
<td></td>
<td>(kcal mol$^{-1}$)</td>
</tr>
<tr>
<td>$M = \text{Ge}$</td>
<td></td>
<td></td>
<td>$M = \text{Sn}$</td>
<td></td>
</tr>
<tr>
<td>($L^5_3$)$_2$MCl$_2$</td>
<td>559a</td>
<td>10.6 490</td>
<td>568a</td>
<td>13.6 1250</td>
</tr>
<tr>
<td>($L^5_3$)$_2$MCl$_2$</td>
<td>559b</td>
<td>12.8 490</td>
<td>568b</td>
<td>13.6 1250</td>
</tr>
<tr>
<td>($L^5_3$)$_2$MCl$_2$</td>
<td>559c</td>
<td>13.6 490</td>
<td>568c</td>
<td>13.9 1210</td>
</tr>
<tr>
<td>($L_2$)$_2$MCl$_2$</td>
<td>561</td>
<td>12.1 1210</td>
<td>571</td>
<td>13.0 1210</td>
</tr>
<tr>
<td>($L^5_3$)$_2$MBr$_2$</td>
<td>560a</td>
<td>10.2 490</td>
<td>569a</td>
<td>13.3 490</td>
</tr>
<tr>
<td>($L^5_3$)$_2$MBr$_2$</td>
<td>560b</td>
<td>12.1 490</td>
<td>569b</td>
<td>13.8 490</td>
</tr>
<tr>
<td>($L^5_3$)$_2$MBr$_2$</td>
<td>560c</td>
<td>12.9 490</td>
<td>569c</td>
<td>13.9 490</td>
</tr>
<tr>
<td>($L^5_3$)$_2$MI$_2$</td>
<td>—</td>
<td>—</td>
<td>570a</td>
<td>12.6 490</td>
</tr>
<tr>
<td>($L^5_3$)$_2$MI$_2$</td>
<td>—</td>
<td>—</td>
<td>570b</td>
<td>13.8 490</td>
</tr>
<tr>
<td>($L^5_3$)$_2$MI$_2$</td>
<td>—</td>
<td>—</td>
<td>570c</td>
<td>13.8 490</td>
</tr>
</tbody>
</table>

$^a$L$^n$ is the n-membered bidentate lactamomethyl C,O-chelating ligand; $L = \text{MeCON(Me)CH}_2$.

![Chemical structures](attachment:chemical_structures.png)

(572a) $R = \text{Me}$
(572b) $R = \text{Bu}$
(574a) $R = \text{Me}, \ R^1 = \text{CCl}_3$
(574b) $R = \text{Bn}, \ R^1 = \text{OMe}$
(574c) $R = \text{Bu}, \ R^1 = \text{Ph}$
sets of Sn–O distances and a C–Sn–C angle of 180° (135–150°), which is best described as skew-trapezoidal bipyramidal (Table 96). Thus, increasing the octahedral distortion (decreasing C–Sn–C and O–Sn–O angles) is associated with a larger difference in the bond length between covalent and coordinate bonds. Closely related structures were found for 4-trichloroacetyl-5-pyrazolones 574a–c. However, they are significantly shifted toward trans-octahedral configuration (skewed trapezoidal bipyramidal) with the C–Sn–C angle of 154–164° (Table 96).

The dihalotin derivatives (Q)2SnX2 (X = F, Cl, Br and I) are probably cis octahedral in the solid state, whereas in solution they exist as a mixture of cis and trans isomers. It is not easily evident why a pseudo-C₃ symmetry exists (or why the trans configuration is not allowed). An apparent reason is the asymmetry of the ligand, since a symmetric β-acetylacetonate anion (acac) stabilizes the trans species (acac)₂Sn(CH₃)₂, which has the metal on an inversion center.

In 575 and 576 the tin atom is in a distorted octahedral environment coordinated by two trans-methyl groups and two bidentate ligands, which coordinate to the metal through the thiolato sulfur and the oxygen atoms. For 575, the Me–Sn–Me bond angle is 139.4° and the linear hypervalent fragment is deformed (161.2, 161.6°). The deviation from the regular geometry is probably due to steric hindrance produced by the trimethylsilyl groups. The corresponding values for 576 are 152.8° and 172.89, 173.90°.

Crystalline studies of neutral bis-chelate diorganotin complexes 577 indicate that the stereochemistry of 577a, 577b, 577c and dimethyl[bis(tetraphenyl-oxothioxodiphosphazane)]tin (574d) are ideal octahedral (X → Sn ← X = X–Sn–X = 180°).

In 575 and 576, the tin atom is in a distorted octahedral environment coordinated by two trans-methyl groups and two bidentate ligands, which coordinate to the metal through the thiolato sulfur and the oxygen atoms. For 575, the Me–Sn–Me bond angle is 139.4° and the linear hypervalent fragment is deformed (161.2, 161.6°). The deviation from the regular geometry is probably due to steric hindrance produced by the trimethylsilyl groups. The corresponding values for 576 are 152.8° and 172.89, 173.90°.

Crystalline studies of neutral bis-chelate diorganotin complexes 577 indicate that the stereochemistry of 577a, 577b, 577c and dimethyl[bis(tetraphenyl-oxothioxodiphosphazane)]tin (574d) are ideal octahedral (X → Sn ← X = X–Sn–X = 180°).
e. Miscellaneous. Complexes of other types were much less investigated. Complexes 578 and 579 are representatives of compounds containing two different bidentate chelating ligands. Selected X-ray data for 578 and 579 are given in Table 97.

### Table 96. Selected structural parameters for octahedral diorganotin bis(ß-diketonate) compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$O\rightarrow Sn$ (Å)</th>
<th>Sn–O (Å)</th>
<th>$\Delta$ (Å)</th>
<th>$O–Sn–O$ (deg)</th>
<th>$O\rightarrow Sn \leftarrow O$ (deg)</th>
<th>$C–Sn–C$ (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph$_2$Sn(Q$^1$)$_2$</td>
<td>2.223</td>
<td>2.143</td>
<td>0.08</td>
<td>91.9</td>
<td>98.6</td>
<td>173.0</td>
<td>1253</td>
</tr>
<tr>
<td></td>
<td>2.26</td>
<td>2.12</td>
<td>0.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bz$_2$Sn(Q$^2$)$_2$</td>
<td>2.359</td>
<td>2.105</td>
<td>0.254</td>
<td>84.1</td>
<td>107.4</td>
<td>164.5</td>
<td>1254</td>
</tr>
<tr>
<td></td>
<td>2.329</td>
<td>2.109</td>
<td>0.220</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Me$_2$Sn(Q$^3$)$_2$</td>
<td>2.288</td>
<td>2.123</td>
<td>0.165</td>
<td>82.7</td>
<td>111.5</td>
<td>162.1</td>
<td>1255</td>
</tr>
<tr>
<td></td>
<td>2.321</td>
<td>2.105</td>
<td>0.216</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Me$_2$Sn(Q$^4$)$_2$</td>
<td>2.39</td>
<td>2.10</td>
<td>0.29</td>
<td>82.0</td>
<td>112.7</td>
<td>157.0</td>
<td>1256</td>
</tr>
<tr>
<td></td>
<td>2.39</td>
<td>2.09</td>
<td>0.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bu$_2$Sn(Q$^5$)$_2$</td>
<td>2.35</td>
<td>2.12</td>
<td>0.23</td>
<td>79.2</td>
<td>118.7</td>
<td>154.7</td>
<td>1257</td>
</tr>
<tr>
<td></td>
<td>2.38</td>
<td>2.11</td>
<td>0.27</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cy$_2$Sn(Q$^6$)$_2$</td>
<td>2.42</td>
<td>2.094</td>
<td>0.326</td>
<td>77.8</td>
<td>121.2</td>
<td>154.6</td>
<td>1252</td>
</tr>
<tr>
<td></td>
<td>2.405</td>
<td>2.132</td>
<td>0.273</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Me$_2$Sn(Q$^1$)$_2$</td>
<td>2.385</td>
<td>2.104</td>
<td>0.281</td>
<td>75.5</td>
<td>126.7</td>
<td>154.5</td>
<td>1258</td>
</tr>
<tr>
<td></td>
<td>2.436</td>
<td>2.099</td>
<td>0.337</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Me$_2$Sn(Q$^5$)$_2$</td>
<td>2.337</td>
<td>2.104</td>
<td>0.233</td>
<td>77.2</td>
<td>121.0</td>
<td>153.3</td>
<td>1259</td>
</tr>
<tr>
<td></td>
<td>2.412</td>
<td>2.103</td>
<td>0.309</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bu$_2$Sn(Q$^5$)$_2$</td>
<td>2.381</td>
<td>2.145</td>
<td>0.236</td>
<td>74.1</td>
<td>127.4</td>
<td>150.0</td>
<td>1260</td>
</tr>
<tr>
<td></td>
<td>2.461</td>
<td>2.135</td>
<td>0.326</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| 573 | 574a | 574b | 574c | 572a | 572b |
| 2.206 | 2.237 | 2.104 | 2.118 | 2.204 | 2.199 |
| 2.237 | 2.105 | 2.108 | 2.118 | 2.204 | 2.189 |
| 2.104 | 2.108 | 2.118 | — | 2.173 | 2.189 |
| 2.204 | 2.173 | 2.173 | 0.03 | 180.0 | 0.01 |
| 2.204 | 2.173 | 2.189 | 0.03 | 180.0 | 0.01 |

$^a$Q$^1$ = 1-phenyl-3-methyl-4-p-bromobenzoylpyrazolon-5-ato.
Q$^2$ = 1-phenyl-3-methyl-4-methoxycarbonylpyrazolon-5-ato.
Q$^3$ = 1-phenyl-3-methyl-4-acetylpyrazolon-5-ato.
Q$^4$ = 1-phenyl-3-methyl-4-isopropoxycarbonylpyrazolon-5-ato.
Q$^5$ = 1-phenyl-3-methyl-4-benzoylpyrazolon-5-ato.
Q$^6$ = 1,3-dimethyl-4-acetylpyrazolon-5-ato.
16. Hypervalent compounds of organic germanium, tin and lead derivatives

TABLE 97. Selected bond distances and angles for complexes $578a$, $578b$ and $579$

<table>
<thead>
<tr>
<th>Compound</th>
<th>O → Sn</th>
<th>S → Sn</th>
<th>O → Sn−Cl</th>
<th>S → Sn−Cl</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$578a$</td>
<td>2.436</td>
<td>2.657</td>
<td>176.2</td>
<td>158.4</td>
<td>1269</td>
</tr>
<tr>
<td>$578b$</td>
<td>2.488</td>
<td>2.632</td>
<td>175.9</td>
<td>161.0</td>
<td>1270</td>
</tr>
<tr>
<td>$579$</td>
<td>2.846</td>
<td>2.370</td>
<td>159.9</td>
<td>167.0</td>
<td>740</td>
</tr>
</tbody>
</table>

XI. HEXACOORDINATE CATIONIC TIN COMPOUNDS

Hexacoordinate cationic organogermanium and organolead complexes, for which structures were established by X-ray crystallography, have not been reported so far.

A. Intermolecular Complexes

The ionic complex $580$ is the first crystallographic example of a species with a hexacoordinate organotin cation 291. The tin atom is bonded to a highly distorted octahedral arrangement of two $trans$-methyl groups (CSnC 158.5°), a chlorine atom and three nitrogen atoms with markedly different Sn−N bond lengths (2.291 (trans to Cl), 2.333 and 2.409 Å). The C−Sn distances of 2.054 and 2.096 Å are shorter than the standard values (2.14 Å)9, while the Sn−Cl bond length (2.65 Å) is one of the longest among hypervalent organotin chlorides. In the anion Me$_2$SnCl$_3^-$, the Sn atom is five-coordinate and has a TBP geometry with both equatorial methyl groups (Section IV, Table 13).

Complexes of the type [R$_2$Sn(D)$_4$]$^{2+}$(X$^-$)$_2$ containing an uncharged O-donor ligand D and noncoordinating anion X$^-$, for example with D = DMSO, Et$_2$SO, Ph$_3$PO, Ph$_3$AsO, HCONMe$_2$ and X$^-$ = Ph$_4$B, have been known for a long time 1271. More recently, a number of species with the same and other O-donor ligands including H$_2$O, DMSO, (H$_2$N)$_2$CO and other anions such as deprotonated dimesylamide and benzene-1,2-disulfonimide were reported 909,1271–1273.

An attempt to prepare dinuclear dication of the type [R$_2$Sn(D)$_2$(µ-OH)]$_2^{2+}$ by treatment of the dimeric hydroxide $581a$ with four equivalents of monodentate O-donor ligands resulted in the mononuclear ionic complexes $582a$, $582b$ 1274 and $582c$ 1272 (equation 91).

Some geometrical parameters for selected cases of cationic species of the type [R$_2$SnD$_4$]$^{2+}$ which were characterized by X-ray analysis are given in Table 98. In all cases, complexes containing a C$_2$O$_4$ moiety (entries 1−5) consist of $trans$-octahedral
centrosymmetric \([R_2SnD_4]^{2+}\) cations (583) with a linear \(C-Sn-C\) bond, near-ideal \(cis\)-angles and somewhat short \(Sn-O\) bonds at 2.18–2.24 \(\AA\), as compared with uncharged hexa- and pentacoordinate complexes, such as \(Me_2SnCl_2(PyO)_2\) (2.25 \(\AA\))\(^{958}\) and \(Me_2SnCl_2(LuO)_2\) (2.29 \(\AA\), LuO = lutidine-N-oxide)\(^1^{69}\), as well as with cationic pentacoordinate intermolecular complexes (2.23–2.33 \(\AA\), Section VIII.B.1). In particular, in cation \([Me_2Sn(H_2O)_4]^{2+}\) (entry 1), the \(CSnC\) angles are 178.9° and 180° for two independent cations, and the mean values of the \(Sn-O\) and \(Sn-C\) bond lengths are 2.229 and 2.088 \(\AA\), respectively\(^{1271}\).

\[
\begin{align*}
[Me_2Sn(A)(\mu-OH)]_2 & \xrightarrow{4 \text{ D}} [Me_2Sn(D)_4]^{2+} \cdot 2[(MeSO_2)_2N]^- \\
(581a) \ A^- = (MeSO_2)_2N^- & \quad (582a) \ D = PyO (pyridine-1-oxide) \\
(581b) \ A^- = \text{o-C}_6\text{H}_4(SO_2)_2N^- & \quad (582b) \ D = DMSO \\
& \quad (582c) \ D = (H_2N)_2C=O
\end{align*}
\]

(583) \(R = \text{Me, Ph}; D = \text{O-donor}\)

In the mixed-ligand complex \([Ph_2Sn(NO_3)(DMSO)_3]^{2+}(NO_3)^-\), the tin atom is hexa-coordinated due to the presence of isobidentate \(NO_3\) ligand\(^{1281}\).

A series of cationic diorganotin complexes 584a–c containing 1-methyl-2(3\(H\))-imidazolinethione (Hmimt) as S-donor ligand were recently synthesized and characterized by IR, Raman, Mössbauer as well as \(^1\)H, \(^{13}\)C and \(^{119}\)Sn NMR spectroscopy\(^{1277–1280}\). Crystallographic studies of 584a–c and 584c · \(H_2O\) (entries 12–15) showed that all four cations have a near-octahedral geometry. The tin atoms lie on a crystallographic center of symmetry and are coordinated to two carbon atoms and to the S atoms of the four Hmimt ligands. The nitrate ions are involved in hydrogen bonding with the NH groups of the ligands. The Hmimt ligand, bound via the S atom, maintains its thione form in the complexes.

\[
\begin{align*}
\text{584a} & \quad R = \text{Me} \\
\text{584b} & \quad R = \text{Et} \\
\text{584c} & \quad R = \text{Ph}
\end{align*}
\]
TABLE 98. Selected X-ray data for hexacoordinate cations R₂SnD₂⁺ in cationic diorganotin complexes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound*</th>
<th>C–Sn (Å)b</th>
<th>cis-angles (deg)</th>
<th>D–Sn (Å)b</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Me₂Sn(H₂O)]²⁺+²(A¹)⁻</td>
<td>2.087</td>
<td>90 ± 1.2</td>
<td>2.208, 2.228</td>
<td>1271</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.089</td>
<td>90 ± 1.2</td>
<td>2.222, 2.260</td>
<td>1271</td>
</tr>
<tr>
<td>2</td>
<td>[Me₂Sn(PyO)₂]²⁺+²(A²)⁻</td>
<td>2.216</td>
<td>90 ± 4.4</td>
<td>2.210, 2.232</td>
<td>1274</td>
</tr>
<tr>
<td>3</td>
<td>[Me₂Sn(DMSO)₂]²⁺+²(A¹)⁻ (582a) · MeCN</td>
<td>2.114</td>
<td>90 ± 3.2</td>
<td>2.200, 2.213</td>
<td>909</td>
</tr>
<tr>
<td>4</td>
<td>[Me₂Sn[(Ur)₂]²⁺+²(A²)⁻ (582c) · MeCNc</td>
<td>2.094</td>
<td>90 ± 2.6</td>
<td>2.225, 2.239</td>
<td>1273</td>
</tr>
<tr>
<td>5</td>
<td>[Me₂Sn[(Ur)₂]²⁺+²(A²)⁻ (582b) · 6Ur</td>
<td>2.106</td>
<td>90 ± 3.5</td>
<td>2.206, 2.212</td>
<td>1275</td>
</tr>
<tr>
<td>6</td>
<td>[Me₂Sn(L₁₂)²⁺+²(A²)⁻ (585)</td>
<td>2.109</td>
<td>90 ± 5.2</td>
<td>2.214, 2.216</td>
<td>1275</td>
</tr>
<tr>
<td>7</td>
<td>[Me₂Sn(L₂₂)²⁺+²(A²)⁻ (586)</td>
<td>2.102</td>
<td>90 ± 7.6</td>
<td>2.204, 2.205</td>
<td>1275</td>
</tr>
<tr>
<td>8</td>
<td>586 · Et₂O · MeCN²</td>
<td>2.102</td>
<td>90 ± 7.6</td>
<td>2.204, 2.205</td>
<td>1275</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.183, 2.214</td>
<td></td>
<td>1276</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Me₂Sn(Ph₃PO)₂(A₁₂) (588)</td>
<td>2.080</td>
<td>90 ± 3.0</td>
<td>2.196, 2.274</td>
<td>1276</td>
</tr>
<tr>
<td>10</td>
<td>Me₂Sn(Ph₃PO)₂(A₁₂)</td>
<td>2.093</td>
<td>90 ± 3.3</td>
<td>2.211, 2.274</td>
<td>901</td>
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<tr>
<td>11</td>
<td>[Me₂Sn(Ph₃PO)₂(A₁₂)</td>
<td>2.125</td>
<td>108.4d</td>
<td>2.268c, 2.280;</td>
<td>1251</td>
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<tr>
<td></td>
<td></td>
<td>2.143</td>
<td></td>
<td>2.322, 2.375c</td>
<td>1251</td>
</tr>
<tr>
<td>12</td>
<td>[Me₂Sn(Hmimt)₁₂]²⁺+²(NO₃)⁻ (584a)</td>
<td>2.145</td>
<td>180.0d</td>
<td>2.731, 2.741</td>
<td>1277</td>
</tr>
<tr>
<td>13</td>
<td>[Et₂Sn(Hmimt)₁₂]²⁺+²(NO₃)⁻ (584b)</td>
<td>2.163</td>
<td>180.0d</td>
<td>2.728, 2.752</td>
<td>1278</td>
</tr>
<tr>
<td>14</td>
<td>[Ph₂Sn(Hmimt)₁₂]²⁺+²(NO₃)⁻ (584c)</td>
<td>2.166</td>
<td>174.3d</td>
<td>2.636, 2.643</td>
<td>1279</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.183</td>
<td></td>
<td>2.737, 2.772</td>
<td>1279</td>
</tr>
<tr>
<td>15</td>
<td>584c · 2H₂O</td>
<td>2.164</td>
<td>178.6d</td>
<td>2.677, 2.695</td>
<td>1280</td>
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<tr>
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<td></td>
<td>2.168</td>
<td></td>
<td>2.734, 2.736</td>
<td>1280</td>
</tr>
</tbody>
</table>

*Anions and ligands: (A¹)⁻ = o-C₆H₄(SO₂)₂N₂⁻, (A²)⁻ = (MeSO₂)₂N⁻, L¹ = [CH₂P(O)Ph₂], L² = [CH₂P(O)Ph₂]₂, Hmimt = 1-methyl-2(3H)-imidazolinethione, Phen = 1,10-phenanthroline, PyO = pyridine-1-oxide, Ur = (HN₂)₂CO.

bAverage value.

cTwo independent cations.

dC₅SnC.
eThe longer bond being trans to a Me group.

The ionic dichelates 585 and 586 were recently described. A solvated variety of 586, 586a · Et₂O · MeCN, was unexpectedly isolated by thermal degradation of 586 in MeCN/Et₂O solution. Crystallographic studies showed all three species (Table 98, entries 6–8) to have a moderately distorted octahedral C₂O₄ geometry similar to the related nonchelate complexes discussed above, with the tin atoms lying on crystallographic inversion centers and short Sn–O bonds of 2.18–2.23 Å.

As in equation 91, destructive complexation of the dimeric hydroxide 581b with two equivalents of 1,10-phenanthroline or Ph₃PO produced, along with Me₂SnO and H₂O, the ionic complex 587 and the neutral compound 588. X-ray analysis showed that the cation of 587 (entry 11) has a severely distorted cis-octahedral C₂N₄ coordination arrangement around tin and it represents an example of a dicaticonic dichelate [R₂Sn(L₂)₂]²⁺ in order to adopt a cis structure (C₅SnC 108.4°).

In the uncharged all-trans complex 588 (entry 9), which may be also considered as a zwitterionic species, the heteroligands are O-bonded in a monodentate fashion to Sn that resides on a crystallographic center of inversion [Sn–O(S) 2.274, Sn–O(P) 2.119 Å, cis-angles = 87–93°]. A similar zwitterionic structure was found for Me₂Sn(OPPh₃)₂[N(SO₂Me)₂] (entry 10), where the dimesylamide groups act as...
\[
\begin{align*}
(585) \quad & A^- = (\text{MeSO}_2)\text{N}^- \\
(586) \quad & A^- = (\text{MeSO}_2)\text{N}^- \\
(587) \\
(588)
\end{align*}
\]
monodentate O-ligands, and the tin atom features an all-trans octahedral geometry with Sn–C 2.093, Sn–O(S) 2.274, Sn–O(P) 2.211 Å, cis-angles of 87–93° and SnOP 165.4°.

**B. Intramolecular Complexes**

A family of ionic 1 : 1 or 2 : 1 or complexes was recently prepared by the reaction of RSnCl3 (R = Me, Ph or n-Bu) and SnX4 (X = Cl, Br, or I) with appropriate amounts of potentially tridentate tris(pyrazol-1-yl)methane ligands (Pz = pyrazole), as shown by equations 92a–d. The stoichiometries of the compounds obtained depend strongly on the number and position of the methyl groups on the azole ring of the neutral ligand.

\[
\begin{align*}
\text{HCl}_3 + 2 \text{RSnCl}_3 & \xrightarrow{\text{Et}_2\text{O}} [\text{RSn(HCl}_3\text{)Cl}_2]^+ \cdot \text{RSnCl}_4^- \\
(\text{589}) & L = 3,5\text{-Me}_2\text{Pz}, 3,4,5\text{-Me}_3\text{Pz} \\
R &= \text{Me}, \text{n-Bu}, \text{Ph} \\
\text{HCl}_3 + 2 \text{SnBr}_4 & \xrightarrow{\text{CH}_2\text{Cl}_2} [\text{Sn(HCl}_3\text{)Br}_3]^+ \cdot \text{SnBr}_5^- \\
(\text{590}) & L = 3,4,5\text{-Me}_3\text{Pz} \\
\text{2HCl}_3 + 3 \text{RSnCl}_3 & \xrightarrow{\text{Et}_2\text{O}} [\{\text{RSn(HCl}_3\text{)Cl}_2]^+\}_2 \cdot \text{RSnCl}_5^{2-} \\
(\text{591}) & L = \text{Pz}, 4\text{-MePz} \\
R &= \text{Me}, \text{n-Bu}, \text{Ph} \\
\text{2HCl}_3 + 3 \text{SnX}_4 & \xrightarrow{\text{CH}_2\text{Cl}_2} [\{\text{Sn(HCl}_3\text{)X}_3]^+\}_2 \cdot \text{SnX}_6^{2-} \\
(\text{592}) & X = \text{Cl, Br, I} \\
L &= \text{Pz}, 4\text{-MePz} \\
R &= \text{Me}, \text{n-Bu}, \text{Ph}
\end{align*}
\]

Crystallographic studies of 589a, 590 and 591a showed that all three cations are very similar. The Sn atom has a strongly distorted octahedral environment with the Sn–N bonds in the range 2.22–2.33 Å (the bonds trans to the carbon atoms are slightly shorter than those trans to halides). The Sn–N, Sn–C (2.214 Å in 589a, 2.17 Å in 591a) and Sn–Cl (2.37–2.40 Å) distances are all markedly different from those found in the cation of 580, presumably owing to the lower Lewis acidity of the R2SnCl+ moiety with respect to that of the RSnCl2+ acceptor. The Sn–Br distances are in the range of 2.51–2.52 Å in the cation and 2.48–2.51 Å (equatorial) and about 2.56 Å (axial) in the anion of 590. In the anions, the Sn atoms are five-coordinate (TBP) in MeSnCl4− and SnBr5− and six-coordinate (octahedral) in n-BuSnCl52−.

Hexacoordinate cation [FMeSn(CH2CH2NHMe)2(CH2CH2NMe)N]+BF4− (449) containing tricyclic atrane framework was discussed in Section VII.C.1877.

A new cation–anionic complex of hypercoordinate tin (593) was obtained by treatment of (L5)2SnCl2 (L5 is a bidentate (2-oxopyrrolidino)methyl C,O-chelating ligand) with AgBF41250. As in the case of (L7)2GeCl2 (Section VIII.A), the reaction occurs with replacement of both Cl atoms. As shown by X-ray crystallography, the reaction product, however, has a dimeric distannoxane structure, in which both tin atoms are stannacenium.
ion moieties stabilized by intraionic $O \rightarrow Sn$ coordination bonds. The $BF_4^-$ anions are bound to the dications through $O-H \cdots F$ hydrogen bonds (the $H-F$ distance is 1.78 Å). The octahedral coordination of the Sn atoms is strongly distorted because of a weak additional interaction with the solvate molecules of dioxane (the Sn–O distance is 3.16 Å).
XII. ACKNOWLEDGMENTS

The authors wish to thank all their colleagues who have been involved in the chemistry of hypervalent compounds of germanium, tin and lead and whose names have been cited in the text. We are indebted to Sergei Pogozhikh for calculations of the deviation of the central metal atom from the equatorial plane and to Sergei Artamkin, Tatyana Baukova, Sergei Bylikin, Evgeniya Kramarova, Nikolai Troitski and Aleksei Shumsky for assistance with the preparation of the manuscript. We are also grateful to RFBR for the financial support for a licence to use CCDB (grant No. 99–07-90133).

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CHAPTER 17

Transition metal complexes of germanium, tin and lead

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I. ABBREVIATIONS

A     alkali metal (also alkali earth metal)
Ac    acetyl
Ar    aryl
bipy  bipyridine
Bu    butyl (also used in t-Bu)
Cp    \( \eta^5 \)-cyclopentadienyl
Cp*   \( \eta^5 \)-pentamethylcyclopentadienyl
DMAP  4-(dimethylamino)pyridine
DME   1,2-dimethoxyethane
DMF   \( N,N \)-dimethylformamide
dppe  1,2-bis(diphenylphosphino)ethane
Et    ethyl
Fc    ferrocenyl
Fp    \( \eta^5 \)-cyclopentadienylirondicarbonyl
Fp*   \( \eta^5 \)-pentamethylcyclopentadienylirondicarbonyl
Hex   hexyl
i-    iso
IR    infrared
L     ligand
LAH   lithium aluminum hydride
LDA   lithium diisopropylamide
M     transition-metal
Me    methyl
Mes   Mesityl(2,4,6-trimethylphenyl)
MS    mass spectrum
n     normal
NMR   nuclear magnetic resonance
Np    naphthyl
OTf   triflate
Ph    phenyl
Pr    propyl (also used in i-Pr)
py    pyridine
R     alkyl
s-    secondary
t-    tertiary
Tb    2,4,6-tris[bis(trimethylsilyl)methyl]phenyl
THF   tetrahydrofuran
Tip   2,4,6-triisopropylphenyl
tmtaa dibenzotetraaza[14]annulene
Tol   tolyl
Triphos PhP(CH\(_2\)CH\(_2\)PPh\(_2\))\(_2\)
UV    ultraviolet
X     halogen

II. INTRODUCTION

Although transition metal germanium\(^1\), tin\(^2\) and lead\(^3\) complexes have been known for a considerable period of time compared to the area of transition metal–silicon chemistry, studies on these systems are less developed. There are a variety of reviews, or
sections of larger reviews, concerning various aspects of Ge$^{4,5,b,c}$, Sn$^5$ and Pb$^{4b,c,5b,c,6}$ transition metal chemistry. It is the purpose of this review to concentrate upon the synthesis and reactivity of Ge−, Sn− and Pb−transition metal complexes. In the case of Sn, we have emphasized the more recent studies, post 1990, except in those topics not covered in the previous reviews. The review is organized in terms of the different synthetic approaches to the metal–E bond (E = Ge, Sn or Pb) followed by selected areas of reactivity for each group 14 element in sequence. We present a limited set of structural and spectroscopic data.

### III. ORGANOGERMANIUM TRANSITION METAL COMPLEXES

#### A. Synthesis of Transition Metal Germanium Single Bond

There is a range of synthetic techniques available for the preparation of such bonds and these are discussed sequentially. In Tables 1–4 we present representative examples of complexes containing metal germanium single bonds: monometallic complexes (Table 1), bimetallic complexes (Table 2), monometallic digermyl, germylsilyl and germylstannyl complexes (Table 3) and bridging germylene bimetallic complexes (Table 4). Similar examples of complexes containing metal–germanium double and triple bonds are presented in Tables 5 and 6, respectively, and selected structural parameters are recorded in Tables 7, 8 and 9. Tables 1–9 appear at the end of this section.

1. Synthesis from transition metal anions and germyl halides

The first transition metal germanium complexes were synthesized by this route from metal carbonylates and triphenylbromo germane and since then, a large number of germyl, oligogermyl/silyl and germole complexes with a range of metals, Cr$^7,8$, Mn$^{1,8–11}$, Fe$^{1,8,9,12–21}$, Co$^{8,9,19,22–25}$, Ni$^{26,27}$, Mo$^{7,8,28–30}$, Rh$^{31,32}$, W$^{7,12,17,28,30}$, Re$^{33–35}$ and Os$^{36,37}$, have been synthesized using this approach. The reactions are usually performed in THF or related ethereal solvents and the products are obtained in good yield. Representative reactions are shown in equations 1–3.

$$\begin{align*}
\text{THF} & \text{M}^{-} \text{Na}^{+} + \text{ClGeR}_3 & \overset{\text{THF}}{\rightarrow} & \text{M}^{\text{GeR}_3} + \text{NaCl} & \quad (1) \\
& (\text{M} = \text{Mo, W}) & & (R = \text{Me, Et, Pr, Ph}) \\
\text{THF} & \text{Re}^{-} \text{Li}^{+} + \text{Cl}_2\text{GePh}_2 & \overset{\text{THF}}{\rightarrow} & \text{Re}^{\text{GePh}_2\text{Cl}} + \text{LiCl} & \quad (2) \\
& & & (1,9) \\
\text{Ge} & \text{Br} + \text{Na} [\text{ML}_n] & \rightarrow & \text{ML}_n^+ & \quad (3)
\end{align*}$$

$\text{ML}_n = \text{Co(CO)}_4, \text{Mn(CO)}_5\text{Fp}$
Functional groups on germanium, including hydrides, can be introduced via the reactivity of the labile Ge−Cl bonds\textsuperscript{17,33}, vide infra.

2. Synthesis from transition metal halides and germyl anions

Germyl metallocene derivatives of the early transition metals, Ti, Zr and Hf (M) have been synthesized by the combination of metallocene halides and germyl anions (equations 4 and 5)\textsuperscript{38−40}. The cyclopentadienyl complexes Cp\textsubscript{2}M(GePh\textsubscript{3})Cl\textsuperscript{39} are difficult to purify due to their instability in solution; however, use of the pentamethylcyclopentadienyl group (Cp\textsuperscript{*}) enhances both the solubility and stability of these complexes\textsuperscript{40,41}.

\[
\text{Cp}_2M \text{Cl} + \text{LiGePh}_3 \rightarrow \text{Cp}_2M\text{GePh}_3 + \text{LiCl} \quad (M = \text{Ti, Zr, Hf})
\]

(4)

\[
\text{Cp}_2M \text{Cl} + \text{LiGe(SiMe}_3)_3 \rightarrow \text{Cp}_2M\text{Ge(SiMe}_3)_3 + \text{LiCl} \quad (M = \text{Zr, Hf})
\]

(5)

Group 10 and 11 transition metal germanium complexes are formed by the same general route (equations 6−8)\textsuperscript{42−48}. Treatment of cis-(Et\textsubscript{3}P)\textsubscript{2}PtCl\textsubscript{2} with one equivalent of bis(trimethylgermyl)mercury resulted in the replacement of one chlorine atom selectively with the inversion of configuration and resulted in the formation of a trans-(Et\textsubscript{3}P)\textsubscript{2}PtCl(GeMe\textsubscript{3}) complex\textsuperscript{44,45}.

\[
\text{trans-}(\text{Et}_3\text{P})_2\text{MCl}_2 + 2\text{LiGePh}_3 \rightarrow \text{trans-}(\text{Et}_3\text{P})_2\text{M}(\text{GePh}_3)_2 + \text{LiCl} \quad (M = \text{Pd, Pt})
\]

(6)

\[
\text{cis-}(\text{Et}_3\text{P})_2\text{PtCl}_2 + (\text{Me}_3\text{Ge})_2\text{Hg} \rightarrow \text{trans-}(\text{Et}_3\text{P})_2\text{Pt}(\text{GeMe}_3)_2\text{Cl} + \text{HgCl}_2 \quad (M = \text{Pd, Pt})
\]

(7)

3. Anionic germyl metal carbonyl complexes

The anionic complexes of Cr, Mo and W were synthesized by the photochemical displacement of CO from M(CO\textsubscript{6}) by the [GeCl\textsubscript{3}]\textsuperscript{−} anion. The resulting anions were stabilized as tetraphenylarsonium salts, [Ph\textsubscript{4}As]\textsuperscript{+}[M(CO\textsubscript{5}GeCl\textsubscript{3})]\textsuperscript{−}\textsuperscript{49,50} and were also prepared by a reaction of Ph\textsubscript{3}GeLi with [M(CO\textsubscript{5}Cl)]\textsuperscript{−}\textsuperscript{51,52}. Anionic diastereomers of Mo and W were obtained from a similar reaction of an optically active germyl lithium MePh(1-naphthyl)GeLi with [(η\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5})M(CO\textsubscript{2}NO)] (M = Mo, W) by the displacement of CO\textsuperscript{53}.

Phosphonium salts of anionic trihydridogermyl metal carbonyl complexes for V, Nb, Cr, Mo, W, Mn, Re, Co and Ni have been synthesized by substitution of carbonyl group with trihydrido germane, −GeH\textsubscript{3}\textsuperscript{54−56} (equation 9). Hydridogermyl metal complexes are the precursors for metal germynes and polynuclear metal germyl complexes\textsuperscript{57,58}.

\[
\text{CpM(CO)}_n + \text{K}^+[\text{GeH}_3]^- \xrightarrow{\text{Ph}_3\text{P}^+\text{Br}^-} [\text{Ph}_4\text{P}]^+[\text{CpM(CO)}_{n-1}\text{GeH}_3]^- \quad (9)
\]

4. Oxidative addition of germyl compounds to metal centers: germyl hydrides, Ge−H

Germyl hydrides readily undergo oxidative addition to the low-valent coordinatively unsaturated transition-metal complexes. Optically active [Co(CO\textsubscript{4})GeMe(1−Np)Ph] was
synthesized with retention of configuration at the asymmetric center from cobalt carbonyl and optically active germane\textsuperscript{59,60}. Germanium derivatives of Mn, Co, Fe, Ru, Os and Pt have been synthesized as illustrated in equation \textsuperscript{10}\textsuperscript{59–72}.

\[
\text{M}_2(\text{CO})_{2n} + 2\text{R}_3\text{Ge} - \text{H} \longrightarrow 2\text{R}_3\text{GeM}(\text{CO})_n + \text{H}_2 \quad (10)
\]

\[\text{M} = \text{Mn}(n = 5), \text{Co}(n = 4); \text{R} = \text{Me}, \text{Ph}, \text{CF}_3\]

The photochemical reaction of bis(hydridodimethylgermyl)methane/ethane, HMe\textsubscript{2}Ge(CH\textsubscript{2})\textsubscript{n}GeMe\textsubscript{2}H (n = 1, 2) with metal carbonyls of Fe, Co and Ru in pentane yielded a series of cyclic derivatives \textsuperscript{1} and \textsuperscript{2}\textsuperscript{73–79}.

\[
\begin{align*}
\text{(CH}_2)_n & \quad \text{Me}_2\text{Ge} \\
\text{M(CO)}_4 & \quad \text{GeMe}_2 \\
\text{(M = Fe, Ru)} \\
\text{(1)}
\end{align*}
\]

\[
\begin{align*}
\text{(CH}_2)_n & \quad \text{Me}_2\text{Ge} \\
\text{GeMe}_2 & \quad \text{(CO)}_3\text{Co} \\
\text{Co(CO)}_3 & \quad \text{CO} \\
\text{(2)}
\end{align*}
\]

Hydrogermoles, like the corresponding hydrosiloles, coordinate oxidatively to the metal centers in the \(\eta^1\) mode via the group 14 element and these complexes can act as catalysts for hydrogermylation reactions. An interesting reaction has been described between dicobaltoctacarbonyl and hydrogermole to afford \textsuperscript{3}, in which the germacyclopentenyl is coordinated to two cobalt carbonyl fragments in \(\eta^1\) mode as well as in rare allylic \(\eta^3\) mode (equation \textsuperscript{11})\textsuperscript{80}. Oxidative addition compounds \textsuperscript{4} and \textsuperscript{5} were obtained from the photolysis of M(CO\textsubscript{2})(PPh\textsubscript{3})\textsubscript{2} (M = Ru, Os) with tris(p-toly兴germane) in benzene in good yield (equation \textsuperscript{12}). The geometry around Os in \textsuperscript{5} is highly distorted and two carbonyl groups are \textit{trans} to each other\textsuperscript{61}.

\[
\begin{align*}
\text{Co}_2(\text{CO})_8 & + \\
\text{CH}_2=\text{CHCHCH}_2-\text{CH}=\text{CHMe} & \quad \rightarrow \text{Co}(\text{CO})_4 \quad \text{Ge} \quad \text{Ph} \\
\text{H} & \quad \text{Co}(\text{CO})_3 \\
\text{(3)}
\end{align*}
\]

\[
\begin{align*}
\text{M(CO)}_2(\text{PPh}_3)_2 + \text{H-Ge(Tol-p)}_3 & \quad \rightarrow \\
\text{Ph}_3\text{P} & \quad \text{M} \quad \text{Ge(Tol-p)}_3 \\
\text{CO} & \quad \text{Ph}_3\text{P} \\
\text{(4) M = Ru} \\
\text{(5) M = Os}
\end{align*}
\]

Fluxional trihydridogermyl complexes of osmium OsH\textsubscript{3}(GeR\textsubscript{3})(CO)(P(Pr-i))\textsubscript{3} have been synthesized by the addition of R\textsubscript{3}GeH to the dihydrido-olefin Os complex OsH\textsubscript{2}(\(\eta^2\)-C\textsubscript{5}H\textsubscript{5})CH\textsubscript{2}=(CH=CH\text{Et})(CO)(P(Pr-i))\textsubscript{3} with the elimination of olefin\textsuperscript{67}. The oxidative addition of R\textsubscript{3}GeH to (\(\eta^5\)-C\textsubscript{5}H\textsubscript{5})OsCl(P(Pr-i))\textsubscript{3} affords a series of Os(IV) derivatives (\(\eta^5\)-C\textsubscript{5}H\textsubscript{5})OsH(GeR\textsubscript{3})(P(Pr-i))\textsubscript{3} with the displacement of one phosphine ligand\textsuperscript{68}. 
The thermal reaction of trans-(PhMe₂P)₂PtHCl with triphenyl germane afforded the trans complex 6 which, on reaction with 2 equivalents of MeLi followed by methanolysis, afforded selectively only the cis-Pt complex 7 (equation 13). The reaction is believed to occur through a platinate intermediate, Li⁺[PtMe₂(GePh₃)(PMe₂Ph)]−, that was characterized spectroscopically.63

\[
\text{trans-(PhMe₂P)₂PtHCl + HGePh₃ } \rightarrow \text{cis-Pt complex 7 (equation 13)}
\]

5. Oxidative addition of germyl-germanes, -silanes and -halides

The oxidative addition of the Ge–Cl bond was reported in square-planar \(d^8\) Pt(II) complexes [PtMe₂(N–N)](N–N = bipyridine, phenanthroline). The additions afforded a series of compounds [PtMe₂Cl(Ge₃Cl₃−n)(N–N)](R = Me, Ph, n = 1, 2, 3)\(^8\). Stereoselective addition of Me₂GeCl₂ to Pt(Pé₃)₃ resulted in the formation of \(\text{trans-(ClMe₂Ge)PtCl(Pé₃)}\)\(^2\). Similarly, 1,2-dichlorotetramethyldigermane, ClMe₂Ge–GeMe₂Cl, adds oxidatively to Pt(PR₃)₃(\(R = \text{Et, Ph}\)) in benzene at room temperature to produce high yields of isomeric mixture of (ClMe₂Ge)₂Pt(PR₃)₂, without the cleavage of Ge–Cl and Ge–C bonds (equation 14)\(^8\).83

\[
\text{Pt(Pé₃)₃ + ClMe₂Ge–GeMe₂Cl } \rightarrow \text{cis/trans-(ClMe₂Ge)₂Pt(Pé₃)₂ (equation 14)}
\]

The addition of the Ge–Ge bond in a strained digermacyclopropane to Pd(PPh₃)₄ is also reported\(^8\). The Si–Ge bonds of 2,2-bis(organosilylgermyl)dithiane 8 undergo facile addition across the Pd⁰ and Pt⁰ complexes.85 The reaction of dithiane 8 with PdL₂ produced a four-membered square-planar bis(germyl) Pd complex 9 with the elimination of disilane, whereas an analogous reaction of dithiane 8 with a platinum–isonitrile complex resulted in the formation of a mixture of octahedral bis(germyl)bis(silyl) platinum 10 along with a tetrakis(germyl) Pt(IV) complex 11 in a low yield (equation 15).
A variety of metal carbonyls, $ML(CO)_n$, $M = Fe, Co, Mo$ and their derivatives undergo oxidative addition of Ge–Cl bonds subsequent to CO elimination (equation 16)\(^{22,86-93}\).

$$LM(CO)_n + GeX_4 \rightarrow (CO)_{n-1}LMGeX_3 + CO$$

(16)

M = Fe, $n = 5$; M = Co, L = Cp, $n = 2$;
M = Mo or W, L = bipy; $n = 4$

Reaction at a higher temperature leads to the formation of bis(germyl)metal carbonyls that exist as a mixture of two isomers (equation 17)\(^{87,88}\). The latter complexes were also synthesized directly by an exchange reaction between Na$_2$Fe(CO)$_4$ and R$_3$GeCl\(^{19}\).

$$2(CO)_4FeGeX_3 + high temp GeX_3(CO)_4FeGeX_3 + FeX_2 + 4 CO$$

(17)


Treatment of Mo(II)\(^{94-96}\), W(II)\(^{94-96}\) and Au(I)\(^{97,98}\) complexes with one equivalent of GeCl$_2$·dioxane, in CH$_2$Cl$_2$ at $-78\,^\circ C$ and subsequent warming to room temperature, resulted in rapid and clean insertion of germynes into the metal–hydrogen or metal–chlorine bond\(^{94-98}\). This is a convenient route to synthesize functionalized transition-metal germanium compounds\(^{99,100}\). The reaction is exemplified in equations 18 and 19.

$$GeCl_2\cdot dioxane + (Ph_3P)AuCl \rightarrow (Ph_3P)AuGeCl_3$$

(18)

$$GeCl_2\cdot dioxane + MOC CO CO RMOC CO CO GeCl_2R$$

(19)

Insertion of highly reactive group 14 carbene analogs into metal–metal bonds is a step toward cluster building and germynes readily insert into the Fe–Fe bond of [CpFe(CO)$_2$]$_2$ under mild conditions (equation 20)\(^{101}\).

7. Elimination reactions using germyl hydrides

Germyl copper compounds, obtained in a very low yield by the salt-elimination method\(^{42}\), can be obtained efficiently from the reaction of germyl hydrides with alkoxy...
copper compounds. The reaction involves elimination of the appropriate alcohol and is performed in DME in the presence of a phosphine (equation 21). Similarly, elimination of methane drives the reaction of Ph₃GeH with dimethyltitanocene resulting in the quantitative formation of 12 (equation 22).

\[ t\text{-BuOCu} + R_3GeH + 2 \text{PPh}_3 \rightarrow R_3GeCu(\text{PPh}_3)_2 + t\text{-BuOH} \]  
(21)

\[ \text{CH}_3\text{TiCH}_3\text{GePh}_3\text{TiCH}_3 \rightarrow \text{Ph}_3\text{GeH} + \text{CH}_4 \]  
(22)

The V–Ge bond has also been synthesized by an analogous reaction.

8. Miscellaneous reactions

Mixed germyl/silyl tungsten complexes Cp₂W(GeR₃)(SiMe₃) have been synthesized by the addition of germanes R₃GeH (R₃Ge = GeMe₃, GeMe₂H, Ge(t-Bu)₂H, GePh₂H) to the tungsten silene complex Cp₂W(η²-SiMe₂=CH₂) (equation 23).

\[ \text{Cp}_2\text{W}_2\text{GeR}_2\text{SiMe}_3 \rightarrow \text{Cp}_2\text{W}_2\text{GeMe}_2\text{Ph} \]  
(25)

Two unusual and complex reactions leading to the formation of a metal germanium bond involve the photochemical treatment of germylsilyl and germylsilylmethyl complexes (equations 24, 25 and 25a).
The reaction illustrated in equation 24 involves a series of 1,3-alkyl, silyl and germyl migrations between the metal–silylene and germylene transients formed subsequent to an \( \alpha \)-elimination reaction initiated by the elimination of CO\textsuperscript{109}.

Metal–germene transients are involved after a \( \beta \)-elimination in the chemistry shown in equation 25. The chemistry of equation 25a is a rare example of the direct \( \beta \)-elimination of a silene to result in the germanium–metal bond formation\textsuperscript{108}.

Another example of an unprecedented synthesis of the Fe–Ge bond involves the thermolysis of the complexes (Me\(_2\)GeGeMe\(_2\))\([\eta^5\text{-C}_5\text{R}_4]\)Fe(CO))\(_2\)(\(\mu\)-CO)\(_2\)(R = H, Me) in xylene leading to the high yield formation of the rearranged cyclic complexes containing Fe–Ge bonds, [Me\(_2\)Ge(\(\eta^5\text{-C}_5\text{R}_4\))Fe(CO)]\(_2\)\textsuperscript{110}.

9. Digermene complexes

The platinum \( \eta^2 \)-digermene complex (Ph\(_3\)P)\(_2\)Pt(\( \eta^2 \)-GeMe\(_2\)GeMe\(_2\)) was obtained by the elimination of ethylene and H\(_2\) from the oxidative addition of tetramethyldigermane HMe\(_2\)GeGeMe\(_2\)H to (Ph\(_3\)P)\(_2\)Pt C\(_2\)H\(_4\) (equation 26)\textsuperscript{111}.

\[
\text{L}_2\text{Pt(C}_2\text{H}_4) + \text{HMe}_2\text{GeGeMe}_2\text{H} \rightarrow \text{L}_2\text{Pt}\left(\begin{array}{c}
\text{GeMe}_2 \\
\text{GeMe}_2
\end{array}\right) + \text{C}_2\text{H}_4 + \text{H}_2
\]

\( (L = \text{PPh}_3, \text{dppe}) \) \hspace{1cm} (26)

B. Synthesis of Bimetallic Bridging Germylene Complexes, LMGeR\(_2\)ML

Data on these compounds are collected in Tables 2, 4 and 8.

1. Complexes with a metal metal bond

The reactions of di- and trihydridogermanes with a range of metal complexes is an attractive route to bimetallic bridging germylene complexes. The triply-bridged germylene iron complex \textbf{13}, containing a metal metal bond, was obtained from the reaction of Me\(_2\)GeH\(_2\) with Fe\(_2\)(CO)\(_9\)\textsuperscript{69,91}, whereas an analogous reaction of Ph\(_2\)GeH\(_2\) with Fe\(_2\)(CO)\(_9\) yielded a yellow crystalline bis(\(\mu\)-germylene)(\(\mu\)-carbonyl) iron complex \textbf{14} (equation 27)\textsuperscript{19,112}.
Similarly, the reaction of Co$_2$(CO)$_8$ with diphenylgermane, Ph$_2$GeH$_2$, gave [Co(CO)$_3$]$_2$(µ-GePh$_2$)(µ-CO) in good yield$^{66}$; no bis(µ-germylene) Co complex was obtained. The use of phenyltrihydridogermane produces $^{15,113}$, and the methylgermane analog $^{16}$ undergoes reversible decarbonylation to the closed cluster Co$_3$(µ$_3$-GeMe)(CO)$_9$ $^{17}$ (equation 28)$^{23,114,115}$. This cluster undergoes addition or substitution reactions with phosphines/arines or metal carbonyls (Mo, W) to produce mixed metal clusters.$^{115}$ A wide variety of such cluster compounds has been reported from the reactions of cobalt carbonyls and monogermanes GeH$_4$, Me$_2$GeH$_2$ and MeGeH$_3$ or digermanes, Ge$_2$H$_6$ or Me$_3$GeGeH$_3$ in different stoichiometry involving extensive rupture of Ge−H, Ge−Ge and Ge−C bonds$^{116–121}$.

![Diagram](image-url)

An interesting series of bridging germylene complexes of Ru and Os, $^{18}$ and $^{19}$, were obtained from the thermolysis of Me$_3$GeH and M$_3$(CO)$_{12}$ (M = Ru, Os) involving cleavage of Ge−C bonds, along with bis-germyl complexes $^{20}$ and $^{21}$ (equation 29). Thermolysis of $^{20}$ or $^{21}$ yielded a mixture of trinuclear metal clusters $^{22}$ and $^{23}$ together with low yields of the binuclear $^{24}$ and $^{25}$ (equation 30)$^{64}$. Low yields of $^{23}$ and $^{25}$ were also obtained from the thermolysis or photolysis of a binuclear bis(µ-germylene) osmium carbonyl complex [OC$_4$Os(GeMe$_2$)]$_2$ in hexane at 100°C and were structurally characterized$^{36}$. The structure of $^{25}$ is similar to that of the iron analog$^{69,91}$. Related trinuclear clusters of Pd and Pt, [M(µ$_3$-Ge(NBu-t)$_2$(CO))$_3$ (M = Pd or Pt)$^{122}$, containing bridging amidogermylenes were obtained from the reaction of metal germynes [M(Ge(NBu-t)$_2$)$_3$] with CO$^{123}$.

![Diagram](image-url)
The photolysis of FpSiMe$_3$ or Fp*SiMe$_3$ in the presence of di- or trihydridogermanes is another attractive route for the synthesis of germylene bridged binuclear iron complexes. The reaction proceeds via initial loss of CO followed by oxidative addition of the germane and results in the formation of the (µ-germylene)(µ-carbonyl) diiron complex 26 and bis(µ-germylene) diiron complex 27 (equation 31)\textsuperscript{124–127}. These bridged complexes exist as the mixture of geometrical isomers in solution which can undergo either thermal or photochemical interconversion. Complexes 28 and 29 were obtained from the photolysis of Fp*SiMe$_3$ in the presence of trihydrido germanes, RGeH$_3$ (R = t-Bu, p-Tol). These diiron Fe⋯H⋯Ge 3-center 2-electron complexes are rare\textsuperscript{128}. Presumably, they are intermediates in the formation of bis(µ-germylene) diiron complexes 27 via H$_2$ expulsion\textsuperscript{124,126}.

\begin{equation}
\text{R}_5\text{FeSiMe}_3\text{OCOCGeFe} + \text{R'RGeH}_2 \xrightarrow{hv} \text{R}_5\text{FeSiMe}_3\text{OCOCGeFe}_{\pm} + \text{R}_5\text{FeSiMe}_3\text{OCOCGeFe}_{\mp}
\end{equation}

\begin{align*}
(26) & \text{R = t-Bu, R' = H} \\
(27) & \text{R = R' = p-Tol} \\
(28) & \text{R = t-Bu} \\
(29) & \text{R = p-Tol}
\end{align*}

2. Complexes without a metal metal bond

Bis(µ-germyl)iron carbonyl complexes without a metal–metal bond were synthesized by the reaction of Fe(CO)$_5$ with germanium tetrahalides and later by an alternate route involving high temperature reaction of Fe(CO)$_5$ with a bis(halogermyl)iron carbonyl complex. Ferrous chloride is a byproduct of these reactions (equation 32)\textsuperscript{86–89}.

\begin{equation}
4 \text{Fe(CO)}_5 + \text{2GeX}_4 \rightarrow \text{(CO)}_4\text{FeGeX}_3 + \text{2Fe(CO)}_5
\end{equation}
Hydrido(methyl)germyl iron complexes undergo elimination of methylgermanes to form four-membered cyclic $\text{Fe}_2\text{Ge}_2$ systems (equation 33)\textsuperscript{129–131}. The tendency for such condensation is directly related to the number of methyl groups on the germanium. The binuclear diiron complex undergoes intramolecular elimination of methylgermane to form a four-membered heterocycle illustrating that the cleavage of Ge—C and Ge—H bonds occurs under mild conditions.

\[
\begin{align*}
\text{(OC)}_4\text{Fe} & \quad \text{GeR}_2\text{H} \\
& \quad \text{GeR}_2\text{H} \\
& \quad -\text{GeR}_2\text{H}_2 \\
\end{align*}
\]

C. Synthesis of Transition Metal Germanium Double Bond Germylene Complexes

Data on these compounds are collected in Table 5.

The early development of transition-metal germylene chemistry is summarized in earlier reviews\textsuperscript{4b–d}. Therefore we summarize the transition-metal germylene chemistry developed after 1990. Such complexes can be divided into seven different types (I–VII) depending upon the nature of bonding between the metal and germanium atom:

1. Base-free metal germylene complexes

The reaction of kinetically stabilized germylenes with metal complexes has proven a useful and not surprising route to complexes containing a metal–germanium double bond. Thus, the reaction of germylenes containing bulky aryl groups with the metal carbonyls
of Fe, Cr and W in THF at room temperature provided the first examples of base-free germyleane complexes of these metals (equation 34)\textsuperscript{132–134}.

\[
\begin{align*}
\text{Ar} & \quad \text{Ge} ; \\
\text{M(CO)}_5/\text{THF} & \quad \xrightarrow{\text{Ar'}} \\
\text{Ar} & \quad \text{Ge} = \text{M(CO)}_5
\end{align*}
\]

Ar = Tb, Ar' = Tip, M = Cr, W
Tb = 2,4,6-tris[bis(trimethylsily1) methyl]phenyl
Tip = 2,4,6-trisopropylphenyl
Ar = Ar' = (2,4,6-tri-t-butylphenyl)seleno, M = W

The internally stabilized silylamide germyleane: Ge[N(SiMe\textsubscript{3})\textsubscript{2}]\textsuperscript{135} reacts with Ni and Pt phosphine complexes yielding Ni\textsuperscript{136} and Pt–germylene complexes (equation 35)\textsuperscript{137–139}.

\[
\begin{align*}
\text{Et}_3\text{P} & \quad \text{Pt(C}_2\text{O}_4) \quad + \quad \text{Ge}[\text{N(SiMe}_3\text{)}\textsubscript{2}] & \quad \xrightarrow{\text{benzene, -2CO}_2} & \quad \text{Et}_3\text{P} \\
\text{C}_2\text{O}_4 & \quad \text{oxalate}
\end{align*}
\]

A stable germyleane containing tetraaza macrocycle, i.e. dibenzotetraaza[14]annulene (tmtaa), and a variety of cyclic germyleanes (such as 30) readily act as two electron donors to form a variety of metal complexes\textsuperscript{101,140–144}.

\[
\begin{align*}
\text{N} & \quad \text{Ge} \quad \text{SiMe}_2 \\
\text{N} & \quad \text{t-Bu} \\
\text{N} & \quad \text{t-Bu}
\end{align*}
\]

Since 30 and related germyleanes have both a filled \(\sigma\)-donor orbital and a low-lying vacant \(\pi\)-orbital, they can act as \(\sigma\)-donor and/or \(\pi\)-acceptor ligands\textsuperscript{101}, and are the building blocks for the formation of unusual, and unpredictable, trimetallic or tetrametallic clusters. For example, the reaction of nickelocene with 30 resulted in the formation of 31, an unprecedented complex in which the two Cp ligands are bound differently and involve the rupture of \(\eta^5\)-bonding between Cp and Ni (equation 36). The two Ge atoms are also in different environments: one is trigonal planar with a short Ge–Ni double bond (2.085(3) Å) while the other is four-coordinated with tetrahedral geometry around Ge and a significantly longer bond between Ni and Ge [2.258(3) Å]\textsuperscript{143}.

\[
\begin{align*}
\text{Ni} + 30 & \quad \xrightarrow{\text{toluene, 80 °C}} \quad \text{Me}_2\text{Si} \\
\text{Me}_2\text{Si} & \quad \text{Ni} \quad \text{Ge} \\
\text{Ge} & \quad \text{Ni} \\
\text{SiMe}_2 & \quad \text{Ge} \\
\text{N} & \quad \text{t-Bu} \\
\text{N} & \quad \text{t-Bu}
\end{align*}
\]
A related cluster \(32\) is obtained from the reaction of \(30\) with \(\text{RhCl}((\text{PPh}_3)_3\). The central Rh has a square-planar arrangement of the four germanium atoms, with two short Rh–Ge bonds [average Rh–Ge bond length 2.337(1) \(\text{Å}\)] having multiple character and the other two Ge atoms [average Rh–Ge bond length (2.373 (2) \(\text{Å}\)] being tetracoordinate bridged by the chlorine atom\(^{142}\).

\[
\text{Ge} \quad \text{Rh} \quad \text{Ge} \\
\text{GeGe} \\
N \\
\text{SiMe}_2
\]

The Pt–Fe heterobimetallic complex \(33\) reacts reversibly with \(30\) to form \(34\), containing both terminal and bridging germylene ligands (equation \(37\))\(^{144}\).

\[
\begin{align*}
\text{Ph}_2\text{P} & \quad \text{PPh}_2 \\
\text{Ph}_3\text{P} & \quad \text{Pt} \quad \text{Fe} \\
& \quad \text{Ge} \quad \text{NBu-t} \\
& \quad \text{t-BuN} \quad \text{SiMe}_2
\end{align*}
\quad \xrightarrow{30 + \text{PPh}_3} 
\begin{align*}
\text{Ph}_2\text{P} & \quad \text{PPh}_2 \\
\text{Ph}_3\text{P} & \quad \text{Pt} \quad \text{Fe} \\
& \quad \text{Ge} \quad \text{NBu-t} \\
& \quad \text{t-BuN} \quad \text{SiMe}_2
\end{align*}
\]

(33) (34) (37)

An interesting (\(\mu\)-germylene)manganese complex \(\left[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}((\text{CO})_2\right]_{2}(\mu\text{-GeCl}_2)\) \(35\) was obtained directly from the treatment of \(\left[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}((\text{CO})_2\right] \cdot \text{THF} \) with \(\text{GeCl}_2 \cdot \text{dioxane}\) in a molar ratio of 2 : 1 in THF (equation \(37a\))\(^{145}\). Complex \(35\) undergoes reductive dehalogenation by zinc dust in the presence of \(\left[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}((\text{CO})_2\right] \cdot \text{THF}\) to give a trinuclear germylene complex \(36\) previously synthesized by the photochemical treatment of \(\left[(\eta^5\text{-C}_5\text{H}_5)((\text{CO})_2\right]_{2}\text{Mn}={\text{Ge}}={\text{Mn}((\text{CO})_2)}(\eta^5\text{-C}_5\text{H}_5)\) in the presence of another molecule of \(\left[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}((\text{CO})_2\right] \cdot \text{THF}\)\(^{57,58}\).

Base-free alkyl-substituted germyl(germylene)tungsten carbonyl complexes \(37\) and \(38\) were synthesized by the photolysis of digermyl complexes of tungsten \(39\) and \(40\) in benzene (equation \(38\)). These complexes are formed by the 1,2-germyl migrations after the initial photodissociation of CO from \(39\) and \(40\)\(^{146}\).
2. Cationic germylene complexes

Cationic germylene complexes are scarce and mononuclear cationic germylene complexes seem limited to only three examples. The cationic iron–germylene complexes 41 and 42 were synthesized by the abstraction of chloride from chlorogermyliron complexes 43 and 44 using a halogen abstracting agent in the presence of a donor molecule (equation 39)\(^{147a}\). A related rhenium complex, 45, was obtained from the exchange reaction of 46 with Me\(_3\)SiOTf (equation 40)\(^{33}\). The X-ray structure of 45 attributes a considerable ionic character to the germanium–triflate bond and double bond character to the germanium–rhenium bond. A variable-temperature-type NMR spectrum indicated that the diastereotopic phenyl groups in 45 coalesce at 268 K and suggest that it is in equilibrium with the cationic rhenium germylene complex 47.

\[ \text{R}_5 = \text{Me}_5 \]  
\[ \text{R}_5 = \text{Me}_4\text{Et} \]
A binuclear donor-stabilized cationic bridged germylene diiron complex \([\text{Cp}_2\text{Fe}_2(\text{CO})_3(\mu-\text{GeBu-t} \cdot \text{DMAP})]^+\text{OTf}^-, \) \(48\), of class VI was obtained from the exchange of an iodine atom on \(\mu\)-germylene bridge \(49\) by silver triflate in the presence of a strong base, 4-dimethylaminopyridine in acetonitrile (equation 41)\(^{147}\). The germanium atom of the \(\mu\)-germylene bridge is pyramidalized due to the coordination of the lone pair of the base. The Fe–Ge bond length of 2.322(2) Å is shorter than those for neutral germylene bridged diiron complexes, indicating a considerable double bond character in the iron–germanium bond.

Thermolysis of \([\text{Cp}_2\text{W}((\text{SiMe}_3))(\text{GeMe}_2\text{OTf})]\) \((50)\) in solution and in the solid state resulted in the formation of a binuclear cationic bridging germylene complex \(51\), type V (equation 42). Structural analysis shows two types of Cp rings and Ge atoms. One of the Ge atoms is tetracoordinated, with a long W–Ge bond [2.583(2) Å] comparable to the W–Ge single bonds. The other planar three-coordinate germanium has a short W–Ge bond of 2.487(2) Å, which suggests that the positive charge at the germanium atom is delocalized by back-bonding to the tungsten atom\(^{148}\).

3. Base-stabilized germylene complexes

As expected, base-free tungsten germylene complex \(37\) reacts with pyridine to afford the base-coordinated tungsten complex \(52\), \(\text{Cp'}\text{W}(\text{CO})_2(=\text{GeMe}_2 \cdot \text{py})(\text{GeMe}_3)\)\(^{146}\). The tungsten–germylene bond of 2.5279(6)Å in \(52\) is significantly longer than the tungsten–germylene bond of 2.4590(16)Å in \(37\).
The base-stabilized diiron germyl analog of allene 53, of class VII, was obtained from treatment of \([\text{Fe}(\text{CO})_4(\mu-\text{GeBr}_2)]_2\) with a pyridine–diethyl ether solution of \(\text{Na}_2\text{Fe}(\text{CO})_4\). The acute \(\text{N}−\text{Ge}−\text{N}\) bond angle of 89°, short \(\text{Fe}−\text{Ge}\) bonds (average 2.35 Å) and widening of the \(\text{Fe}−\text{Ge}−\text{Fe}\) angle to 131° demonstrate the multiple bonding between \(\text{Fe}\) and \(\text{Ge}\) in 53\(^\text{149}\).

\[
\text{py} \quad \text{py} \\
\begin{array}{c}
\text{(CO)}_4\text{Fe} \\
\downarrow \\
\text{Ge} \\
\downarrow \\
\text{Fe} \quad \text{(CO)}_4
\end{array}
\]

(53)

Intramolecularly alkoxy base-stabilized bis(germylene)-, 54, or (germylene)(silylene)-, 55, iron complexes, of type IV, were obtained from the photolysis of digermyl or germysilyl iron complexes (equation 43)\(^\text{14}\). These are the same type of complexes noted above for base-free tungsten analogs\(^\text{146}\) involving \(\alpha\)-elimination subsequent to photochemical elimination of CO as noted below.

\[
\begin{array}{c}
\text{Me}_5\text{Fe} \quad \text{OC} \\
\downarrow \\
\text{GeMe}_2\text{EMe}_2\text{OMe} \\
\downarrow \\
\text{OC}
\end{array} \quad \begin{array}{c}
\text{Me}_5\text{Fe} \quad \text{OC} \\
\downarrow \\
\text{GeMe}_2\text{EMe}_2\text{OMe} \\
\downarrow \\
\text{OC}
\end{array}
\xrightarrow{\text{hv benzene}} \begin{array}{c}
\text{Me}_5\text{Fe} \quad \text{OC} \\
\downarrow \\
\text{GeMe}_2\text{EMe}_2\text{OMe} \\
\downarrow \\
\text{OC}
\end{array}
\xrightarrow{-\text{CO}} \begin{array}{c}
\text{Me}_5\text{Fe} \quad \text{OC} \\
\downarrow \\
\text{GeMe}_2\text{EMe}_2\text{OMe} \\
\downarrow \\
\text{OC}
\end{array}
\]

(43)

\[
\begin{array}{c}
\text{Me}_5\text{Fe} \quad \text{OC} \\
\downarrow \\
\text{GeMe}_2\text{EMe}_2\text{OMe} \\
\downarrow \\
\text{OC}
\end{array}
\xrightarrow{\text{hv benzene}} \begin{array}{c}
\text{Me}_5\text{Fe} \quad \text{OC} \\
\downarrow \\
\text{GeMe}_2\text{EMe}_2\text{OMe} \\
\downarrow \\
\text{OC}
\end{array}
\]

(54) \(E = \text{Ge}\)

(55) \(E = \text{Si}\)

In the case of the iron system, base stabilization is required for their isolation. Variable temperature NMR studies suggest that the methoxy-bridged bis(silylene) complexes do not undergo the silylene rotation whereas bis(germylene) iron complexes undergo the germylene–methyl group exchange. A mechanism involving cleavage of the germium–oxygen bond followed by rotation of the germylene group to interchange the methyl groups reasonably explains the fluxional behavior of 54 and 55. This difference also reflects the greater stability of the M=Ge bond in comparison to the M=Si bond and the weaker Ge–O bond than the Si–O bond.
D. Synthesis of Transition Metal Germanium Triple Bond Germlyyne Complexes

Data on these compounds are collected in Tables 6 and 8. Stable mononuclear transition-metal germlyne complexes with a formal triple bond between the Ge and metal atoms (Cr, Mo, W, 56–62) have been synthesized by a combination of salt-elimination and decarbonylation reaction (equation 44)\(^{150,151}\). The decarbonylation process for the Cr and W intermediates can involve either a thermal or a photochemical reaction; the molybdenum germlyne complexes 56 and 57 were obtained directly, even at low temperatures.

![Diagram](image)

\[ \text{(56)} M = \text{Mo, Ar} = 2,6\text{-bis(Mes)phenyl} \\
\text{(57)} M = \text{Mo, Ar} = 2,6\text{-bis(triisopropylphenyl)phenyl} \\
\text{(58)} M = \text{Cr, Ar} = 2,6\text{-bis(triisopropylphenyl)phenyl} \\
\text{(59)} M = \text{W, Ar} = 2,6\text{-bis(triisopropylphenyl)phenyl} \\
\text{(60)} M = \text{W, Ar} = 2,6\text{-bis(Mes)phenyl} \\
\]

Ar = 2, 6-bis(triisopropylphenyl)phenyl

The metal–germanium bond distances in 58 [2.1666(4) \( \text{Å} \)] and 60 [2.2767(14) \( \text{Å} \)] are \( \text{ca} \sim 0.41 \text{ Å} \) shorter than the M–Ge bond distances in the metallogermlynes 61 and 62. The metal germlynes have almost linear (M–Ge–C) angles in the range of 170.9(3)–175.99(6) whereas the (M–Ge–C) bond angles of metallogermlynes 61 and 62 are bent at 114.7(6)\( ^{5} \) and 117.8(2)\( ^{5} \), respectively. These structural features strongly suggest a formal triple bond between the 15-electron \( (\eta^{5}\text{-C}_{5}\text{H}_{5}\text{M})\text{(CO)}_{2} \) fragment and the Ge–Ar moiety.

E. The Reactivity of the Transition Metal Germanium Single Bond

1. Cleavage reactions

The cleavage of the metal–germanium bond occurs under mild conditions with both electrophilic and nucleophilic reagents. Halogens, halogen acids, organic halides, phenyllithium, Grignard reagents, \( \text{H}_{2} \) and lithium aluminum hydride easily cleave the Pd–Ge \(^{33} \), Pt–Ge \(^{44–46,111} \), Mo–Ge \(^{28,53} \), W–Ge \(^{28} \) and Co–Ge \(^{19,59} \) bonds. Mercuric salts also cleave the Mo–Ge and W–Ge bonds with the formation of M–Hg bonds (equation 45)\(^{28} \).
Such cleavage reactions of Pt−Ge complexes are believed to proceed through oxidative addition and a reductive elimination mechanism involving octahedral Pt (IV) complex (equation 46). In methyl/phenyl mixed germyl platinum complexes, selective cleavage of the Me₃Ge group occurred in preference to cleavage of a Ph₃Ge group. The M−Ge bond of the group 11 complexes, (R₃P)ₙM−GePh₃ (M = Cu, Ag, Au), are readily cleaved by 1,2-dibromoethane producing ethylene, Ph₃GeBr and R₃PMBr. Cleavage reactions of M−Ge bonds suggest that their stability order is Au−Ge > Ag−Ge > Cu−Ge.

The zirconocene complex, CpCp*Zr−GePh₃(Cl) undergoes hydrogenolysis of the Zr−Ge bond, giving zirconocene hydrochloride and triphenylgermane. The reaction is slow in comparison with the hydrogenolysis of the Zr−Si bond in an analogous complex (equation 47).

The germanium heterocycles of Co, Fe and Ru also undergo cleavage of the M−Ge bond with halogens, alcohols, organic halides, metal halides, PbCl₂, HgCl₂ and Bu₃SnH.
17. Transition metal complexes of germanium, tin and lead

They also react with 1,2-quinone through a radical process with the expulsion of metal carbonyls to form dioxo-metallacycles, the adducts of the biradicals \( \text{Me}_2\text{Ge}-(\text{CH}_2)_n-\text{GeMe}_2 \) \( (n = 1, 2) \) with quinones:\textsuperscript{75–79}

\[
\text{PbCl}_2 \quad \text{Me}_2\text{ClGe}(\text{CH}_2)_n\text{GeClMe}_2 + \text{M}_3(\text{CO})_{12} + \text{Pb}
\]

\[
\text{Me}_2\text{XGe}(\text{CH}_2)_n\text{GeXMe}_2
\]

\[
\text{Me}_2\text{HGe}(\text{CH}_2)_n\text{GeHMe}_2
\]

\[
\text{Me}_2(\text{OMe})\text{Ge}(\text{CH}_2)_n\text{Ge}(\text{OMe})\text{Me}_2 + \text{M}_3(\text{CO})_{12}
\]

\[
(M = \text{Fe}, \text{Ru})
\]

(48)

2. Metal digermyl, germylsilyl and germylstannyl complexes

Data on these compounds are given in Table 3.

Transition-metal complexes with direct metal–germanium bonds in which the germanium atom is also bonded to another group 14 element are of considerable interest. They are readily formed by salt-elimination reaction involving a transition metallate and the appropriate chlorogermyl compound (equation 49)\textsuperscript{13,15}. The complexes are thermally stable and may be handled in air for limited periods; however, they exhibit photochemical behavior reminiscent of that of the related oligosilyl complexes. Thus, subsequent to initial CO elimination followed by an \( \alpha \)-elimination of the silyl (or stannyl) group silyl (stannyl) germylene transients are formed. These can undergo a series of 1,3-migrations to form the isomeric germyl silylene (stannylene) complexes. Final elimination of the group 14 carbene analog upon recoordination of CO results in the formation of a mono-group 14 substituted metal compound, \( \text{Fe} = (\eta^5-\text{C}_5\text{H}_5)\text{Fe(CO)}_2 \) (equation 50).

As noted above, this reaction is very specific since, regardless of the initial complexes used, \( \text{FeGeMe}_2\text{SiMe}_3 \) or the isomeric \( \text{FeSiMe}_2\text{GeMe}_3 \), only the \( \text{FeSiMe}_3 \) compound is obtained. The greater stability for \( \text{Ge(II)} \) vs \( \text{Si(II)} \) intermediate compounds can be used to understand this selectivity, coupled to the greater thermodynamic driving force for the formation of \( \text{Si–C} \) vs \( \text{Ge–C} \) bonds. The 1,3-alkyl group migration is thus unidirectional, favoring the formation of the germylene complex.

In the case of the \( \text{FeGeMe}_2\text{SnMe}_3 \), this compound rearranges prior to loss of the group 14 carbene analog to form \( \text{FeSnMe}_2\text{GeMe}_3 \). This illustrates the more or less equal stability of the stannylene and germylene intermediates, as may be expected.

\[
\text{OC} \quad \text{Fe} \quad \text{Na}^+ \quad \text{ClGeMe}_2\text{SiMe}_3 \quad \text{OC}
\]

\[
\text{Fe} \quad \text{GeMe}_2\text{SiMe}_3 \quad \text{OC}
\]

(49)
3. Chemistry at the metal center

A series of transition-metal carbene complexes can be obtained from the neutral and anionic transition-metal germanium complexes. Treatment of \((\eta^5\text{-C}_5\text{H}_5)M(\text{CO})_3\text{−GePh}_3\) with organolithium reagents followed by alkylation resulted in the formation of a series of carbene compounds, \((\eta^5\text{-C}_5\text{H}_5)M(\text{CO})_3\text{−GePh}_3\text{C}(\text{OR}_1\text{)}\text{R}\) (equation 51)\(^{152,155}\). Carbene complexes can be obtained in a single step by the direct reaction of anionic germyl transition-metal complexes with dichlorocyclopropene by a substitution reaction\(^{154}\).

4. Intramolecular migration of the germyl group from the metal center

In some of the carbene formation chemistry noted above, a secondary reaction has been observed. Thus, treatment of \((\eta^5\text{-C}_5\text{H}_5)M(\text{CO})_n\text{GeR}_3\) (M = Mo, W, \(n = 3\); M = Fe, \(n = 2\)) with bases such as LDA, MeLi etc., followed by alkylation with RX, resulted in the formation of a series of products derived from germyl migration to the cyclopentadienyl ring, \([(\eta^5\text{-C}_5\text{H}_4\text{GeR}_3)M(\text{CO})_n\text{R}]\) (equation 52)\(^{153,155}\).

5. Photolysis/thermolysis of metal carbonyl germyl complexes

Photolysis of mononuclear chlorogermyl metal carbonyl complexes yields binuclear bis(\(\mu\)-germylene) metal carbonyl compounds (equation 53). The dimerization is believed to occur through a radical process\(^8\).
The photolysis of the related chlorogermyl iron complex, FpGeMe2Cl, mainly gives \( 63 \), which exist as a 4 : 1 mixture of the cis and trans isomers in solution\(^8,156,157\). Photolysis of the bimetallic \([\text{CpFe(CO)}_2\text{]}_2\text{GeMe}_2\) also yields \( 63 \) and such chemistry is typical of many such bimetallic germyl complexes (equation 54)\(^8,16,156–159\). In contrast, the related molybdenum complex, \([\text{CpMo(CO)}_3\text{]}_2\text{GeMe}_2\), simply undergoes cleavage of the Mo–Ge bond on photolysis\(^8\). The dynamic NMR and structure of \( 63 \) was reported and nonbridged terminal germylene intermediates were proposed to rationalize its cis–trans isomerization in solution\(^159\).

\[
\text{ML}_n(\text{CO})-\text{GeMe}_2-\text{ML}_n(\text{CO}) \xrightarrow{\text{hv}} \text{L}_n\text{M} \quad (54)
\]

\[
\text{ML}_n = \text{Co(CO)}_3, \text{Mn(CO)}_5
\]

Photolysis of the bimetallic iron complex FpGeMe2SiMe2Fp, \( 64 \), selectively gives a (\( \mu \)-germylene)(\( \mu \)-carbonyl) diiron complex \( 65 \) as a mixture of three equilibrating geometrical isomers. Prolonged photolysis of \( 65 \) transforms it to a mixture of cis and trans isomers of (\( \mu \)-germylene)(\( \mu \)-silylene) diiron complex \( 66 \) (equation 55)\(^15\). The proposed mechanism involves germylene and silylene intermediates and is closely related to the photochemical transformations of the disilyl diiron complex, FpSiMe2SiMe2Fp\(^{160,161}\).

A binuclear bis(\( \mu \)-germylene) osmium carbonyl complex \([\text{(OC)}_4\text{Os(GeMe}_2\text{)}]\)_2 on photolysis or thermolysis yields a mixture of an interesting series of (\( \mu \)-germylene) osmium clusters\(^36\). Bis(metalcarbonyl)germacyclopentene complexes on photolysis or thermolysis
also undergo a loss of CO with the formation of a carbonyl-bridged metal–metal bond (equation 56)\(^9\)\(^{162}\); thermolysis of the related Mn complex results in the cleavage of Ge–C bonds with the extrusion of a metal germylene which can be trapped with dienes\(^9\)\(^a\).

\[
\begin{align*}
\text{Fe} & \quad \text{GeMe}_2\text{SiMe}_2 & \quad \text{Fe} \\
\text{OC} & \quad \text{OC} & \quad \text{OC} \\
(64) & \quad (65)
\end{align*}
\]

6. Reactivity of germa-heterocycles

Bis[(dimethylgermyl)methane]metal carbonyls \((M = \text{Fe, Ru})\) undergo facile ring expansion with aldehydes\(^{73,75–79}\). The reactions occur faster under UV light and 1,2-insertions resulting in the ring expansion occur almost quantitatively (equation 57). The six-membered metallacycles are stable at room temperature but decompose thermally into a mixture of alkenes, germanium oxides and metal carbonyls. The proposed mechanism involves initial loss of CO under photolytic conditions, coordination of aldehyde to the metal center, insertion of the carbonyl group of the aldehyde into the metal–germanium bond and finally the recoordination of CO to form the metallacycles.

\[
\begin{align*}
\text{ML}_n & = \text{Mn(CO)}_4, \text{CpFe(CO)}, \text{Co(CO)}_3 \\
\text{ML}_n & = \text{Mn(CO)}_5 \\
\end{align*}
\]
F. Chemistry of the Transition Metal Germanium Double Bond, $M=\text{Ge}$

The platinum germylene complex 67 has been extensively studied and an array of interesting chemistry has been developed. The chemistry, outlined in equation 58, is predominantly addition to the $M=\text{Ge}$ bond, e.g. to give 68–71. The rearrangement of the 1,2-dioxametallocycle in 68 to the 1,3 isomer 72 is understood in terms of forming two $M-O$ bonds at the expense of the relatively weak $O-O$ bond\textsuperscript{136–139}.

\[
\begin{align*}
\text{(70)} & \\
\text{(67)} & \\
\text{(71)} & \\
\text{(68)} & \\
\text{(72)} & 
\end{align*}
\]
<table>
<thead>
<tr>
<th>Compound</th>
<th>Available data</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp₂Ti(Cl)GePh₃</td>
<td>NMR</td>
<td>38</td>
</tr>
<tr>
<td>Cp₂TiMe(GePh₃)</td>
<td>NMR, MS</td>
<td>104</td>
</tr>
<tr>
<td>Cp₂Zr(η²-COMe)GePh₃</td>
<td>NMR, MS, X-ray</td>
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<td>Cp₂Zr(Cl)Ge(SiMe₃)₃</td>
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<td>Cp₂Hf(Cl)GePh₃</td>
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<td>39</td>
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<td>Cp²Hf(Cl)₂Ge(SiMe₃)₃</td>
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<td>CpCr(CO)₃GeMe₂Cl</td>
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<td>IR, NMR</td>
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<td>CpMo(CO)₃GeCl₃</td>
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<tr>
<td>CpMo(CO)₃GeCl₂H</td>
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<td>CpW(CO)₃GeMe₂Cl</td>
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<td>CpW(CO)₃GePh₂H</td>
<td>IR, NMR, MS</td>
<td>17b</td>
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<td>cis-Cp²W(CO)₂(PMe₃)Ge(Cl)₃</td>
<td>IR, NMR, MS, X-ray</td>
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<td>Mn(CO)₅GeCl₃</td>
<td>IR, NMR, X-ray</td>
<td>9b</td>
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<tr>
<td>Mn(CO)₅Ge(H)(CF₃)₃</td>
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<td>62</td>
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<td>Mn(CO)₅GeH₃</td>
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<td>Re(CO)₅GeBr₃</td>
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<td>Re(CO)₅GePh₃</td>
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<td>CpRe(NO)(PPh₃)GePh₂Cl</td>
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<td>CpFe(CO)₅GeMe₃</td>
<td>IR, NMR, MS</td>
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<td>IR, NMR</td>
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<td>Fe(CO)₂CpGe(CO)₅Pr</td>
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<td>CpFe(CO)$_2$GePhH$_2$</td>
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<td>CpFe(CO)$_2$GePh$_2$Cl</td>
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<td>CpFe(CO)$_2$GePhCl$_2$</td>
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<td><em>trans</em>-Fe(CO)$_4$(GeCl$_3$)$_2$</td>
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<td>CpFe(CO)$_2$Ge(NBu-t)$_2$Me</td>
<td>IR, NMR, MS, X-ray</td>
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<td>Ru(CO)$_4$(GeMe$_3$)$_2$</td>
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<td>Ru(CO)$_4$(GeCl$_3$)$_2$</td>
<td>IR, NMR, X-ray</td>
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<td>Ru(CO)$_4$I(GeMe$_3$)</td>
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<td>Ru(CO)$_2$(PPh$_3$)$_2$(GeMe$_3$)$_2$</td>
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<td>(PP$_3$h$_2$)Ru(CO)$_2$Ge(Tol-p)$_3$</td>
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<td>Os(CO)$_3$(GeMe$_3$)$_2$</td>
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<tr>
<td>Os(CO)$_3$IGeMe$_3$</td>
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<td>CpCo(CO)(GeBr$_3$)$_2$</td>
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<td>86</td>
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<tr>
<td>CpCo(CO)Br(GeBr$_3$)$_2$</td>
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<td>IR, NMR, X-ray</td>
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<tr>
<td>Co(CO)$_3$Ge(CF$_3$)$_3$</td>
<td>IR, NMR, MS</td>
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<td>CpRh(CO)(GeMe$_3$)$_2$</td>
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<td>Cl</td>
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<td>IR, NMR, X-ray</td>
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<td>(CO)$_2$Hlr</td>
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<td>Ge[N(SiMe$_3$)$_2$]$_2$</td>
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<td>CpNi(PPh$_3$)$_3$GeEt$_3$</td>
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<td>CpNi(PPh$_3$)$_3$GeCl$_3$</td>
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<tr>
<td>(Et$_3$P)$_2$Pd(GePh$_3$)$_2$</td>
<td>IR, NMR, X-ray</td>
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<td>(Et$_3$P)$_2$Pt(GePh$_3$)$_2$</td>
<td>IR, NMR</td>
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<td>(Et$_3$P)$_2$Pt(GePh$_3$)$_2$Cl</td>
<td>IR, NMR</td>
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<td>(Et$_3$P)$_2$Pt(GeMe$_2$Cl)$_2$</td>
<td>IR, NMR, X-ray</td>
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<tr>
<td>(Et$_3$P)$_2$ClPtGeMe$_2$Cl</td>
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<td><em>trans</em>-(Et$_3$P)$_2$Pt(Cl)GeMe$_3$</td>
<td>IR, NMR, MS</td>
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<td><em>trans</em>-(Et$_3$P)$_2$Pt(GePh$_3$)GeMe$_3$</td>
<td>IR, NMR, MS</td>
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<td>(PP$_3$h$_2$)$_3$CuGePh$_3$</td>
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<td>(PP$_3$h$_2$)$_3$AgGePh$_3$</td>
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<td>(PP$_3$h$_2$)$_3$AuGePh$_3$</td>
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<td>(Ph$_3$P)$_3$AuGeCl$_3$</td>
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<td>(Ph$_3$P)$_3$AuGeCl$_3$</td>
<td>NMR, X-ray</td>
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**TABLE 2. Bimetallic transition metal germanium complexes**

<table>
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<tr>
<th>Compound</th>
<th>Available data</th>
<th>Reference</th>
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<tbody>
<tr>
<td>Me₂Ge[Mn(CO)₅]₂</td>
<td>IR, NMR, MS</td>
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<tr>
<td>H₂Ge[Mn(CO)₅]₂</td>
<td>IR, NMR, Ge−H, ν = 2083 cm⁻¹</td>
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<td>Me₂Ge[Cr(CO)₃Cp]₂</td>
<td>IR, NMR, MS</td>
<td>8</td>
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<tr>
<td>Me₂Ge[Mo(CO)₃Cp]₂</td>
<td>IR, NMR, MS</td>
<td>8</td>
</tr>
<tr>
<td>(NMe₂)₄W₂(GePh₃)₂</td>
<td>IR, NMR, X-ray</td>
<td>166</td>
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<td>Cl₂Ge[Fe(CO)₂Cp]₂</td>
<td>IR, NMR, X-ray</td>
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<td>Me₂Ge[Fe(CO)₂Cp]₂</td>
<td>IR, NMR</td>
<td>8, 20</td>
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<tr>
<td>Cl₂Ge[Co(CO)₄]₂</td>
<td>IR, NMR</td>
<td>22</td>
</tr>
<tr>
<td>Me₂Si(t-BuN)₂Ge[(CpFe(CO)₂)]₂</td>
<td>NMR, MS, X-ray</td>
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<tr>
<td>[(Me₃Ge)Ru(CO)₃Br]₂</td>
<td>IR, NMR</td>
<td>163</td>
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<tr>
<td>[(Me₃Ge)Os(CO)₃Br]₂</td>
<td>IR, NMR</td>
<td>163</td>
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<tr>
<td>Me₂Ge[Co(CO)₄]₂</td>
<td>IR, NMR</td>
<td>8, 22</td>
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<tr>
<td>Cl₂Ge[Co(CO)₄]₂</td>
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<td>Ph₂Ge[Co(CO)₄]₂</td>
<td>IR, MS</td>
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<td>Ge&lt;Co(CO)₄&lt;Co(CO)₄&lt;Co(CO)₄&lt;Co(CO)₄</td>
<td>IR, NMR</td>
<td>9b</td>
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<tr>
<td>Ge&lt;Co(CO)₄&lt;Co(CO)₄&lt;Co(CO)₄&lt;Co(CO)₄</td>
<td>IR, NMR, X-ray</td>
<td>9b</td>
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</table>

**TABLE 3. Transition metal digermyl, −germylsilyl and −germylstannyl complexes**

<table>
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<tr>
<th>Compound</th>
<th>Available data</th>
<th>Reference</th>
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<tr>
<td>Mn(CO)₅GeH₂GeH₃</td>
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<td>167</td>
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<td>FpGeMe₂GeMe₃</td>
<td>IR, NMR, MS</td>
<td>14a</td>
</tr>
<tr>
<td>FpGeMe₂GePh₃</td>
<td>IR, NMR</td>
<td>13</td>
</tr>
<tr>
<td>FpGeMe₂SiPh₃</td>
<td>IR, NMR</td>
<td>13</td>
</tr>
<tr>
<td>FpGeMe₂SiMe₃</td>
<td>IR, NMR</td>
<td>13</td>
</tr>
<tr>
<td>FpGePh₂GePh₂H</td>
<td>IR, NMR, MS</td>
<td>17b</td>
</tr>
<tr>
<td>FpGeMe₂GeMe₂Cl</td>
<td>IR, NMR, MS</td>
<td>14a</td>
</tr>
<tr>
<td>Fp⁺GeMe₂GeMe₂Cl</td>
<td>IR, NMR, MS</td>
<td>14a</td>
</tr>
<tr>
<td>Fp⁺GeMe₂GeMe₂OmMe</td>
<td>IR, NMR, MS</td>
<td>14a</td>
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<td>Fp⁺GeMe₂GeMe₂Et</td>
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<td>14a</td>
</tr>
<tr>
<td>Fp⁺GeMe₂SiMe₂Cl</td>
<td>IR, NMR, MS</td>
<td>14a</td>
</tr>
<tr>
<td>Fp⁺GeMe₂SiMe₂OmMe</td>
<td>IR, NMR, MS</td>
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### TABLE 3. Transition metal complexes of germanium, tin and lead (continued)

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<tr>
<td>FpGeMe$_2$SnMe$_3$</td>
<td>IR, NMR, MS</td>
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<tr>
<td>Wp*-GeMe$_2$GeMe$_3$</td>
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<tr>
<td>WpGePh$_2$GePh$_2$H</td>
<td>IR, NMR, MS</td>
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![Diagram of FpGeMe$_2$GeMe$_2$Fp](image)

### TABLE 4. Transition metal complexes with bridging germylene ligands

<table>
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<th>Compound</th>
<th>Available data</th>
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</thead>
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<tr>
<td>[CpCr(CO)$_2$]$_2$(µ-GeMe$_2$)$_2$</td>
<td>IR, NMR</td>
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<tr>
<td>[CpMo(CO)$_2$]$_2$(µ-GeMe$_2$)$_2$</td>
<td>IR, NMR</td>
<td>8</td>
</tr>
<tr>
<td><a href="%C2%B5-GeMe$_2$">Mn$_2$(CO)$_3$</a>(µ-CO)</td>
<td>IR, NMR, X-ray</td>
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</tr>
<tr>
<td><a href="%C2%B5-GeMe$_2$">Mn$_2$(CO)$_3$</a>$_2$</td>
<td>IR, NMR</td>
<td>8</td>
</tr>
<tr>
<td>[CpMn(CO)$_2$]$_2$(µ-GeMe$_2$)(µ-CO)</td>
<td>IR, NMR, X-ray</td>
<td>8, 159</td>
</tr>
<tr>
<td><a href="%C2%B5-GeCl$_2$">CpFe(CO)$_2$</a>(µ-CO)</td>
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<td>IR, NMR, X-ray</td>
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</tr>
<tr>
<td><a href="%C2%B5-GeMe$_2$">CpFe(CO)$_2$</a>$_2$</td>
<td>IR, NMR</td>
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<tr>
<td><a href="%C2%B5-GePh$_2$">CpFe(CO)$_2$</a>(µ-CO)</td>
<td>IR, NMR, MS</td>
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<tr>
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<td>IR, NMR, MS</td>
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<td><a href="%C2%B5-GeHBu-t">CpFe(CO)$_2$</a>(µ-CO)</td>
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<tr>
<td><a href="%C2%B5-GeHBu-t">CpFe(CO)$_2$</a>$_2$</td>
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<tr>
<td><a href="%C2%B5-Ge(Tol-p)$_2$">Cp*Fe(CO)$_2$</a>(µ-CO)</td>
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<tr>
<td><a href="%C2%B5-GeHTol-p">Cp*Fe(CO)$_2$</a>$_2$</td>
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![Diagram of [CpFe(CO)$_2$](µ-GeMe$_2$)(µ-CO)](image)

![Diagram of [Cp*Fe(CO)$_2$](µ-Ge(Tol-p)$_2$)(µ-CO)](image)

![Diagram of [Cp*Fe(CO)$_2$](µ-η$_2$-HGe(Tol-p)$_2$) ](image)

(continued overleaf)
### TABLE 4. (continued)

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<th>Compound</th>
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<td>[Me$_3$GeRu(CO)$_3$(µ-GeMe$_2$)]$_2$</td>
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<td>Os$_2$(CO)$_6$(µ-GeMe$_2$)$_3$</td>
<td>IR, NMR, X-ray</td>
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<td>[Os(CO)$_4$(µ-GeMe$_2$)]$_2$</td>
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<td>[Os(CO)$_3$(µ-GeMe$_2$)]$_3$</td>
<td>IR, NMR, X-ray</td>
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![Diagram of a transition metal germylene complex]

### TABLE 5. Transition metal germylene complexes

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<th>Compound</th>
<th>Available data</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>[Cp(NO)(PPh$_3$)Re=GePh$_2$.py]OTf</td>
<td>IR, NMR</td>
<td>33</td>
</tr>
<tr>
<td>Cr(CO)$_5$=GeTb(Tip)</td>
<td>IR, UV, NMR</td>
<td>134</td>
</tr>
<tr>
<td>Cr(CO)$_5$=Ge(tmtaa)</td>
<td>NMR, X-ray</td>
<td>141</td>
</tr>
<tr>
<td>Cp$^*$GeMe$_3$(CO)$_2$W=GeMe$_2$</td>
<td>IR, NMR, MS, X-ray</td>
<td>146</td>
</tr>
<tr>
<td>Cp$^*$GeMe$_3$(CO)$_2$W=GeMe$_2$.py</td>
<td>IR, NMR, MS, X-ray</td>
<td>146</td>
</tr>
<tr>
<td>W(CO)$_5$=Ge[SeC$_6$H$_2$(Bu-t)$_3$-2,4,6]$_2$</td>
<td>IR, NMR, MS, X-ray</td>
<td>133</td>
</tr>
<tr>
<td>W(CO)$_5$=GeTb(Tip)</td>
<td>IR, UV, NMR, X-ray</td>
<td>134</td>
</tr>
<tr>
<td>Cp$^*$Fe(CO)[GeMe$_2$OMeGeMe$_2$]</td>
<td>IR, NMR, MS</td>
<td>14a</td>
</tr>
<tr>
<td>Cp$^*$Fe(CO)[GeMe$_2$OMeSiMe$_2$]</td>
<td>IR, NMR, MS</td>
<td>14b</td>
</tr>
<tr>
<td>((CO)$_4$Fe)$_2$Ge.2py</td>
<td>IR, NMR, X-ray</td>
<td>149</td>
</tr>
<tr>
<td>(Et$_3$P)$_2$Ni=Ge[(CH(SiMe$_3$)]$_2$]$_2$</td>
<td>NMR</td>
<td>136</td>
</tr>
<tr>
<td>(Et$_3$P)$_2$Ni=Ge[(N(SiMe$_3$)]$_2$]$_2$</td>
<td>NMR, X-ray</td>
<td>136</td>
</tr>
<tr>
<td>(Et$_3$P)$_2$Pt=Ge[(N(SiMe$_3$)]$_2$]$_2$</td>
<td>NMR, X-ray</td>
<td>138, 139</td>
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### TABLE 6. Transition metal germlyne complexes

<table>
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<th>Compound</th>
<th>Available data</th>
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<tr>
<td>CpCr(CO)$_2$≡GeTrip$^a$</td>
<td>IR, NMR, X-ray</td>
<td>151</td>
</tr>
<tr>
<td>CpMo(CO)$_2$≡GeTrip$^a$</td>
<td>IR, NMR, X-ray</td>
<td>151</td>
</tr>
<tr>
<td>CpMo(CO)$_2$≡GeMes</td>
<td>IR, NMR, X-ray</td>
<td>150, 151</td>
</tr>
<tr>
<td>CpW(CO)$_2$≡GeMes</td>
<td>IR, NMR, X-ray</td>
<td>150, 151</td>
</tr>
<tr>
<td>CpW(CO)$_2$≡GeTrip$^a$</td>
<td>IR, NMR</td>
<td>151</td>
</tr>
<tr>
<td>[Cp$_2$Fe$_2$(CO)$_3$(µ-GeBu-t).B] OTf</td>
<td>IR, NMR, MS, X-ray</td>
<td>147b</td>
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$^a$Trip = 2,6-bis(2,4,6-triisopropylphenyl)phenyl; B = DMAP.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond</th>
<th>Bond length (Å)</th>
<th>L-M-Ge angle (deg)</th>
<th>X-Ge-X angle (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp₂Ti(η²-COCH₃)GePh₃</td>
<td>Ti—Ge</td>
<td>2.710(2)</td>
<td>109.0(4)</td>
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<td>104</td>
</tr>
<tr>
<td>Cp³Cl₂HfGe(SiMe₃)₃</td>
<td>Hf—Ge</td>
<td>2.740(1)</td>
<td>99.9(1)</td>
<td>109.0(2)</td>
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<tr>
<td>CpMo(CO)₂GeCl₃</td>
<td>Mo—Ge</td>
<td>2.545(10)</td>
<td>75.2(2)</td>
<td>102.5(11)</td>
<td>94</td>
</tr>
<tr>
<td>trans-CpMo(CO)₂(PMe₃)GeCl₃</td>
<td>Mo—Ge</td>
<td>2.510(6)</td>
<td>131.8—116.1</td>
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<td>94</td>
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<tr>
<td>Cp(NO)Mo(η³-hexenyl)GePh₃</td>
<td>Mo—Ge</td>
<td>2.658(2)</td>
<td>70.8—131.8</td>
<td>109.8—116.1</td>
<td>152</td>
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<tr>
<td>Cp²W(CO)₃GeCl₃</td>
<td>W—Ge</td>
<td>2.563(2)</td>
<td>85.9(1)</td>
<td>109.5(1)</td>
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<tr>
<td>trans-Cp²W(CO)₂(PMe₃)GeCl₃</td>
<td>W—Ge</td>
<td>2.487(3)</td>
<td>124.6(6)</td>
<td>120.0(13)</td>
<td>96</td>
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<tr>
<td>W(CO)₃(Br)GeBr₃-bipy</td>
<td>W—Ge</td>
<td>2.608(6)</td>
<td>78.8(2)</td>
<td>102.6(4)</td>
<td>169</td>
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<tr>
<td>Cp₂W(SiMe₃)(GeMe₂Cl)</td>
<td>W—Si</td>
<td>2.591(3)</td>
<td>187</td>
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<tr>
<td>Mn(CO)₅GeH₃</td>
<td>Mn—Ge</td>
<td>2.49</td>
<td></td>
<td></td>
<td>170</td>
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<tr>
<td>Mn(CO)₅GePh₃</td>
<td>Mn—Ge</td>
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<td>171a</td>
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<td>Mn(CO)₅GeBr₃</td>
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<td>2.44</td>
<td>113</td>
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<tr>
<td>Mn(CO)₅Ge(CF₃)₃</td>
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<td>2.413(9)</td>
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<td>Mn(CO)₅GeBr</td>
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<tr>
<td>Mn(CO)₅Ge</td>
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<tr>
<td>(CO)₅ReGeH₃</td>
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<tr>
<td>[Fe(CO)₂Cp]₂GeCl₂</td>
<td>Fe—Ge</td>
<td>2.357(4)</td>
<td>128.4</td>
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<td>Cp⁶Fe(CO)₅FeGeMe₂Cl</td>
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<td>2.339(1)</td>
<td>85.75</td>
<td>111.38(7)</td>
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<tr>
<td>(η⁵-C₅H₅)(η⁴-C₄H₆)FeGeMeCl₂</td>
<td>Fe—Ge</td>
<td>2.28(1)</td>
<td>130</td>
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<td>173</td>
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<tr>
<td>(η⁵-C₅H₅)(η⁴-C₄H₆)FeGeCl₃</td>
<td>Fe—Ge</td>
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<td>112.3</td>
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<tr>
<td>PhFe(CO)₂CpPh</td>
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<td>2.308(1)</td>
<td>89.2(2)</td>
<td>111.4(0)</td>
<td>12</td>
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<tr>
<td>C₂Rf(CO)₂[Ge(NBu-t)₂SiMe₂]Me</td>
<td>Fe—Ge</td>
<td>2.390(2)</td>
<td>88.2(2)</td>
<td>118.4(2)</td>
<td>101</td>
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<tr>
<td>trans-Ru(CO)₂(GeCl₃)₂</td>
<td>Ru—Ge</td>
<td>2.477(1)</td>
<td>90.0(1)</td>
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<td>175</td>
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<td>(η⁵-C₅H₅)Ru(CO)(GeCl₃)₂</td>
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<td>2.408(2)</td>
<td>90.3(7)</td>
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<tr>
<td>(C₅H₅)₉(CO)₂RuGeMe₃</td>
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<td>171.7(2)</td>
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<td>(PH₃P)₂OsH(CO)₂Ge(Tol-p)₃</td>
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<td>2.560(3)</td>
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<tr>
<td>Co(CO)₄GeBr</td>
<td>Co—Ge</td>
<td>2.367(1)</td>
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<td>(CO)₄CoGeCl₃</td>
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<td>(CO)₄CoGeH₃</td>
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(continued overleaf)
TABLE 7. (continued)

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<tr>
<th>Compound</th>
<th>Bond</th>
<th>L-M-Ge (Å)</th>
<th>X-Ge-X angle (deg)</th>
<th>Reference</th>
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<tr>
<td>Ph₃P(CO)₃CoGePh₃</td>
<td>Co–Ge</td>
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<td>180</td>
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<tr>
<td>(Me₃Si)₂NGeClN(SiMe₃)₂</td>
<td>Ir–Ge</td>
<td>2.418(1)</td>
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<tr>
<td>cis-(Et₃P)₂Pt(GeMe₂Cl)₂</td>
<td>Pt–Ge</td>
<td>2.427(15)</td>
<td>158.4(10)</td>
<td>123.7(5)</td>
</tr>
<tr>
<td>(Ph₃P)₃AuGeCl₃</td>
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<tr>
<td>[CpMn(CO)₂]₂(µ-GeCl₂)</td>
<td>Mn–Ge</td>
<td>2.357(0)</td>
<td>3.08(1)</td>
<td>80.66(1)</td>
</tr>
<tr>
<td>Mn₂(CO)₈(µ-CO)(µ-GeMe₂)</td>
<td>Mn–Ge</td>
<td>2.432(2)</td>
<td>2.854(5)</td>
<td>71.13(5)</td>
</tr>
<tr>
<td>[CpFe(CO)]₂(µ-GeMe₂)(µ-CO)</td>
<td>Fe–Ge</td>
<td>2.345(1)</td>
<td>2.628(1)</td>
<td>68.15(3)</td>
</tr>
<tr>
<td>[Fe(CO)₃]₃(µ-GeMe₂)(µ-CO)</td>
<td>Fe–Ge</td>
<td>2.347(1)</td>
<td>2.750(11)</td>
<td>70.0(2)</td>
</tr>
<tr>
<td>Fe₂(CO)₇(GePh₂)</td>
<td>Fe–Ge</td>
<td>2.402–2.440</td>
<td>2.666(3)</td>
<td>66.8(1)</td>
</tr>
<tr>
<td>Fe(CO)₆(µ-GeCl₂)</td>
<td>Co–Ge</td>
<td>2.341(9)</td>
<td>2.439(5)</td>
<td>123.6(8)</td>
</tr>
<tr>
<td>[Ru(CO)]₃(µ-GeMe₂)₃</td>
<td>Ru–Ge</td>
<td>2.49(1)</td>
<td>2.926(9)</td>
<td>71.9(3)</td>
</tr>
<tr>
<td>Os₂(CO)₆(µ-GeMe₂)₃</td>
<td>Os–Ge</td>
<td>2.545(1)</td>
<td>2.994(1)</td>
<td>70.68(4)</td>
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<tr>
<td>[Os(CO)₄(µ-GeMe₂)]₂</td>
<td>Os–Ge</td>
<td>2.588(1)</td>
<td>104.80(4)</td>
<td>36</td>
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<tr>
<td>[Os(CO)₅(µ-GeMe₂)]₃</td>
<td>Os–Ge</td>
<td>2.514(1)</td>
<td>2.920(1)</td>
<td>70.82(4)</td>
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<tr>
<td>Os₄(CO)₁₂(µ-GeMe₂)₄</td>
<td>Os–Ge</td>
<td>2.557(2)</td>
<td>3.069(1)</td>
<td>69.40(6)</td>
</tr>
<tr>
<td>[(CO)₃Co]₂(µ-Co(CO)₃(µ-Ge-Co(CO)₄)</td>
<td>Co–Ge</td>
<td>2.281(1)</td>
<td>2.613(1)</td>
<td>69.89</td>
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</table>

TABLE 8. X-ray structural data of transition metal germanium complexes with bridging germylene ligands

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<tr>
<th>Compound</th>
<th>Bond</th>
<th>Bond length (Å)</th>
<th>M–M bond length (Å)</th>
<th>M–Ge–M angle (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CpMn(CO)₂]₂(µ-GeCl₂)</td>
<td>Mn–Ge</td>
<td>2.357(0)</td>
<td>3.08(1)</td>
<td>80.66(1)</td>
<td>145</td>
</tr>
<tr>
<td>Mn₂(CO)₈(µ-CO)(µ-GeMe₂)</td>
<td>Mn–Ge</td>
<td>2.432(2)</td>
<td>2.854(5)</td>
<td>71.13(5)</td>
<td>156</td>
</tr>
<tr>
<td>[CpFe(CO)]₂(µ-GeMe₂)(µ-CO)</td>
<td>Fe–Ge</td>
<td>2.345(1)</td>
<td>2.628(1)</td>
<td>68.15(3)</td>
<td>159</td>
</tr>
<tr>
<td>[Fe(CO)₃]₃(µ-GeMe₂)(µ-CO)</td>
<td>Fe–Ge</td>
<td>2.347(1)</td>
<td>2.750(11)</td>
<td>70.0(2)</td>
<td>69, 91</td>
</tr>
<tr>
<td>Fe₂(CO)₇(GePh₂)</td>
<td>Fe–Ge</td>
<td>2.402–2.440</td>
<td>2.666(3)</td>
<td>66.8(1)</td>
<td>112</td>
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<tr>
<td>Fe(CO)₆(µ-GeCl₂)</td>
<td>Co–Ge</td>
<td>2.341(9)</td>
<td>2.439(5)</td>
<td>123.6(8)</td>
<td>89, 90</td>
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<tr>
<td>[Ru(CO)]₃(µ-GeMe₂)₃</td>
<td>Ru–Ge</td>
<td>2.49(1)</td>
<td>2.926(9)</td>
<td>71.9(3)</td>
<td>181, 182</td>
</tr>
<tr>
<td>Os₂(CO)₆(µ-GeMe₂)₃</td>
<td>Os–Ge</td>
<td>2.545(1)</td>
<td>2.994(1)</td>
<td>70.68(4)</td>
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</tr>
<tr>
<td>[Os(CO)₄(µ-GeMe₂)]₂</td>
<td>Os–Ge</td>
<td>2.588(1)</td>
<td>104.80(4)</td>
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<tr>
<td>[Os(CO)₅(µ-GeMe₂)]₃</td>
<td>Os–Ge</td>
<td>2.514(1)</td>
<td>2.920(1)</td>
<td>70.82(4)</td>
<td>36</td>
</tr>
<tr>
<td>Os₄(CO)₁₂(µ-GeMe₂)₄</td>
<td>Os–Ge</td>
<td>2.557(2)</td>
<td>3.069(1)</td>
<td>69.40(6)</td>
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</tr>
<tr>
<td>[(CO)₃Co]₂(µ-Co(CO)₃(µ-Ge-Co(CO)₄)</td>
<td>Co–Ge</td>
<td>2.281(1)</td>
<td>2.613(1)</td>
<td>69.89</td>
<td>183</td>
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</table>
**TABLE 8.** (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond</th>
<th>Bond length Å</th>
<th>Bond length M−M Å</th>
<th>M−Ge−M angle</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₂Si(NBu-t)₂Ge(O)(Si(OMe)₂)Pt₂</td>
<td>Pd−Ge</td>
<td>2.36(5)</td>
<td>2.304(1)</td>
<td>137</td>
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<tr>
<td>[Et₃P]₂Ni=Ge[N(SiMe₃)₂]₂</td>
<td>Ni−Ge</td>
<td>2.258(3)</td>
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<td>(Et₃P)₂Ni=Ge[N(SiMe₃)₂]₂</td>
<td>Ni−Ge</td>
<td>2.206(1)</td>
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<tr>
<td>[CpNi(Ge[NBu-t]₂SiMe₂)₂(μ-Cp)]</td>
<td>Ni−Ge</td>
<td>2.085(3)</td>
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<tr>
<td>[(CO)₄Fe]₂Ge·2py</td>
<td>Fe−Ge</td>
<td>2.339(4)</td>
<td>149</td>
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<tr>
<td>Cp⁺W(CO)₂=GeMe₂(GeMe₃)·py</td>
<td>W−Ge</td>
<td>2.5279(6)</td>
<td>122.81(2)</td>
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<td></td>
</tr>
<tr>
<td>Cr(CO)₅=Ge(tmtaa)</td>
<td>Cr−Ge</td>
<td>2.500(2)</td>
<td>140</td>
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<td></td>
</tr>
<tr>
<td>(CO)₅W=Ge(Se-2,4,6-tri-t-butylphenyl)_₂</td>
<td>W−Ge</td>
<td>2.528(1)</td>
<td>133</td>
<td></td>
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<tr>
<td>(CO)₅W=Ge(Tb(Tip))</td>
<td>W−Ge</td>
<td>2.5934(8)</td>
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<tr>
<td>Cp⁺²W(CO)₂=GeMe₂(GeMe₃)³⁺</td>
<td>W−Ge</td>
<td>2.4590(16)</td>
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<tr>
<td>RhCl[Ge(NBu-t)₂(SiMe₂)₄]</td>
<td>Rh−Ge</td>
<td>2.337(3)</td>
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<td></td>
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<tr>
<td>[Cp⁺Fe(CO)₂=GeMe₂·DMAP]BPh₄</td>
<td>Fe−Ge</td>
<td>2.329(3)</td>
<td>147a</td>
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<tr>
<td>[(CO)₃Fe]₂Ge·2py</td>
<td>Fe−Ge</td>
<td>2.339(4)</td>
<td>149</td>
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<td></td>
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<tr>
<td>[CpFe(CO)]₂(μ-GeBBu-t)(μ-CO)</td>
<td>Fe−Ge</td>
<td>2.322(2)</td>
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<tr>
<td>Cp⁺²W(CO)₂=GeMe₂(GeMe₃)·py</td>
<td>W−Ge</td>
<td>2.5279(6)</td>
<td>122.81(2)</td>
<td>146</td>
<td></td>
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<tr>
<td>Cp⁺²W(CO)₂=GeMe₂(GeMe₃)·py</td>
<td>W−Ge</td>
<td>2.5279(6)</td>
<td>122.81(2)</td>
<td>146</td>
<td></td>
</tr>
<tr>
<td>Cp⁺²W(CO)₂=GeMe₂(GeMe₃)·py</td>
<td>W−Ge</td>
<td>2.5279(6)</td>
<td>122.81(2)</td>
<td>146</td>
<td></td>
</tr>
<tr>
<td>Cp⁺²W(CO)₂=GeMe₂(GeMe₃)·py</td>
<td>W−Ge</td>
<td>2.5279(6)</td>
<td>122.81(2)</td>
<td>146</td>
<td></td>
</tr>
<tr>
<td>Cp⁺²W(CO)₂=GeMe₂(GeMe₃)·py</td>
<td>W−Ge</td>
<td>2.5279(6)</td>
<td>122.81(2)</td>
<td>146</td>
<td></td>
</tr>
<tr>
<td>Cp⁺²W(CO)₂=GeMe₂(GeMe₃)·py</td>
<td>W−Ge</td>
<td>2.5279(6)</td>
<td>122.81(2)</td>
<td>146</td>
<td></td>
</tr>
<tr>
<td>Cp⁺²W(CO)₂=GeMe₂(GeMe₃)·py</td>
<td>W−Ge</td>
<td>2.5279(6)</td>
<td>122.81(2)</td>
<td>146</td>
<td></td>
</tr>
<tr>
<td>Cp⁺²W(CO)₂=GeMe₂(GeMe₃)·py</td>
<td>W−Ge</td>
<td>2.5279(6)</td>
<td>122.81(2)</td>
<td>146</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 9.** X-ray structural data of transition metal germylene complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond</th>
<th>Bond length Å</th>
<th>M−M bond length Å</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(CO)₅=Ge(tmtaa)</td>
<td>Cr−Ge</td>
<td>2.500(2)</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>(CO)₅W=Ge(Se-2,4,6-tri-t-butylphenyl)₂</td>
<td>W−Ge</td>
<td>2.528(1)</td>
<td>133</td>
<td></td>
</tr>
<tr>
<td>(CO)₅W=Ge(Tb(Tip))</td>
<td>W−Ge</td>
<td>2.5934(8)</td>
<td>134</td>
<td></td>
</tr>
<tr>
<td>Cp⁺²W(CO)₂=GeMe₂(GeMe₃)³⁺</td>
<td>W−Ge</td>
<td>2.4590(16)</td>
<td>146</td>
<td></td>
</tr>
<tr>
<td>Cp⁺²W(CO)₂=GeMe₂(GeMe₃)·py</td>
<td>W−Ge</td>
<td>2.5279(6)</td>
<td>122.81(2)</td>
<td>146</td>
</tr>
<tr>
<td>Cp⁺²W(CO)₂=GeMe₂(GeMe₃)·py</td>
<td>W−Ge</td>
<td>2.5279(6)</td>
<td>122.81(2)</td>
<td>146</td>
</tr>
<tr>
<td>Cp⁺²W(CO)₂=GeMe₂(GeMe₃)·py</td>
<td>W−Ge</td>
<td>2.5279(6)</td>
<td>122.81(2)</td>
<td>146</td>
</tr>
<tr>
<td>Cp⁺²W(CO)₂=GeMe₂(GeMe₃)·py</td>
<td>W−Ge</td>
<td>2.5279(6)</td>
<td>122.81(2)</td>
<td>146</td>
</tr>
<tr>
<td>Cp⁺²W(CO)₂=GeMe₂(GeMe₃)·py</td>
<td>W−Ge</td>
<td>2.5279(6)</td>
<td>122.81(2)</td>
<td>146</td>
</tr>
<tr>
<td>Cp⁺²W(CO)₂=GeMe₂(GeMe₃)·py</td>
<td>W−Ge</td>
<td>2.5279(6)</td>
<td>122.81(2)</td>
<td>146</td>
</tr>
<tr>
<td>Cp⁺²W(CO)₂=GeMe₂(GeMe₃)·py</td>
<td>W−Ge</td>
<td>2.5279(6)</td>
<td>122.81(2)</td>
<td>146</td>
</tr>
</tbody>
</table>

*a*Cp²⁺ = A mono ethyl-substituted Cp.
There have been several significant reviews of this area of chemistry\textsuperscript{5}. It is the purpose of this review to summarize primarily the synthesis and reactivity of transition metal–tin complexes, with emphasis on the activity since the last of the previous reviews in 1989, and those aspects not previously covered.

A. Synthesis of the Transition Metal Tin Single Bond

1. Salt-elimination reactions between transition metal anions and tin halides

Examples of the use of the salt-elimination reaction between an alkali metal transition metallate and haloorganotin compounds, usually the chlorides, can be found for almost each group of the transition elements and has been widely used since the initial studies on transition-metal tin chemistry. The resulting complexes can be neutral or anionic as noted in the representative selection illustrated in equations 59–61 and usually result in good yield transformations. Indeed, a large number of such complexes have been synthesized for the purposes of proving the existence of the various metallate systems, such as the efficiency of the process and the general stability of the resulting complexes. The method works well for the characterization of highly reduced metal carbonyl anions including those of Ti, Cr, Mo and W\textsuperscript{184–187}.

\[
[Ti(CO)_{6}]^{2-} + ClSnR_{3} \longrightarrow [R_{3}SnTi(CO)_{6}]^{-}
\]

\(R = Me, Ph, Cy\) \hspace{1cm} (59)

\[
[M(CO)_{5}]^{2-} + ClSnR_{3} \longrightarrow [(CO)_{5}MSnR_{3}]^{-}
\] \(M = Cr, Mo, W; R = Me, Ph\) \hspace{1cm} (60)

\[
[M(CO)_{4}]^{-4} + ClSnPh_{3} \longrightarrow cis-[(CO)_{4}M(SnPh_{3})_{2}]^{-2}
\] \(M = Cr, Mo, W\) \hspace{1cm} (61)

New group 4 cyclopentadienylmetal carbonylate derivatives were also reported (equation 62)\textsuperscript{188,189}.

\[
[Cp^{R}M(CO)_{4}]^{-} + ClSnPh_{3} \longrightarrow Cp^{R}(CO)_{4}MSnPh_{3}
\] \(M = Ti, Zr; R = H, Me\) \hspace{1cm} (62)

Of particular interest is the capacity to utilize hydridometallate salts to form bifunctional stannyl(hydrido) metal derivatives (equation 63)\textsuperscript{190}.

\[
Li[Cp_{2}NbH_{2}] + ClSnMe_{3} \longrightarrow [Cp_{2}NbH_{2}SnMe_{3}]
\] \hspace{1cm} (63)

\(\pi\)-Arene metal carbylnates react both with the maintenance of the aromatic ring (equations 64\textsuperscript{191} and 65\textsuperscript{192}) but there are also examples in which they are transformed to an \(\eta^{5}\)-cyclohexadienyl group (equation 66)\textsuperscript{193}.

\[
[(\eta^{6}-C_{6}H_{6})Cr(CO)_{2}]^{-2} + ClSnPh_{3} \longrightarrow [(\eta^{6}-C_{6}H_{6})(CO)_{2}Cr(SnPh_{3})_{2}]^{-}
\] \hspace{1cm} (64)

\[
[(\eta^{6}-arene)(CO)_{2}CrSnPh_{3}]^{-} + ClSnMe_{3} \longrightarrow [(\eta^{6}-arene)(CO)_{2}Cr(SnPh_{3})(SnMe_{3})]
\] \hspace{1cm} (65)
The salt-elimination reactions are usually performed in THF or related ethereal solvents and the range of metallates is very large. The method continues to be useful as noted from the additional recent examples collected in Table 10.

In general these salt-elimination reactions are straightforward, however, an occasional surprise is noted. For example, the reaction of \([\text{PPh}_3)_2\text{Mn(CO)}_3^-\) with BrSnMe\(_3\) gives a mixture of fac-cis and mer-trans isomers of \([\text{PPh}_3)_2\text{Mn(CO)}_3\text{SnMe}_3\) at room temperature\(^{219}\), but in refluxing THF \([\text{PPh}_3)_2\text{(CO)}_3\text{MnSnMe}_2\text{Br}\] is obtained, illustrating the weakness of the Sn–C bond\(^{220}\).

Salt-elimination reactions also produce multimetal complexes, e.g. 73 (equation 67)\(^{221}\).

\[
\text{Na}_2[\text{Os(CO)}_4] + \text{R}_2\text{SnCl}_2 \xrightarrow{-2 \text{NaCl}} \text{R}_2\text{Sn} \begin{array}{c}\text{Os(CO)}_4\end{array} \text{Sn} \begin{array}{c}\text{Os(CO)}_4\end{array}\]  

(67)

R = Me, Ph

Unprecedented twelve-membered metallocycle Os\(_6\)Sn\(_6\) 74 is formed from the reaction between Na\(_2\)[Os(CO)]\(_4\)] with Cl\(_2\)SnPh\(_2\) in THF\(^{222}\).

Dimetallate salts can also be used to form extended metal–metal bonded complexes. Thus, the reactions of K\(_2\)[Fe\(_2\)(CO)]\(_8\)] with ClSnPh\(_3\) and Cl\(_2\)SnPh\(_2\) gave Ph\(_3\)Sn(CO)]\(_4\)Fe–Fe(CO)]\(_4\)SnPh\(_3\) and ClPh\(_2\)Sn(CO)]\(_4\)Fe–Fe(CO)]\(_4\)SnPh\(_2\)Cl, respectively (equation 68)\(^{223}\).

Transition metal–tin clusters can be formed from similar reactions and K\(_2\)[Fe\(_3\)S(CO)]\(_9\)] mixed with Me\(_2\)SnBr\(_2\) resulted in the formation of a double-bridged cluster 75. Similarly,
**TABLE 10.** Recent tin metal compounds prepared from transition metal anions and organotin halides

<table>
<thead>
<tr>
<th>Anion</th>
<th>XₙSnR₄₋ₙ</th>
<th>Product</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group 5: V, Nb, Ta</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[M(CO)₅]⁻³</td>
<td>ClSnPh₃</td>
<td>[(CO)₅MSnPh₃]⁻²</td>
<td>194, 195</td>
</tr>
<tr>
<td>M = Nb, Ta</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[CpM(CO)₃]⁻²</td>
<td>ClSnPh₃</td>
<td>[Cp(CO)₃MSnPh₃]⁻</td>
<td>196</td>
</tr>
<tr>
<td>Group 6: Cr, Mo, W</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(CO)₃M(SnPh₃)₃]⁻³</td>
<td>ClSnPh₃</td>
<td>[(CO)₃M(SnPh₃)₄]⁻²</td>
<td>197</td>
</tr>
<tr>
<td>M = Mo, W</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(Ab)(M(CO)₃)]⁻</td>
<td>ClSnMe₃</td>
<td>[(Ab)(CO)₃MSnMe₃]</td>
<td>198</td>
</tr>
<tr>
<td>Ab = 1-But-2-Me-1,2-, azaboroliny M = Cr, Mo, W</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(fcp)(M(CO)₃)]⁻</td>
<td>Cl₂SnMe₂</td>
<td>(fcp)(CO)₃MSnMe₂Cl</td>
<td>199</td>
</tr>
<tr>
<td>fcp = formylcyclo-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pentadienyl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M = Cr, Mo, W</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(η⁶-arene)(CO)₂CrSnPh₃]</td>
<td>ClSnR₂</td>
<td>[(η⁶-arene)(CO)₂CrSnPh₃]</td>
<td>200</td>
</tr>
<tr>
<td>R = Me, Cl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R₂SnCl₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cr(CO)₄(NO)]⁻</td>
<td>ClSnPh₃</td>
<td>[(CO)₄(NO)CrSnPh₃]</td>
<td>201</td>
</tr>
<tr>
<td>M = Cr, Mo</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R = Me, Ph</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[CO]₅W]⁻²</td>
<td>ClSnR₃</td>
<td>[(CO)₅WSnR₃]⁻</td>
<td>203</td>
</tr>
<tr>
<td>Group 7: Mn, Tc, Re</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Mn(CNAr)₃]⁻</td>
<td>ClSnPh₃</td>
<td>[Mn(CNAr)₃SnPh₃]</td>
<td>204</td>
</tr>
<tr>
<td>Ar = 2, 6-Me₂C₆H₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Mn(CO)₃(NO)]⁻²</td>
<td>ClSnPh₃</td>
<td>[(CO)₃(NO)MnSnPh₃]⁻²</td>
<td>205</td>
</tr>
<tr>
<td>[CpRe(CO)₂]⁻²</td>
<td>ClSnMe₃</td>
<td>Cp(CO)₂Re(SnMe₃)</td>
<td>206</td>
</tr>
<tr>
<td>Group 8: Fe, Ru, Os</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Fe(CO)₃(PR₃)(SiR₃)]⁻</td>
<td>ClSnMe₃</td>
<td>[Me₃SnFe(CO)₃(PR₃)(SiR₃)]</td>
<td>207</td>
</tr>
<tr>
<td>[HFe(CO)₄]⁻</td>
<td>ClSnR₅</td>
<td>[Me₃SnFe(CO)₃(PR₃)(SiR₃)]</td>
<td>207</td>
</tr>
<tr>
<td>R = Ph, 4-Tol</td>
<td>R = Ph, 4-Tol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[HFe(CO)₄]⁻</td>
<td>Cl₂SnPh₂</td>
<td>[Cl₂SnFe(CO)₄]⁻</td>
<td>208</td>
</tr>
<tr>
<td>SnCl₄</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[HFe(CO)₅(PR₃)]⁻</td>
<td>ClSnPh₃</td>
<td>[Ph₃SnFe(CO)₅(PR₃)]⁻</td>
<td>209</td>
</tr>
<tr>
<td>R = Me, Ph</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Os(CO)₅]⁻²</td>
<td>ClSnR₃</td>
<td>(R₃Sn)₂Os(CO)₅</td>
<td>210, 211</td>
</tr>
<tr>
<td>R = n-Bu, t-Bu, Ph</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[HO₅S(CO)₁₁]⁻</td>
<td>ClSnPh₃</td>
<td>HO₅S(CO)₁₁(SnPh₃)</td>
<td>212</td>
</tr>
<tr>
<td>Group 9: Co, Rh, Ir</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Co(CO)₃L]⁻</td>
<td>ClSnMe₃</td>
<td>Me₃SnCo(CO)₃L</td>
<td>213, 214</td>
</tr>
<tr>
<td>L = PPh₃, P(OPh)₃, AsPh₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[CO(CNAr)₄]⁻</td>
<td>ClSnPh₃</td>
<td>[(ArNC)₃CoSnPh₃]⁻</td>
<td>215, 216</td>
</tr>
<tr>
<td>Ar = 2,6-Me₂C₆H₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Rh(CO)(triphos)]⁻</td>
<td>ClSnMe₃</td>
<td>Me₃SnRh(CO)(triphos)</td>
<td>217</td>
</tr>
<tr>
<td>[Cr*IrH(PMe₃)]⁻</td>
<td>ClSnR₃</td>
<td>R₃SnCr*IrH(PMe₃)</td>
<td>218</td>
</tr>
</tbody>
</table>
K$_2$[Fe$_3$(CO)$_9$PR] (R = Ph, Tol) with Br$_2$SnMe$_2$ gave 76 (equation 69)$^{224}$. 

\[
\begin{align*}
K_2[&\text{CO)}_4\text{Fe-Fe(CO)}_4] & \xrightarrow{2 \text{Ph}_2\text{SnCl}_2} \text{Ph}_3\text{Sn(CO)}_4\text{Fe-Fe(CO)}_4\text{SnPh}_3 \\
\xrightarrow{2 \text{Ph}_2\text{SnCl}_2} & \text{ClPh}_2\text{Sn(CO)}_4\text{Fe-Fe(CO)}_4\text{SnPh}_2\text{Cl}
\end{align*}
\]

(68)

\[
\begin{align*}
\text{(CO)}_3\text{Fe} & \xrightarrow{\text{Me}_2\text{SnBr}_2} \text{(CO)}_3\text{Fe} \\
\text{E} & \xrightarrow{\text{(CO)}_3\text{Fe}} \text{E}
\end{align*}
\]

(69) $E = S$

(75) $E = PR, R = \text{Ph, } p$-Tol

Reduction of (butadiene)Fe(CO)$_3$ and (1-Ph-butadiene)Fe(CO)$_3$ with Li[HBEt$_3$] in THF, followed by treatment with ClSnMe$_3$, afforded (anti-methallyl)(CO)$_3$FeSnMe$_3$ and (anti-1-Me-syn-3-Ph-allyl)(CO)$_3$FeSnMe$_3$, which thermally isomerized to their syn isomers (equations 70 and 71)$^{225}$.

\[
\begin{align*}
\text{Fe(CO)}_3 & \xrightarrow{1. \text{BHEt}_3^-} \text{(CO)}_3\text{Fe-SnMe}_3 \xrightarrow{2. \text{ClSnMe}_3} \text{(CO)}_3\text{Fe-SnMe}_3 \\
\text{(CO)}_3\text{Fe-SnMe}_3 & \xrightarrow{\text{syn}} \text{(CO)}_3\text{Fe-SnMe}_3 \xrightarrow{\text{anti}} \text{Fe(CO)}_3
\end{align*}
\]

(70)

\[
\begin{align*}
\text{Fe(CO)}_3 & \xrightarrow{1. \text{BHEt}_3^-} \text{(CO)}_3\text{Fe-SnMe}_3 \xrightarrow{2. \text{ClSnMe}_3} \text{(CO)}_3\text{Fe-SnMe}_3 \\
\text{(CO)}_3\text{Fe-SnMe}_3 & \xrightarrow{\text{syn}} \text{(CO)}_3\text{Fe-SnMe}_3 \xrightarrow{\text{anti-syn}} \text{Fe(CO)}_3
\end{align*}
\]

(71)

As noted above, the lability of the Sn–C bond is often a factor determining the outcome of such reactions and this is well illustrated in a very early reaction between Na$_2$[Fe(CO)$_4$] with MeSnCl$_3$, where redistribution of methyl groups took place to form 77 and 78$^{226}$. An unusual hypercoordinated tin compound 79 was obtained by reacting K[Fe(CO)$_3$[Si(OMe)$_3$][Ph$_2$P(2-pyridyl)] with Cl$_2$SnPh$_2$, which involved an unusual silicon–tin exchange$^{227}$.

\[
\begin{align*}
\text{(CO)}_4\text{Fe} & \xrightarrow{\text{Me}_2\text{Sn}} \text{(CO)}_4\text{Fe} \\
\text{Sn} & \xrightarrow{\text{Me}_2\text{Sn}} \text{Sn}
\end{align*}
\]

(77)

\[
\begin{align*}
\text{(CO)}_4\text{Fe} & \xrightarrow{\text{Me}_2\text{Sn}} \text{(CO)}_4\text{Fe} \\
\text{Sn} & \xrightarrow{\text{Me}_2\text{Sn}} \text{Sn}
\end{align*}
\]

(78)
The ferrate-borole derivative \( [(C_4H_4BPh)Fe(CO)_2(SnPh_3)]^- \) (as tetraethylammonium salt) was obtained from the anion \( [(C_4H_4BPh)Fe(CO)_2]^- \), and similarly the 1,1-dimethylsilole and 1,1,3,4-tetramethylsilole (L) derivatives \( [(\eta^4-L)Co(CO)_2]_2 \) can be converted to anions, which react with ClSnPh_3 to form derivatives \( (\eta^4-L)(CO)_2CoSnPh_3 \). Cobalt derivatives of some tin-containing cyclosiloxanes, 80 and 81, were prepared from the corresponding Sn–Cl compounds by similar procedures, using \([Co(CO)_4]^-\). The reaction of the cluster \([Ni_6(CO)_{12}]^-\) with trialkyltin halides form \([Ni(SnRCl_2)_4(CO)]^-\) (R = Me, Bu), which are precursors of polynuclear \([Ni_{11}(SnR)_2(CO)_{18}]^-\), based upon a Ni-centered Ni_{10}Sn_2 icosahedral cage.

2. Synthesis from transition metal complexes and organotin anions

Triorganotin salts of general formula \([R_3Sn]^+\), A = alkali metal, are readily obtained from the reaction of the corresponding chlorotin compounds with the alkali metal. Reaction of these compounds with transition-metal halides is thus another useful salt-elimination reaction for the formation of tin–metal bonds. A representative selection of such reactions is illustrated in equation 72–74.

\[
\begin{align*}
\text{LiSnR}_3 + [\text{CIM(CO)}_5][\text{NEt}_4]^+ & \rightarrow [(\text{CO})_5\text{MSnR}_3][\text{NEt}_4]^+ \quad (72) \\
\text{M} = \text{Cr, Mo, W}; \ R = \text{Me, Ph} \\
\text{LiSnPh}_3 + \text{Cp}_2\text{MCl}_2 & \rightarrow \text{Cp}_2\text{M(SnPh}_3)\text{Cl} \quad (73) \\
\text{Cp}' = \text{C}_5\text{H}_5, \text{C}_5\text{Me}_5; \ M = \text{Zr, Hf} \\
\text{LiSnPh}_3 + \text{M}_2\text{Cl}_2(\text{NMe}_2)_4 & \rightarrow (\text{Me}_2\text{N})_4\text{M}_2(\text{SnPh}_3)_2 \quad (74) \\
\text{M} = \text{Mo, W}
\end{align*}
\]
A similar reaction involves the use of transition-metal complexes containing other good leaving groups, or systems that can readily provide increased coordination numbers by accommodating the Lewis base tin nucleophile, \([R_3Sn]^{-}\). The latter reactions usually lead to metal–tin bonds in anionic metallate products, as illustrated in equations 75 and 76 using sodium triphenyltin\(^{233,234}\).

\[
\text{NaSnPh}_3 + \text{Ti(CO)}_5(\text{dmpe}) \rightarrow [\text{Na}]^+[\text{Ph}_3\text{SnTi(CO)}_5(\text{dmpe})]^-
\]

\[
\text{NaSnPh}_3 + \text{MCl}_4 \cdot 2\text{THF} + \text{CO} \rightarrow [\text{Na}^+]_2[(\text{Ph}_3\text{Sn})_2\text{M(CO)}_4]^-
\]

\(M = \text{Zr, Hf}\)

In the case of copper complexes, the use of organotin lithium salts provided a route to the coordination of the stannylate system to neutral Cu(I) to form the corresponding cuprates (equations 77\(^{235}\) and 78\(^{236}\)).

\[
\text{LiSnPh}_3 + \text{CuPh} \rightarrow [\text{Li}]^+[\text{PhCuSnPh}_3]^{-}
\]

\[
\text{LiSnMe}_3 + \text{CuSPh} \rightarrow [\text{Li}]^+[\text{PhSCuSnMe}_3]^{-}
\]

Trimethylstannyl potassium, \(\text{KSnMe}_3\), reacts with bis(naphthalene)titanium(0) (obtained by reducing \(\text{TiCl}_4 \cdot 2\text{THF}\) by \(\text{KC}_{10}\text{H}_8\)) to give \([\text{Ti(C}_{10}\text{H}_8)_2(\text{SnMe}_3)_2]^{2-}\) in very good yield\(^{237}\). Solutions containing equimolar concentrations of \(\text{LiMe, LiSnMe}_3\), and \(\text{CuCN}\), or the reaction products of \(\text{Sn}_2\text{Me}_6\) with \(\text{Li}_2[\text{Me}_2\text{Cu(CN)}]\) form higher order stannylcuprates \(\text{Me}_3\text{Sn(Me)Cu(CN)}_2\text{Li}_2\), useful as reagents for delivering \(\text{SnMe}_3\) groups to various substrates\(^{238}\).

### 3. Elimination of \(\text{H}_2\), HCl, amines, hydrocarbons, silanes, etc.

The well-established reducing properties of the \(\text{Sn–H}\) bond have led to a number of useful synthetic methods for forming a tin–metal bond. In particular, many early transition-metal hydrides, -amides and -silanes readily eliminate \(\text{H}_2/\text{amines/silanes}\) upon treatment with the \(\text{Sn–H}\) bond. Some examples are illustrated in equations 79–83 for titanium\(^{232,239a}\), zirconium\(^{232}\), niobium\(^{239b}\) and manganese\(^{239c}\) complexes.

\[
\text{Cp^*_2TiH} + \text{HSnPh}_3 \rightarrow \text{Cp^*_2SnTiPh}_3 + \text{H}_2
\]

\[
(Et_2\text{N})_2\text{Ti(OBu-t)}_2 + 2 \text{HSnBu}_3 \rightarrow (\text{Bu}_3\text{Sn})_2\text{Ti(OBu-t)}_2 + 2 \text{Et}_2\text{NH}
\]

\[
\text{CpCp’Zr[Si(SiMe)_3]Cl + HSnPh}_3 \rightarrow \text{CpCp’Zr(SnPh}_3\text{Cl + (SiMe}_3\text{)_3SiH}
\]

\[
\text{HSnPh}_3 + [(\text{Me}_3\text{SiC}_5\text{H}_4)_2\text{NbH}_3] \rightarrow [(\text{Me}_3\text{SiC}_5\text{H}_4)_2(\text{H})_2\text{NbSnPh}_3]
\]

\[
\text{Mn}_2(\text{CO})_8\text{L}_2 + \text{HSnBu}_3 \rightarrow 2(\text{CO})_4\text{LMnSnBu}_3 + \text{H}_2
\]

\(L = \text{CO, PR}_3; R = \text{Me, Bu, i-Pr}\)

An unusual reaction, with loss of a phenyl group from \(\text{HSnPh}_3\), occurs with some dinuclear manganese–hydride carbonyl complexes (equation 84)\(^{240}\). The chemistry outlined in the previous equations, involving elimination of \(\text{H}_2\), occurs in many regions of the periodic table and produces good yields of the metal–tin bonded complex.
Related reactions involving elimination of hydrocarbons are also known, but appear much less general and this route has been used mostly for vanadium\textsuperscript{105}, zinc\textsuperscript{241a,241b}, cadmium\textsuperscript{241c} and mercury\textsuperscript{242} derivatives (equations 85–89).

\[
\begin{align*}
\text{HSnEt}_3 + \text{Cp}_2\text{VCH}_2\text{CH}_2\text{SiMe}_3 & \rightarrow \text{Cp}_2\text{VSnEt}_3 + \text{EtSiMe}_3 \quad (85) \\
\text{EtZnCl} + 2 \text{HSnPh}_3 & \rightarrow \text{Zn(SnPh}_3)_2 + \text{C}_2\text{H}_6 + \text{HCl} \quad (87) \\
\text{Et}_2\text{Cd} + 2 \text{HSn(CH}_2\text{SiMe}_3)_3 & \rightarrow \text{Cd[Sn(CH}_2\text{SiMe}_3)_3]}_2 + \text{C}_2\text{H}_6 \quad (88) \\
\text{R} = \text{Me, Et, Pr, Bu}, & \text{ Ph} \\
\text{Hg(Bu-t)}_2 + 2 \text{HSnR}_3 & \rightarrow \text{Hg(SnR}_3)_2 + 2\text{r-BuH} \quad (89)
\end{align*}
\]

The elimination reaction between metal hydrides and tin halides is another useful route to the formation of the tin–metal bond (equations 90 and 91)\textsuperscript{243,244,294}. The presence of a base to remove the hydrogen halide is often necessary to prevent decomposition reactions.

\[
\begin{align*}
\text{X}_n\text{SnR}_{4-n} + \text{CpNbH}_3 & \rightarrow [\text{Cp}_2(\text{H})_2\text{NbSnR}_n\text{X}_3-n] \quad (90) \\
\text{R} = \text{Me, X} = \text{Cl, n} = 2, 3; \text{R} = \text{Et, X} = \text{Br, n} = 2 \\
2\text{Cl}_2\text{SnMe}_2 + \text{Cp}_2\text{WH}_2 + 2 \text{NEt}_3 & \rightarrow \text{Cp}_2\text{W(SnMe}_2\text{Cl})_2 + 2 \text{Et}_3\text{N-HCl} \quad (91a) \\
(\text{Cp}_2\text{Zr})_4 + 4 \text{Me}_3\text{SnCl} & \rightarrow [\text{Cp}_2\text{ZrSnMe}_3]_2 + 2\text{Cp}_2\text{ZrCl}_2 + (\text{Me}_3\text{Sn})_2 \quad (91b)
\end{align*}
\]

The elimination of amines may also be accomplished by using the reactions of organotin amides and transition-metal hydrides, or transition-metal amides and tin hydrides\textsuperscript{4}. Neither route has attracted much attention recently.

There are few elimination reactions involving oxygen-containing leaving groups. One interesting example is the loss of water that occurred when $[\text{L(CO)}_4\text{WH}]^-$, $\text{L} = \text{CO, P(OMe})_3$, reacted with $\text{Ph}_3\text{SnOH}$ to form $[\text{L(CO)}_4\text{WSnPh}_3]^-$. The presence of a base is often necessary to prevent decomposition reactions.

4. Addition of HSnR\textsubscript{3} to metal centers and related reactions

The addition of the Sn–H bond to a transition-metal center can lead to the formation of metal–tin bonds and this route has been widely investigated recently. In some cases the M–H bond is retained, while in others further chemistry is observed. Such reactions can be likened to oxidative addition reactions that can occur with and without the loss of ligands from the metal center. Some representative examples, involving chromium,
molybdenum and tungsten, iron, ruthenium, osmium, rhodium, and iridium complexes, are provided in equations 92–99.

\[
[(L)(CO)_4W(THF)] + HSnR_3 \rightarrow [(L)(CO)_4W(H)SnR_3]
\]  
(L = PPh_3, PPh_2Me; M = Cr, Mo, W; R = Me, Ph)

\[
[CpFe(CO)_2]_2 + HSnBu_3 \rightarrow Cp(CO)_2FeSnBu_3 + Cp(CO)Fe(H)(SnBu_3)_2
\]  
Fe(CO)_2[P(OPh)_3]_2 + HSnR_3 \rightarrow cis-[(PhO)_3P]_2(CO)_2(H)FeSnR_3
\]  
R = Me, Ph

\[
M(CO)_2(PPh_3)_3 + HSnR_3 \rightarrow R_3SnM(H)(CO)_2(PPh_3)_2
\]  
M = Ru, Os; R = p-Tol

\[
OsCl(NO)(PPh_3)_2 + HSnR_3 \rightarrow R_3SnOsH(Cl)(NO)(PPh_3)_2
\]  
R = p-Tol

\[
CpOsCl(PPr_i)_2 + HSnR_3 \rightarrow CpOsH(Cl)(PPr_i)SnR_3
\]  
R = Bu, Ph

\[
RhH(PPh_3)_4 + HSnR_3 \rightarrow Rh(H)((\mu-H)(SnR_3)_2)(PPh_3)_2 \rightarrow
\]  
R = Bu, Ph

\[
IrH(PPh_3)_2 + 2 HSnPh_3 \rightarrow
\]  
Ph_3Sn

Of particular interest with respect to addition of the Sn−H bond are the reactions of tin hydrides with areneM(CO)_3 (M = Cr, Mo, W) complexes. In these reactions the Sn−H bond coordinates to the metal in the \(\eta^2\)-fashion as illustrated for Cr in equation 101.

The reducing power of the Sn−H bond can interfere with oxidative additions when metal-halogen bonds are present. For example, the reaction of cis- or trans-CpRe(CO)_2Br_2 with HSnPh_3 yielded the dihydride CpRe(CO)_2H_2 and BrSnPh_3.
When the same reaction was performed in the presence of pyridine or Et₃N, trans-Cp(CO)₂Re(SnPh₃)₂ was obtained²⁵⁷.

\[
\text{Me} \quad \text{Me} \quad \text{Cr(CO)₃} \quad + \quad \text{HSnPh₃} \quad \xrightarrow{\text{hv} - \text{CO}} \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Cr} - \text{H} \quad \text{Sn Ph₃}
\]

(101)

\[
\text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Cr(CO)₃} \quad + \quad \text{HSnPh₃} \quad \xrightarrow{\text{hv} - \text{CO}} \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Cr} - \text{H} \quad \text{Sn Ph₃}
\]

(82)

The reactions of tin hydrides with metal–metal bonded clusters has proven to be a successful route to a range of metal–tin bonded complexes. Products usually result in the cleavage of the M–M bond; however, under special conditions, for example with bridging ligands, the bond can remain intact and result in either bridging or terminal tin groups, as shown for some ruthenium²⁵⁸ and osmium²⁵⁹ clusters (equations 102 and 103).

\[
[Ru₃(μ-praz)(μ-CO)₃(CO)₁] + 2 \text{HSnR₃} \rightarrow
\text{praz} = \text{pyridazine}; R = \text{Bu}, \text{Ph}
\]

(102)

\[
\text{Os₃(μ-H)₂(CO)₁₀ + 2 HSnMe₃} \rightarrow \text{Os₃(μ-H)₂(CO)₁₀(SnMe₃)₂}
\]

(103)

Displacement of MeCN from M₃(CO)₁₂₋₈(MeCN)ₙ (M = Ru, Os; n = 1, 2) by organotin hydrides affords M₃(H)(CO)₁₁(SnR₃) (M = Ru, Os; R = alkyl, aryl) and Os₃(H)(CO)₁₀(MeCN)(SnR₃)²⁶⁰, as shown below.

\[
\begin{array}{c}
\text{(CO)}₄\text{M} \\
\text{H} \\
\text{SnR₃}
\end{array}
\quad \xrightarrow{\text{MeCN}} 
\begin{array}{c}
\text{(CO)}₄\text{Os} \\
\text{H} \\
\text{SnR₃}
\end{array}
\]

Similar displacement of ethylene from Cp*M(C₂H₄)₂ by HSnR₃ (M = Rh, Ir; R = Me, Bu) afforded Cp*M(H)₂(SnR₃)₂ (equation 104). An intermediate Cp*Ir(H)(SnR₃) (C₂H₄) was identified spectrally, and the same product was obtained from the reaction of the tin hydride with Cp₂*M₂Cl₄ (equation 105)²⁶¹.

\[
\text{Cp}^*\text{M(C₂H₄)₂ + 2 HSnR₃} \rightarrow \text{Cp}^*\text{M(H)₂(SnR₃)₂ + 2 C₂H₄}
\]

(104)

\[
\text{M} = \text{Rh, Ir}; R = \text{Me, Bu}
\]

\[
\text{Cp}^*\text{M₂Cl₄ + 4 HSnR₃} \rightarrow 2 \text{Cp}^*\text{M(H)₂(SnR₃)₂ + 4HCl}
\]

(105)
There are many individual reactions of tin hydrides with metal complexes that are not readily categorized. For example, the salt \([\text{Ru}_3(\mu\text{-NO})(\text{CO})_{10}]^-[\text{PPN}]^+\) reacts with one or two equivalents of HSnR₃ to form the oxidative addition products \(83\) and \(84\) (R = Bu, Ph) (equation 106)[262]. Similarly, the reaction between \(\text{RuH}(\eta^2\text{-H}_2\text{BH}_2)(\text{CO})(\text{P(Pr-i)}_3)\) and HSnPh₃, in a 1:3 molar ratio under a hydrogen atmosphere, results in the formation of \(85\) in which the \(\text{H}_2\) ligand can be easily displaced by \(\text{CO}\) or \(\text{P(OMe)}_3\) (equation 107).

\[
\begin{align*}
\text{CO} & \quad \text{Ru} \quad \text{CO} \\
\text{OC} & \quad \text{Ru} \quad \text{CO} \\
\text{OC} & \quad \text{Ru} \quad \text{CO} \\
\text{OC} & \quad \text{Ru} \quad \text{CO} \\
\text{OC} & \quad \text{Ru} \quad \text{CO} \\
\text{OC} & \quad \text{Ru} \quad \text{CO} \\
\text{OC} & \quad \text{Ru} \quad \text{CO} \\
\text{OC} & \quad \text{Ru} \quad \text{CO}
\end{align*}
\]

\(83\)

\[
\begin{align*}
\text{CO} & \quad \text{Ru} \quad \text{CO} \\
\text{OC} & \quad \text{Ru} \quad \text{CO} \\
\text{OC} & \quad \text{Ru} \quad \text{CO} \\
\text{OC} & \quad \text{Ru} \quad \text{CO} \\
\text{OC} & \quad \text{Ru} \quad \text{CO} \\
\text{OC} & \quad \text{Ru} \quad \text{CO} \\
\text{OC} & \quad \text{Ru} \quad \text{CO} \\
\text{OC} & \quad \text{Ru} \quad \text{CO}
\end{align*}
\]

\(84\)

\[
\begin{align*}
\text{OC} & \quad \text{Ru} \quad \text{CO} \\
\text{OC} & \quad \text{Ru} \quad \text{CO} \\
\text{OC} & \quad \text{Ru} \quad \text{CO} \\
\text{OC} & \quad \text{Ru} \quad \text{CO} \\
\text{OC} & \quad \text{Ru} \quad \text{CO} \\
\text{OC} & \quad \text{Ru} \quad \text{CO} \\
\text{OC} & \quad \text{Ru} \quad \text{CO} \\
\text{OC} & \quad \text{Ru} \quad \text{CO}
\end{align*}
\]

\(85\)

The borohydride reduction of BrRe(CO)₅ in the presence of PPhMe₂ and HSnBu₃ forms (CO)₄Re(PMe₂Ph)H. The tin hydride adduct could not be isolated, but upon water work-up a cyclic dirhenium distannoxane \(86\) was isolated[264].

\[
\begin{align*}
\text{(CO)}_4\text{Re} & \quad \text{Re(CO)}_4 \\
\text{Bu}_2\text{Sn} & \quad \text{SnBu}_2
\end{align*}
\]

\(86\)

5. Insertion of Sn(II) species into \(M-X\) bonds

The stability of Sn(II) compounds led to their use to form Sn(IV) derivatives of the transition metals via insertion reactions (equations 108[253], 109, 110[49,265] and 111[164]),

\[
\text{Cp}_2(\text{CO})\text{NbCl} + \text{SnCl}_2 \rightarrow \text{Cp}_2(\text{CO})\text{NbSnCl}_3 \quad \text{(108)}
\]
\[
[XW(CO)_5]^- + SnX_2 \rightarrow [(CO)_5WSnX_3]^- \\
M = Cr, Mo, W; X = Cl, Br
\]

\[
[Cp(CO)_3MoMe] + Sn(CH(SiMe_3)_2)_2 \rightarrow [Cp(CO)_3MoSn(CH(SiMe_3)_2)_2Me]
\]

\[
CpFe(\text{diphos})Cl + SnX_2 \rightarrow Cp(\text{diphos})FeSnX_2Cl
\]

More recently, interesting Os–H–Sn and Os–H–Os bridging species, 87 and 88, were obtained from the reaction of Sn[CH(SiMe_3)_2]_2 with OsH_2(CO)_10 (equation 112)\(^{266,267}\). The insertion of SnCl_2 into the metal–metal bonds of Me_2E[\(\eta^5\)-C_5H_4M(CO)_2]_2(\(\mu\)-CO)_2 (E = Si, M = Ru; E = Ge, M = Fe, Ru) affords heteronuclear cyclic complexes 89\(^{268}\).

\[
\text{OsH}_2(CO)_{10} + SnR_2 \rightarrow \text{reflux n-pentane}
\]

6. Use of distannane and distannoxane reagents

Hexamethylditin, Me_3SnSnMe_3, with its weak Sn–Sn bond, has proven a very useful reagent to form direct transition metal–tin bonds. Selected examples are noted in equations 113, \(^{269,270}\) 114 and 115\(^{271,272}\).

\[
\text{Me}_3\text{SnSnMe}_3 + Ru_3(CO)_{12} \rightarrow (CO)_4Ru(SnMe)_3 + \text{Me}_{10}\text{Sn}_4\text{Ru}_2(CO)_6
\]

\[
\text{Me}_3\text{SnSnMe}_3 + ML_2(\text{PMe}_3) \rightarrow ML_2(SnMe)_2
\]

\[
\text{Me}_3\text{SnSnMe}_3 + Co_2(CO)_8 \rightarrow \text{Me}_3\text{SnCo}(CO)_4 + \text{Me}_2\text{Sn}[Co(CO)_4]_2
\]
Recent examples include the insertion of platinum into the Sn–Sn bond of hexamethyldistannane (equation 116) and of a distannaferrocenophane, 90 (equation 117)\(^{273,274}\).

\[
\text{Me}_3\text{SnSnMe}_3 + (\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_2\text{H}_4) \rightarrow \text{Me}_3\text{SnPPh}_3 \quad \text{(116)}
\]

\[
\text{Me}_3\text{SnSnMe}_3 + (\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_2\text{H}_4) \rightarrow \text{Me}_3\text{SnPPh}_3 \quad \text{(117)}
\]

Similar reactions of organolanthanide reagents, RLn (Ln = Yb, Eu, Sm), with hexaalkyl(aryl) distannanes resulted in formation of reactive organometallic derivatives with Sn–Ln bonds, R\(_3\)SnLn\(^{275,276}\).

Several examples of the use of hexamethyldistannoxane as a Me\(_3\)Sn group transfer agent are reported. Thus the dimetallic carbonyl dimers of Mo, Mn, Fe, Co, and Ni react with Me\(_3\)SnOSnMe\(_3\) [and also with tris(trimethylstannyl)amine, N(SnMe\(_3\))\(_3\)] to form metal-carbonyl derivatives containing tin complexes (equation 118)\(^{277}\).

\[
\text{Mn}_2(\text{CO})_{10} + \text{Me}_3\text{SnOSnMe}_3 \rightarrow 2(\text{CO})_5\text{MnSnMe}_3 \quad \text{(118)}
\]

The reaction depicted in equation 119 is an interesting example of an oxygen transfer from tin; the diorganotin sulfides and acetates react similarly under the same conditions (refluxing iron pentacarbonyl)\(^{278}\).

\[
2\text{Fe}(\text{CO})_5 + 2/n(\text{Bu}_2\text{SnO})_n \rightarrow [\text{Bu}_2\text{SnFe}(\text{CO})_4]_2 + 2\text{CO}_2 \quad \text{(119)}
\]

7. Organotin group transfer via Sn–C bond cleavage

As noted in several instances in the foregoing chemistry, the tin–carbon bond is often quite labile. This is particularly true for the Sn–C(sp\(^1\), sp\(^2\)) linkages and has been used to synthesize metal–tin bonds. The reactions of alkylnitin compounds with iron carbynols result in Sn–C(alkyne) bond cleavage with formation of \([\text{R}_2\text{SnFe}(\text{CO})_4]_2\) and \([\text{R}_2\text{SnFe}(\text{CO})_3(\text{PPh}_3)]_2\)^{279}. Trimethylcyclopentadienyltin, CpSnMe\(_3\), reacts with bi- and polynuclear metal carbonyls to form MSnMe\(_3\), where M = Mn(\text{CO})\(_5\), Re(\text{CO})\(_5\), Co(\text{CO})\(_4\), CpMo(\text{CO})\(_3\), CpFe(\text{CO})\(_2\), CpNi(\text{CO}) and Fe(\text{CO})\(_4\), via cleavage of the M–M bond and transfer of the SnR\(_3\) group to the metal\(^{93}\).

More recently vinyltin derivatives, H\(_2\)C=CHSnR\(_3\), were found to transfer SnR\(_3\) groups to ruthenium and osmium. Thus, high yields of R\(_3\)SnRuCl(\text{CO})(\text{PPh}_3)_2 (R = Me, Bu, p-Tol) are obtained from H\(_2\)C=CHSnR\(_3\) and RuHCl(\text{CO})(\text{PPh}_3)_3, probably via insertion of the vinylstannane into the Ru–H bond, followed by a \(\beta\)-elimination of ethylene from the \(\beta\)-stannyethyl complex formed\(^{280}\). Similarly, the osmium complex, Me\(_3\)SnOsCl(\text{CO})(\text{PPh}_3)_2, was obtained from OsHCl(\text{CO})(\text{PPh}_3)_3 and H\(_2\)C=CHSnMe\(_3\)^{281}. 
A relatively unusual cleavage of the Sn−C(sp³) bond is illustrated in equation 120\textsuperscript{282}.

\[
\text{Ru}_3(\text{CO})_{12} + \text{Me}_3\text{SnCH}_2\text{NMe}_2 \rightarrow (\text{Me}_3\text{Sn})_2\text{Ru}(\text{CO})_4 + \text{HRu}_3(\text{CO})_{10}(\text{:CNMe}_2)
\] (120)

The migration of a triphenyltin group from a carbene (CO),\textsubscript{5}Cr:C(SnPh\textsubscript{3})NE\textsubscript{t}_2, on treatment with PPh\textsubscript{3} with loss of CO, leads to a carbyne complex, \textit{trans}-[(CO)\textsubscript{4}Cr(SnPh\textsubscript{3})(:CNE\textsubscript{t}_2)]; the reaction follows a first order kinetics\textsuperscript{283,284}.

### 8. Miscellaneous reactions

Recent studies have illustrated a number of interesting synthetic pathways to metal–tin bonds. For example the metal exchange reaction involving Yb and Sm complexes leads to new rhenium–tin compounds (equation 121)\textsuperscript{285}.

\[
2\text{CpRe}(\text{CO})_2(\text{MI}) + 2\text{ClSnPh}_3 \rightarrow \text{Cp}(\text{CO})_2\text{Re}(\text{SnPh}_3)_2 + \text{CpRe}(\text{CO})_2\text{I}_2 + \text{MCl}_2 + \text{MI}_2 (\text{M} = \text{Yb}, \text{Sm})
\] (121)

The oxidative decarbonylation reaction of \text{Cp}^R\text{Ti}(\text{CO})_2(\text{R} = \text{H, Me}) with aryltin halides, e.g. \text{Cl}_2\text{SnPh}_2 and \text{XSnPh}_3 (\text{X} = \text{Cl, Br, I}), gave the insertion product \text{Cp}^R(\text{X})\text{TiSnR}_2\text{X}' (\text{X}' = \text{R, X})\textsuperscript{286}. Similarly, \text{bis}(3,5\text{-dimethylpyrazolyl})\text{ethane (bmpze)} complexes of the type \text{M}(\text{CO})_4(\text{bmpze}) (\text{M} = \text{Mo, W}) react with \text{RSnCl}_3 (\text{R} = \text{Cl or Ph}) in CH\text{Cl}_2 at room temperature to give seven-coordinate insertion products \text{[(bmpze)(CO)\textsubscript{3}(Cl)M(SnRCl\textsubscript{2})]}\textsuperscript{287}. Related nitrile complexes \text{[M(CO)\textsubscript{3}(NCR)_\textsubscript{3}]} react with organotin trichlorides \text{R'SnCl}_3 to form \text{[CO]_\textsubscript{3}M(NCR)_\textsubscript{2}(Cl)M(SnR'\textsubscript{2}Cl\textsubscript{2})]} (where \text{M} = \text{Mo, W, R = Me or Et, R' = Bu or Ph) involving elimination of the nitrile}\textsuperscript{288,289}.

An unusual insertion occurs in a reaction of a substituted bipyridyl complex of dimethylplatinum with cyclic chalcogenotin compounds to form 91 (equation 122)\textsuperscript{290}.

\[
\text{t-Bu} \quad \text{Pt} \quad \text{Me} \\
\text{t-Bu} \quad \text{Me} \\
\text{E} \quad \text{Sn} \\
\text{E} \\
\text{R}_2 \quad \text{Sn} \\
\text{E} \\
\text{R}_2 \quad \text{SnR}_2
\]

\[
\text{t-Bu} \quad \text{Pt} \quad \text{Me} \\
\text{t-Bu} \quad \text{Me} \\
\text{E} \quad \text{Sn} \\
\text{E} \\
\text{SnR}_2 \\
\text{E} \\
\text{SnR}_2
\]

\[
\text{t-Bu} \quad \text{Pt} \quad \text{Me} \\
\text{t-Bu} \quad \text{Me} \\
\text{E} \quad \text{Sn} \\
\text{E} \\
\text{SnR}_2 \\
\text{E} \\
\text{SnR}_2
\]

\[
\text{t-Bu} \quad \text{Pt} \quad \text{Me} \\
\text{t-Bu} \quad \text{Me} \\
\text{E} \quad \text{Sn} \\
\text{E} \\
\text{SnR}_2 \\
\text{E} \\
\text{SnR}_2
\]

\[
\text{t-Bu} \quad \text{Pt} \quad \text{Me} \\
\text{t-Bu} \quad \text{Me} \\
\text{E} \quad \text{Sn} \\
\text{E} \\
\text{SnR}_2 \\
\text{E} \\
\text{SnR}_2
\]

\[
\text{t-Bu} \quad \text{Pt} \quad \text{Me} \\
\text{t-Bu} \quad \text{Me} \\
\text{E} \quad \text{Sn} \\
\text{E} \\
\text{SnR}_2 \\
\text{E} \\
\text{SnR}_2
\]

\[
\text{t-Bu} \quad \text{Pt} \quad \text{Me} \\
\text{t-Bu} \quad \text{Me} \\
\text{E} \quad \text{Sn} \\
\text{E} \\
\text{SnR}_2 \\
\text{E} \\
\text{SnR}_2
\]

\[
\text{t-Bu} \quad \text{Pt} \quad \text{Me} \\
\text{t-Bu} \quad \text{Me} \\
\text{E} \quad \text{Sn} \\
\text{E} \\
\text{SnR}_2 \\
\text{E} \\
\text{SnR}_2
\]
The dinuclear carbonyl Fe$_2$(CO)$_9$ reacts with Ph$_2$PCH$_2$CH$_2$SnPh$_3$ to form a chelated complex 92 via (CO)$_4$FePPh$_2$CH$_2$CH$_2$SnPh$_3$; the same compound is formed in the reaction of (CO)$_4$Fe(H)SiMePh$_2$ with Ph$_2$PCH$_2$CH$_2$SnPh$_3$ via a silyl group elimination.$^{291}$

\[ \text{Ph}_2\text{Fe} \quad \text{Ph}_2\text{P} \quad \text{SnPh}_2 \quad \text{OC} \quad \text{OC} \]

(92) \hspace{1cm} (93)

In a similar manner Fe$_2$(CO)$_9$ also reacted with Ph$_2$P(CH$_2$)$_n$SnR$_2$R$^\prime$ ($n = 2$, R$' = \text{Ph}$; R$_2 = \text{Ph}_2$, MePh; R$' = \text{Me}$, R$_2 = \text{Me}_2$; $n = 1$, 3, R$_2$R$' = \text{Ph}_3$) to give (CO)$_x$Fe[Ph$_2$P(CH$_2$)$_n$SnR$_2$R$'$]$_{5-x}$ ($x = 1$, 2) which, upon UV irradiation, gave the chelated phosphinoalkyl complexes (CO)$_3$Fe[Ph$_2$P(CH$_2$)$_n$SnR$_2$] by intramolecular oxidative addition of the SnR$'$ group$^{292}$. Similar compounds, 94–96, have been recently reported for nickel and platinum chemistry involving loss of a tin–phenyl group$^{293}$.

\[ \text{R}_3\text{SnCH}_2\text{CH}_2\text{P} \quad \text{R}_2\text{P} \quad \text{SnSn} \quad \text{Ni} \quad \text{Ph}_2 \quad \text{Ph}_2 \]

(94) R = Ph, M = Ni

(95) R = Me, M = Pt

The compound Cp(CO)$_2$FeSnMe$_2$GeMe$_3$, which can be prepared directly, was also formed by photoisomerization of its isomer Cp(CO)$_2$FeGeMe$_2$SnMe$_3$, prior to photoelimination of GeMe$_2$ and SnMe$_2$, to form Cp(CO)$_2$SnMe$_3$ (40%) and Cp(CO)$_2$FeGeMe$_3$ (60%)$^{15}$. This rearrangement (equation 123) contrasts the behavior of the related SiGe isomers where only photoelimination of the germylene was observed$^{13}$.

\[ \text{Fp-GeMe}_2\text{SnMe}_3 \quad \text{Fp-SnMe}_2\text{GeMe}_3 \]

(123)
The insertion of platinum into a Sn–C bond, presumably relieves the strain of a ferrocenophane and forms the metallocycle 97 (equation 124).

\[
\begin{align*}
\text{Fe} & \quad \text{Sn(Bu-\text{t})}_2 \\
\text{Fe} & \quad \text{Pt} \quad \text{Pt} \\
\text{Sn(Bu-\text{t})}_2 & \\
\end{align*}
\]

\[\text{Pt}(1,5-\text{COD})_2\]

(124)

B. Synthesis of Stannylene Complexes

The stannynes and their transition metal complexes have been dealt with in a series of recent reviews. We concentrate upon the most recent developments which chiefly involve direct reactions of preformed stannynes with various metal complexes (equation 125). The addition of SnCp₂ or SnCp′₂ to THF solutions of M(CO)₅THF (M = Cr, Mo, W) yields stannylene complexes R₂SnM(CO)₅ (R = Cp, M = Cr, Mo; R = Cp′, M = Cr, W).  

\[
\begin{align*}
\text{M(CO)}_5\text{L} + \text{R}_2\text{Sn} & \rightarrow \text{R}_2\text{SnM(CO)}_5 \\
(M = \text{Cr, Mo, W}; \text{L} = \text{CO}; \text{R} = \text{Me, t-Bu})
\end{align*}
\]

(125)

This is a very general procedure and a variety of stannynes have been used to form donor-free complexes, Sn[CH(SiMe₃)₂]₂; alkylarylstitannylene SnRR′(R = 2, 4, 6-(t-Bu)₃C₆H₂, R′ = CH₂CMe₂-C₆H₃(Bu-t)₂-3, 5); SnCp₂ and SnCp′₂. In the latter case the pentahapto bonding of the cyclopentadienyl rings to tin is retained. The Mössbauer spectra demonstrate a synergic tin–metal σ and metal–tin π bonding along the tin–metal axis.

The reaction of Cp₄Co(η²-C₂H₄)₂ (R = H, Me) with Sn[CH(SiMe₃)₂]₂ leads to the formation of a stannylene complex, 98 (equation 126).

\[
\begin{align*}
\text{Co} & \quad \text{Sn} \\
\text{CH(SiMe₃)₂} & \quad \text{CH(SiMe₃)₂} \\
\end{align*}
\]

(98)

Although cationic stannylene manganese complexes are well established, e.g. Me₂Sn=Mn(CO)₅⁺BF₄⁻, only recently was it shown that treatment of Mn₂(CO)₁₀ with SnRR′(R = 2, 4, 6-(t-Bu)₃C₆H₂; R′ = CH₂CMe₂(C₆H₃(Bu-t)₂-3, 5) provides a tetracarbonylstannylene complex 99 containing a heterocyclic moiety formed in the
process of cyclometallation (equation 127).\(^{303}\)

\[
\text{Mn}_2(\text{CO})_{10} + \text{SnRR}' \rightarrow \text{R'OC CO} \quad \text{Sn} \quad \text{R} \quad \text{Mn} \quad \text{Sn} \quad \text{OC CO} \\
\text{Bu-t} \quad \text{Bu-t} \quad \text{Me} \quad \text{Me} \quad \text{t-Bu} \quad \text{t-Bu} \\
(99) \quad \text{(127)}
\]

The reaction of Sn(\(\eta^1\text{-Cp})_2\) with diiron enneacarbonyl produces bridging stannylene complexes (equation 128).\(^{298,304,305}\)

\[
\text{Sn}(\eta^1\text{-Cp})_2 + \text{Fe}_2(\text{CO})_9 \rightarrow [(\eta^1\text{-Cp})_2\text{SnFe(\text{CO})}_4]_2 + \text{CO} \quad (128)
\]

Similarly, Sn(C\(_5\)Me\(_5\))\(_2\) and CpSnX (X = Cl, Br) react with Fe\(_2\)(CO)\(_9\) in benzene to give cyclic dimers [Cp\(^2\)*SnFe(CO)\(_4\)]\(_2\) and [CpXSnFe(CO)\(_4\)]\(_2\), respectively.\(^{306}\) The homolytic cleavage of these dimers, with even relatively weak Lewis bases, produce base-stabilized stannylene complexes of the type (CO)\(_4\)FeSnR\(_2\).\(^{298,306}\) The relative cleavage propensity for metals is: Ge > Sn > Pb and for bases is: Py > acetone > THF > Et\(_2\)O.\(^{307}\)

A rare metal atom synthesis was used for the preparation of \((R_2\text{Sn})_2\text{Fe}(\eta^6\text{-toluene})\), \(R = 2\text{-}(t\text{-Bu})-3,4,5\text{-Me}_3\text{C}_6\text{H}\), from Fe atoms, toluene and the stannylene SnR\(_2\).\(^{308}\) and for the synthesis of \((R_2\text{Sn})\text{Fe}(\mu^2\text{-C}_2\text{H}_4)(\eta^6\text{-toluene})\) where \(R = 2\text{-}(t\text{-Bu})-4,5,6\text{-Me}_3\text{C}_6\text{H}\) or CH(SiMe\(_3\))\(_2\). The latter reacts with CO at \(-20^\circ\text{C}\) in toluene to form \(R_2\text{SnFe}(\text{CO})_4\) and \((R_2\text{Sn})_2\text{Fe}(\text{CO})_3\). A metal atom route, involving solvated nickel atoms, was used to prepare red to purple, crystalline stannylene complexes of the type Ni(SnR\(_2\))\(_4\), with \(R = \text{CH(SiMe}_3)\(_2\)\) and C\(_6\)H(Bu-t)\(_2\)Me\(_3\)-4,5,6 at \(-78^\circ\text{C}\) in 58 and 33% yields, respectively.\(^{310}\)

The stannylene Sn[CH(SiMe\(_3\))\(_2\)] behaves as a Lewis base in its reactions with [CpFe(CO)\(_2\)]\(_2\) to form Cp\(_2\)Fe(CO)\(_3\)(SnR\(_2\)). Pyridine, 4-methylpyridine and piperidine form dissociable 1 : 1 adducts.\(^{265}\)

On the other hand, the mixed nitrile/carbonyl complexes of the three metals all react; \([\text{Fe}_3(\text{CO})_{11}\text{MeCN}] \rightarrow [\text{Fe}_2(\text{CO})_6(\mu\text{-SnR}_2)_2]\); \([\text{Ru}_3(\text{CO})_{10}\text{MeCN}] \rightarrow [\text{Ru}_3(\text{CO})_{10}(\mu\text{-SnR}_2)_2]\); \([\text{Os}_3(\text{CO})_{10}\text{MeCN}] \rightarrow [\text{Os}_3(\text{CO})_{10}(\mu\text{-SnR}_2)_2]\).\(^{311}\)

Treatment of Cp(\(\text{CO}\))(SnMe\(_3\))Fe{PN(Me)CH\(_2\)CH\(_2\)NM(e OR)}\(_2\)(R = Me, Et) with Me\(_3\)SiOSO\(_2\)CF\(_3\) resulted in P–OR bond cleavage and migration of a methyl group from tin to phosphorus, to yield an unusual stannylene complex.\(^{100,312}\)
Cyclic diazastannynes, Sn(NBu-t)₂SiMe₂, afford a series of interesting stannylene complexes. They insert into the Fe–Me bond of Cp(CO)₂FeMe, to form the corresponding stannylene complex 101.

A reaction of the four-membered cyclic stannylene with nickelocene gave compound 102 with a Sn–Ni–Sn fragment.

With NiBr₂, PdCl₂ and PtCl₂ the cyclic diazastannylene, Sn(NBu-t)₂SiMe₂ form compounds containing four Sn–M bonds, 103, but with MX₂ (M = Cr, Fe, Co, Zn; X = Cl, Br) the compounds formed are totally different and do not contain M–Sn bonds.

More sophisticated structures 104 and 105 are obtained by reactions of the cyclic diazastannylene, Sn(NBu-t)₂SiMe₂ with [(CO)₃Fe(μ-CO)(μ-Ph₂PXPh₂)Pt(PR₃)] (X = CH₂ or NH) and mer-[(CO)₂Fe{μ-Si(OMe)₂(OMe)}(μ-dppm)M(Me)] (M = Pd, Pt), respectively.

The stannylene Sn[CH(SiMe₃)₂]₂ reacts with [Os₃(CO)₈(μ-H)(μ-C₆H₄PhCH₂CH₂PPh₂)] and reverses the orthometallation used for its formation, to afford [Os₃(SnR₂)₂(μ-dppm)(CO)₈].
The ethylene complex \( \text{Cp}^\ast\text{Co}(\eta^2-\text{C}_2\text{H}_4)_2 \) reacts with the stannylene \( \text{SnR}_2 \), \( R = 6-t\text{-Bu-2,3,4-Me}_3\text{C}_6\text{H} \), to form \( \text{Cp}^\ast(\eta^2-\text{C}_2\text{H}_4)\text{CoSnR}_2 \), 106, which can be converted to the trinuclear \( \text{bis[bis}[6\text{-}t\text{-} \text{Bu-2,3,4\text{-}trimethylphenyl}]]\text{stannio} (\eta^5\text{-pentamethylcyclopentadienyl})\text{-cobalt(I)} \) 107 \( (\text{R}_2\text{Sn})_2\text{CoCp}^\ast \) upon heating 316.

The stannylene \( \text{SnR}_2 \) with \( R = \text{CH}\left(\text{SiMe}_3\right)_2 \) reacts with \( \text{RhCl(PPh}_3)_3 \) to form the addition product \( \text{R}_2\text{SnRhCl(PPh}_3)_2 \) 2265.

The stannylene \( \text{Sn}[\text{CH}\left(\text{SiMe}_3\right)_2]_2 \) reacts with \( \text{Ni(C}_2\text{H}_4)_3 \) and affords \( (\text{C}_2\text{H}_4)_2\text{NiSn}[\text{CH}(\text{SiMe}_3)_2]_2 \)-L with \( L = \text{NH}_3, \text{pyridine}, \text{OP(NMe}_2)_3 \), could be obtained 317. The ethene ligand can be displaced by CO to form \( \text{(CO)}_3\text{NiSn}[\text{CH(\text{SiMe}_3)_2}]_2 \), from which adducts \( \text{(CO)}_3\text{NiSn}[\text{CH(\text{SiMe}_3)_2}]_2 \)-L can also be prepared 317.

With toluene solvated nickel atoms, the stannylenes \( \text{Sn}[\text{CH(\text{SiMe}_3)_2}]_2 \) and \( \text{Sn(\text{C}_6\text{H}-2-t\text{-Bu-3, 4, 5-Me}_3)_2} \) at \(-78^\circ \text{C} \) form homoleptic stannylene analogs of nickel tetracarbonyl, \( \text{Ni(SnR}_2)_4 \) with \( R = \text{CH(\text{SiMe}_3)_2} \) and \( 2,3,4\text{-Me}_3-6-t\text{-BuC}_6\text{H}_3 \). The four membered cyclic stannylene \( \text{Sn(NBu-t}_2)\text{SiMe}_2 \) can also form a similar homoleptic complex 319.
The dimer \([\text{CpNi(PEt}_3])_2\) adds the stannylene \(\text{Sn}[\text{CH(SiMe}_3]_2]\) and eliminates the tri-ethylphosphine to form tetranuclear \([\text{CpNiSn}[\text{CH(SiMe}_3]_2]\) with a butterfly molecular structure which preserves the Ni–Ni bond. Alternatively, the same compound can be obtained directly from nickelocene and \(\text{Sn}[\text{CH(SiMe}_3]_2\) in 83% yield. The acetylene diphosphine chelate complex \(\text{Ni}(\text{HC}≡\text{CH})(\text{i-Pr})_2\text{PCH}_2\text{CH}_2\text{P(Pr-)}_2\) reacts with the stannylene \(\text{Sn}[\text{CH(SiMe}_3]_2\) (below \(-30^\circ\text{C}\)) in a different manner, by forming a stanna(I)nickela(II)cyclobutene complex (equation 131) which dissociates reversibly (up to \(20^\circ\text{C}\)) in solution to the starting components.

\[
\begin{align*}
\text{Ni} & \quad \text{P} \quad \text{P} \quad \text{Ni} \\
i-\text{Pr} & \quad \text{Pr-}i \quad \text{H} \quad \text{H} \\
i-\text{Pr} & \quad \text{Pr-}i
\end{align*}
\]

The four-membered cyclic stannylene \(\text{Sn(NBu}_-t)_2\text{SiMe}_2\) reacts with nickelocene to give an 87% yield of insertion product containing a CpNi moiety bridging two tin atoms. The structure was established by single crystal X-ray diffraction.
Tin(II) chloride behaves as a stannylene by inserting into the Ni–Ni bond of \([\text{CpNi(PEt}_3\text{)}]_2\) to form 108, in which both chlorine atoms can be replaced by alkyl groups in reactions with LiR (R = Me, Bu)\(^{322}\).

![Image of 108](image)

The reaction of \((\text{CO})_5\text{MnSnMe}_3\) with BF\(_3\) gives the stannylene complex \([\text{Me}_2\text{Sn:Mn(\text{CO})}_5]\text{BF}_4\); the same compound can be obtained from \((\text{CO})_5\text{MnSnMe}_2\text{Cl}\) with AgBF\(_4\) (equation 132)\(^{302}\).

\[
\begin{align*}
\text{(CO)}_5\text{MnSnMe}_3 + \text{BF}_3 & \rightarrow [\text{Me}_2\text{Sn:Mn(\text{CO})}_5]\text{BF}_4 \\
\text{(CO)}_5\text{MnSnMe}_2\text{Cl} + \text{AgBF}_4 & \rightarrow [\text{Me}_2\text{Sn:Mn(\text{CO})}_5]\text{BF}_4
\end{align*}
\]

\(\text{(132)}\)

C. The Reactivity of the Transition Metal Tin Single Bond

1. Thermal stability

There are widespread reports concerning the thermal stability of various M–Sn bonds; however, no systematic studies are apparent involving the effect on this stability of the metal component. A common decomposition pathway of triorganotin complexes involves the formation of ditin compounds as noted below for V and Hg complexes (equations 133\(^{323}\) and 134\(^{241,324}\)).

\[
\begin{align*}
2\text{Cp}_2\text{VSnEt}_3 & \rightarrow \text{Et}_3\text{SnSnEt}_3 + 2\text{Cp}_2\text{V} \\
\text{Hg}(\text{SnR}_3)_2 & \rightarrow \text{Hg} + \text{R}_3\text{SnSnR}_3
\end{align*}
\]

\(\text{(133)}\) \quad \text{(134)}

(R = Me, Et, Pr, Bu, Ph)

A study of the chemistry in equation 134 showed that the bulkier the R group, the more stable the complex, a typical feature of bulky ligands increasing the kinetic stability of many transition-metal and main group element complexes. The related thermal decomposition of alkyl(trimethyltin)mercury complexes, RHgSnMe\(_3\) (R = Me, Et, Pr, i-Pr, t-Bu), was investigated using CIDNP techniques and showed that the mechanism, not surprisingly, involved the formation of free radicals\(^{325,326}\). The very bulky arrangement of bis(tris-trimethylsilylmethyltin) mercury results in a distinctive decomposition route, presumably due to the instability of the related ditin compound (equation 135)\(^{327}\).

\[
\text{Hg}[\text{Sn(CH}_2\text{SiMe}_3)_3\text{]}_2 \rightarrow \text{Sn(CH}_2\text{SiMe}_3)_4 + \text{Hg}
\]

\(\text{(135)}\)

Solutions of \([\text{Zr(\text{CO})}_5(\text{SnMe}_3)_2]\)\(^{-2}\) in acetonitrile decompose within hours at 20\(^{\circ}\)C, to give the more stable anion \([\text{Zr(\text{CO})}_4(\text{SnMe}_3)_4]\)\(^{-2}\) containing eight-coordinate zirconium\(^{328}\).
A limited number of thermal redistribution reactions are reported, involving redistribution at both the tin and metal centers of the Sn–M complex (equations 136 and 137). The product in equation 137 contains a cyclic Os₃Sn₃ skeleton. A similar multimetal product 109 was obtained by the pyrolysis of the stannylene complex \([\eta^1\text{Cp}_2\text{SnFe(}CO\text{)}_4]_2\).

\[
\begin{align*}
2 \quad \text{Mo} & \quad \text{SnMe}_3 \\
\text{L} & \quad \text{CO} \quad \text{CO} \\
\text{L} & \quad \text{CO} \quad \text{CO} \\
\text{L} & \quad \text{CO} \quad \text{CO} \\
\end{align*}
\]

\[\text{(L = PPh}_3\text{)}\]

\[3 \ [\text{Me}_2\text{SnOs(}CO\text{)}_4]_2 \longrightarrow 2 \ [\text{Me}_2\text{SnOs(}CO\text{)}_3]_3\]  

(137)

2. Photostability

The limited data on the photostability of metal–tin complexes suggest that a process similar to that occurring in the thermal decompositions can take place. For example, RHgSnMe₃ (R = Me, Et, Pr, i-Pr, t-Bu) complexes produce ditin compounds via a radical process and Hg(SnR₃)₂ (R = Me, Et, Bu, Ph, CH₂C(Bu-t)₃, t-Bu) exhibit a stability proportional to the bulk of the organic radical substituent.

Interestingly, irradiation of \([\text{Me}_2\text{SnOs(}CO\text{)}_4]_2\) produced a different cluster compound than that obtained thermally in equation 137, i.e. 110 (equation 138).

\[
\begin{align*}
\text{Fe(}CO\text{)}_2\text{Cp} & \\
\text{(}CO\text{)}_3\text{Fe} & \quad \text{Sn} \\
\text{(}CO\text{)}_3\text{Fe} & \quad \text{Sn} \\
\text{Fe(}CO\text{)}_2\text{Cp} & \\
\end{align*}
\]

(109)

\[\text{hv} \quad [\text{Me}_2\text{SnOs(}CO\text{)}_4]_2 \longrightarrow (\text{Me}_2\text{Sn})_4\text{Os}_4(}CO\text{)_14\]  

(110)

The new cluster compound contains a planar Os₄Sn₄ skeleton consisting of a central rhomboidal Os₂Sn₂ unit fused to two outer Os₂Sn triangles.

Photolysis of Me₂Sn[Mn(CO)₅]₂ proceeds with loss of carbon monoxide and four-membered ring closure to form 111, and similar bridging stannylene complexes 112 and 113 are formed by the photochemical treatment of related Fe and Co complexes.

Photolysis of \([\text{(L)}_2(}CO\text{)_3\text{MnSnR}_3\text{]}\), R = Me, Et, L = P(OPh)₃, resulted in loss of the stannyl group and formation of an orthometallation product 114 involving the phosphite
3. Insertion reactions

A variety of simple insertion reactions are reported for the M–Sn bond, involving species as disparate as Te\textsuperscript{239}, CS\textsubscript{2}\textsuperscript{2337}, SO\textsubscript{2}\textsuperscript{203,338}, dienes and acetylenes (equations 140–143).

\[
\text{Cp}_2^+\text{Ti}–\text{SnPh}_3 + \text{Te} \rightarrow \text{Cp}_2^+\text{Ti}–\text{Te}–\text{SnPh}_3 \quad (140)
\]

\[
\text{(triphos)CuSnMe}_3 + \text{CS}_2 \rightarrow \text{(triphos)CuS}_2\text{CSnMe}_3·\text{CS}_2 \quad (141)
\]

\[
[(\text{CO})_5\text{WSnMe}_3]^- + \text{SO}_2 \rightarrow [(\text{CO})_5\text{WS(O)SnMe}_3]^- \quad (142)
\]

\[
\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{MoSnR}_3 + \text{SO}_2 \rightarrow \text{Cp}(\text{CO})_2(\text{PPh}_3)\text{MoOS(O)SnR}_3 \quad (143)
\]

\[(R = \text{Me, Ph})\]

The insertion chemistry noted in equation 141 relies upon the steric bulk imparted by the phosphine ligand. The related nonphosphine-containing complexes, Cp(\text{CO})_3\text{MSnPh}_3 (M = \text{Mo, W}), react with liquid sulfur dioxide to give dimersion products formulated as Cp(\text{CO})_3\text{MSnPh}_3·\text{SO}_2, in which insertion takes place into both the M–Sn and C–Sn bonds. Similarly, depending upon the temperature, the methyl analogs \text{Cp}(\text{CO})_3\text{MSnMe}_3 insert either one or two moles of SO\textsubscript{2}. The related bimetals, Ph\textsubscript{2}Sn[M(\text{CO})_5\text{Cp}_2], more bulky materials, do not react with SO\textsubscript{2}; however, the tungsten salt [(\text{CO})_5\text{WSnMe}_3]^- reacts at ambient temperature to form the mono-insertion product [(\text{CO})_5\text{WS(O)SnMe}_3]^-\textsuperscript{203,338}.

Reactions of (\text{CO})_5\text{MnSnR}_3 (M = \text{Mn, R = Me, Ph; M = Re, R = Me}) with liquid sulfur dioxide resulted in the formation of various products with insertions into the Sn–C bonds as well as the Sn–M bond\textsuperscript{339,340}. This type of chemistry exemplifies the relatively reactive nature of the Sn–C bond compared to the metal–Sn bond, \textit{vide supra}. In (\text{CO})_5\text{MnSnMe}_3 only the Mn–Sn bond reacts, but (\text{CO})_5\text{ReSnMe}_3 undergoes insertion into one Sn–C bond; Ph\textsubscript{2}Sn[Mn(\text{CO})_5]_2 incorporates three equivalents of SO\textsubscript{2} inserting into the Mn–Sn bond and two Sn–C bonds, whereas under the same conditions the
methyl analog, \( \text{Me}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2 \), decomposes. In the case of iron complexes, insertion occurs only into the Sn–C bond (equation 144)\(^{341a}\).

\[
\text{CpFe(CO)}_2\text{SnPh}_3 + 2\text{SO}_2 \rightarrow \text{CpFe(CO)}_2\text{SnPh[OS(O)Ph]}_2
\] (144)

Fluoroalkenes and fluoroalkynes, e.g. perfluoropropene, perfluoro-2-butyne and perfluorocyclobutene, insert into M–Sn bonds, M = Mn, Fe (equation 145)\(^{341b}\).

\[
\text{Me}_3\text{SnMn(CO)}_5 + \text{CF}_3\text{C≡CCF}_3 \rightarrow \text{Me}_3\text{Sn(CF}_3\text{)}_2\text{C} = \text{C(CF}_3\text{)}\text{Mn(CO)}_5
\] (145)

Similar chemistry occurs with \( \text{R}_3\text{SnCo(CO)}_4 \) if the reaction is performed photochemically in hexane; however, when conducted thermally in polar solvents, cobalt fluorides, \( \text{R}_3\text{SnF} \) and cobalt cluster compounds are formed\(^{342}\). In the case of an attempted insertion into a Rh–Sn bond under photochemical conditions, ligand exchange chemistry occurred (equation 146)\(^{343}\).

\[
\text{F}_2\text{C} = \text{CF}_2 + \text{Me}_3\text{SnRh(CO)}_2(\text{PPh}_3)_2 \rightarrow \text{Rh(CF} = \text{CF}_2)(\text{CO})_2(\text{PPh}_3)_2 + \text{FSnMe}_3
\] (146)

Attempted insertions of fluorocarbenes into Sn–Mn and Sn–Fe bonds were unsuccessful; thus, the thermal reaction of \( (\text{CO})_3\text{MnSnMe}_3 \) with \( \text{Me}_3\text{SnCF}_3 \) (a good source of carbene \( \text{CF}_2 \)) led instead to a disproportionation reaction involving formation of \( (\text{CO})_3\text{MnSnMe}_2(\text{CF}_3) \) and \( \text{SnMe}_4 \)\(^{344}\).

A very high yield insertion of a reactive, coordinatively unsaturated, metallic species into the Hg–Sn bond has been reported (equation 147)\(^{345,346}\).

\[
\text{Hg}[\text{Sn(C}_6\text{F}_5)_3]_2 + \text{M}(\text{PPh}_3)_2 \rightarrow (\text{C}_6\text{F}_5)_3\text{SnHgM(PPh}_3)_2\text{Sn(}C_6\text{F}_5)_3
\] (M = Pd, Pt) (147)

Similarly, from a mixed germyl(stannyl)mercury compound, the tetrametallic complex \( (\text{C}_6\text{F}_5)_3\text{SnHgM(PPh}_3)_2\text{Ge(}C_6\text{F}_5)_3 \) was obtained as a mixture of cis and trans isomers\(^{345}\).

4. Metal tin bond cleavage

The metal–tin bond is readily cleaved by a variety of reagents, e.g. \( \text{I}_2 \), \( \text{HgX}_2 \) (\( \text{X} = \text{Cl}, \text{OCOCF}_3 \)), \( \text{ClSiR}_3 \), \( \text{SiCl}_4 \), \( \text{SnCl}_4 \), \( \text{TiCl}_4 \). For example, upon treatment with either \( \text{I}_2 \) or \( \text{HgX}_2 \), the tin complexes \( \text{Cp(CO)}_3\text{MnSnR}_3 \) (\( \text{M} = \text{Cr}, \text{Mo}, \text{W}; \text{R} = \text{Me}, \text{Bu}, \text{Ph} \)) form the corresponding \( \text{Cp(CO)}_3\text{MI(HgX)} \) and \( \text{R}_3\text{SnX} \) compounds. Both processes involve charge transfer or adduct intermediates and although cleavage by iodine is accompanied by some CO evolution, this is not the case for the cleavage by \( \text{HgX}_2 \)\(^{347−352}\). Treatment of the same tin complexes with organomercury halides, \( \text{RHgCl} \) (\( \text{R} = \text{Me}, \text{Ph}, \text{allyl} \)), in acetone results in the initial formation of \( \text{Cp(CO)}_3\text{MHgR} \) followed by symmetrization (\( \text{M} = \text{Mo}, \text{W} \)) (equations 148 and 149)\(^{250}\).

\[
\text{Cp(CO)}_3\text{MnSnMe}_3 + \text{RHgCl} \rightarrow \text{Cp(CO)}_3\text{MHgR} + \text{ClSnMe}_3
\] (148)

\[
2 \text{Cp(CO)}_3\text{MHgR} \rightarrow \text{HgR}_2 + \text{Hg}[\text{M(CO)}_3\text{Cp}]_2
\] (149)

The reactions between \( \text{I}_2 \), \( \text{Br}_2 \), \( \text{ICl}, \text{IBr} \) and \( (\text{CO})_5\text{MnSnMe}_3 \), \( \text{Cp(CO)}_3\text{WSnMe}_3 \), \( \text{Me}_3\text{SnRe(}CO)_5 \) and \( \text{Cp(CO)}_3\text{FeSnMe}_3 \) have been studied as have been the reactions with \( \text{RMe}_2\text{SnMn(CO)}_5 \) [\( \text{R} = \text{CpMo(CO)}, \text{CpFe(CO)}_2, \text{Co(CO)}_4 \)]\(^{349,353−360}\). The following reactivity sequence for bond cleavage was observed with iodine:

\[
\text{Sn–Co} \sim \text{Sn–Fe} > \text{Sn–Mo} \sim \text{Sn–W} > \text{Sn–Mn}
\]
Phosphonium ylides, $R_3P-CHR'$ ($R = H, Et, Bu; R' = H, Me, SiMe_3$)$^{361}$, and phosphorus halides also cleave the Mo–Sn, Fe–Sn and Co–Sn bonds$^{362}$. (equation 150 and 151).

$$\text{Cp(CO)}_n\text{MSnMe}_3 + R_3PCHR' \longrightarrow [R'\text{CH_2R}_3\text{P}]^+[\text{CpM(CO)}_n]^– + R_3\text{PCR'SnMe}_3$$

$$\text{(M = Mo, n = 3; M = Fe, n = 2)}$$

$$2\text{Me}_3\text{SnCo(CO)}_4 + 2\text{Ph}_2\text{PCl} \longrightarrow (\text{CO})_3\text{Co(μ-PPh}_2)_2\text{Co(CO)}_3 + 2\text{Me}_3\text{SnCl}$$

The analogous reaction to equation 151, using $R_2\text{AsX}$, $R = \text{CF}_3, \text{CH}_3; X = \text{Cl}, \text{I}$, gave $\text{Me}_2\text{SnX}$ and a variety of different arsenic metallic products, e.g. $[\text{Me}_2\text{AsCo(CO)}_3]_n$ and $(\text{CF}_3)_2\text{AsCo(CO)}_4$.$^{362,363}$

Mercury–tin bonds are readily cleaved by the halogenos to yield haloorganotins. The bulky complex $\text{Hg}[\text{Sn(CH(Bu-t))}_3]_2$ reacts with $\text{HgCl}_2$, iodine and $\text{Hg(CH}_2\text{COOMe})_2$ to give the respective tin-chloride (90% yield), -iodide (74% yield) and -methyl acetate (88% yield)$^{364}$.

Both cadmium and mercury compounds $M[\text{SnR}_3]_2$ ($R = \text{Me, Et, Pr, t-Bu, Ph}$) are oxidized by air to the related stannoxanes and $\text{MO}$ ($M = \text{Cd}$) or $M$ ($M = \text{Hg}$)$^{239,241}$. Peroxides, e.g. $\text{Bz}_2\text{O}_2$, also perform similar oxidations to form $\text{M(OBz)}_2(M = \text{Cd})$ and $\text{BzOSnR}_3$$^{365}$. Even the thermally stable complexes with bulky ligands ($R = \text{Me}_3\text{SiCH}_2$) are also oxidized$^{333}$.

In an interesting report, 1,2-dibromocyclohexane cleaves the $\text{Hg–Sn}$ bond in $\text{Hg}[\text{Sn(CH}_2\text{(Bu-t))}_3]$ to form $\text{Hg}$, $\text{BrSn(CH}_2\text{(Bu-t))}_3$ and cyclohexene$^{333}$. Also noteworthy is the formation of carbene complexes ($η^6$-arene)$\text{(CO)}_2\text{Cr:CrF}_2$ formed in the substitution/elimination reactions of stannyl complexes $K[(η^6$-arene)$\text{(CO)}_2\text{CrSnPh}_3]$ with activated $C$–$X$ bond in organic dihalogeno derivatives $\text{R}_2\text{CX}_2$ or ionic halides $[\text{R}_2\text{CX}]_2\text{Y}$$^{366}$.

There are reports of nominal two-electron donors cleaving the metal–tin bond. Thus, methyl cyanide displaces a $\text{SnPh}_3$ group from $[\text{NEt}_4]_2[(\text{CO})_4\text{M(SnPh}_3)_2]$ to give the complex $[\text{NEt}_4][(\text{CO})_2\text{M(SnPh}_3)_2][\text{MeCN}]$, and $\text{PPh}_3$ in turn replaces the methyl cyanide ligand to form $[\text{NEt}_4][(\text{CO})_4\text{M(SnPh}_3)_2][\text{PPh}_3]$.$^{367}$ Loss of a triphenyltin group also occurs on treating seven-coordinate $[(\text{CO})_4\text{Cr(SnPh}_3)_3]$– with $\text{LiSnPh}_3$, $\text{LiMe}$, $\text{PPh}_3$ and $(\text{Me}_2\text{N})_3\text{PO}$, with formation of the six-co-ordinate $[(\text{CO})_4\text{Cr(SnPh}_3)_2]_2$$^{2,367}$.

The metal–tin bond is readily cleaved by alkali metals to form the anionic salts of both the transition-metal and tin moieties. The complex $[(\text{dppe})\text{(CO)}_4\text{VSnPh}_3]$ is reduced by sodium metal in THF to give, after treatment with $[\text{Et}_4\text{N}]\text{Cl}$, the salt $[\text{Et}_4\text{N}][(\text{V(CO)}_4(\text{dppe})]$ and $\text{Ph}_3\text{SnSnPh}_3$, and $[(\text{triphos})\text{(CO)}_4\text{VSnPh}_3]$ is reduced to $\text{Na}[\text{V(CO)}_4(\text{triphos})].$$^{358}$ Similarly, $[(\text{PPh}_3)(\text{CO})_5\text{VSnPh}_3]$, $[(\text{dppe})(\text{CO})_4\text{NbSnPh}_3]$ and $[(\text{PPh}_3)(\text{CO})_5\text{TaSnPh}_3]$ were also reduced by sodium in THF but the products were not isolated$^{368}$.

The reduction of seven-coordinate $[\text{Et}_4\text{N}][(\text{CO})_5\text{V(SnPh}_3)_2]$ produced the six-coordinate dinegative anion $[(\text{CO})_5\text{VSnPh}_3]^–$$^{2,369}$. Many similar reductions are reported, including those of $\text{Cd}[\text{Sn(CH}_2\text{SiMe}_3)_3]_2$ and $\text{Hg}[\text{Sn(CH}_2\text{SiMe}_3)_3]_2$ by $\text{Li}$ in THF to form the tin anionic species$^{370}$.

5. Chemistry at tin

As noted above, the insertion of $\text{SO}_2$ in metal–tin complexes can occur into both the $\text{M–Sn}$ and $\text{C–Sn}$ bonds. This speaks to the reactivity of the $\text{C–Sn}$ bond in metal
complexes and indeed many reagents illustrate the robust nature of the metal–tin bond at the expense of the C–Sn bond. Thus, various acids will selectively react to cleave the tin–carbon bond (equations 152–154).

\[
\text{Cp}_2(\text{CO})\text{NbSnEt}_3 + 3\text{HCl} \rightarrow \text{Cp}_2(\text{CO})\text{NbSnCl}_3 + 3\text{C}_2\text{H}_6 \quad (152)
\]

\[
\text{Ph}_2\text{Sn}[\text{Mn(OCO)}_5]_2 + 2\text{AcOH} \rightarrow (\text{AcO})_2\text{Sn}[\text{Mn(OCO)}_5]_2 + 2\text{PhH} \quad (153)
\]

\[
\text{Ph}_2\text{Sn}[\text{Mn(OCO)}_4(\text{CNR})]_2 + 2\text{HCl} \rightarrow \text{Cl}_2\text{Sn}[\text{Mn(OCO)}_4(\text{CNR})]_2 + 2\text{PhH} \quad (154)
\]

\(R = \text{Me}, \text{Et}\)

As a further illustration of this chemistry, the complexes \(\text{Cp}'(\text{CO})_3\text{MnSnPh}_3\) and \(\text{Cp}(\text{CO})_3\text{MnSnPh}_2\text{X} (M = \text{Mo, W}; X = \text{Cl, Br})\) react with HCl or HBr to yield trihalogenotin derivatives. There are even examples of the cleavage of Sn–C bonds preferentially to the M–Sn bond by iodine (equation 155).

\[
(\text{CO})_5\text{MnSn(allyl)}_3 + 3\text{I}_2 \rightarrow (\text{CO})_5\text{MnSnI}_3 + 3\text{CH}_2=\text{CHCH}_2\text{I} \quad (155)
\]

Tin–carbon bonds in \([(\text{CO})_5\text{MnSnMe}_3]\) are cleaved by LiAlH\(_4\) or NaBH\(_4\) to form hydrides and the reaction of CF\(_3\)COCl and HSiCl\(_3\) with the same compound results in the formation of \([(\text{CO})_5\text{MnSnMe}_2\text{Cl}\)]\(_3\) (equations 156–159).

\[
[\text{Cp}_2(\text{H})\text{Nb}(\text{SnMe}_3)_2] + \text{Cl}_2\text{SnMe}_2 \rightarrow [\text{Cp}_2(\text{H})\text{Nb}(\text{SnMe}_2\text{Cl})_2] + \text{Me}_3\text{SnCl} \quad (156)
\]

\[
[(\text{CO})_5\text{WSnPh}_3]^- + [(\text{CO})_5\text{WSnCl}_3]^- \rightarrow [(\text{CO})_5\text{WSnPh}_3-n\text{Cl}_n]^- \quad (n = 1, 2, 3) \quad (157)
\]

\[
[\text{Cp}(\text{CO})_2\text{Fe}]_2\text{SnCl}_2 + [\text{Cp}(\text{CO})_2\text{Fe}]_2\text{SnPh}_2 \rightarrow [\text{Cp}(\text{CO})_2\text{Fe}]_2\text{SnPhCl} \quad (158)
\]

\[
\text{Hg}(\text{SnPh}_3)_2 + \text{RHgCl} \rightarrow \text{RHgSnPh}_3 + \text{ClSnPh}_3 \quad (159)
\]

\(R = \text{Me}, \text{Et}, \text{Ph}\)

A redistribution reaction between the Me\(_3\)Sn and I\(_2\)MeSn osmium complexes yields IMe\(_2\)SnOs(η\(^2\)–SnCNEt\(_2\))\((\text{CO})\)(PPh\(_3\))\(_2\) and further derivatization of the organotin halides is possible with a variety of reagents (pyridinium tribromide, catechol, potassium hydroxide, triethanolamine, nitrilotriacetic acid) to give the corresponding substitution compounds. The compound Hg[Sn(CH\(_2\)Bu-t\(_3\))]\(_2\) reacts reversibly with Hg(GeEt\(_3\))\(_2\) to form Et\(_3\)GeHgSn(CH\(_2\)Bu-t\(_3\))\(_3\) (equations 156–159).

A redistribution reaction between the metal–tin complexes not only provide extremely useful transition-metal-substituted organotin chlorides, but also demonstrate the chemical robustness of the M–Sn bonds. For example, whereas the W–Sn bond in \([(\text{CO})_5\text{WSnPh}_3]^-\) resists attack by dry HCl, the silicon and germanium analogs are cleaved to \([\text{ClW(OCO)}_5]-\) (49). An interesting reaction is the I\(_2\) cleavage of one Sn–Me bond in Me\(_3\)SnRuCl(\(p\)-tolyl) to give \((\text{ClMe}_2\text{Sn})\text{Ru}(\text{I})(\text{CO})(\text{CNR})(\text{PPh}_3)_2\). The final product involves the migration of chlorine from ruthenium to tin. Treatment of this chloro derivative with aqueous KOH affords a rare transition-metal hydroxo-tin derivative, \((\text{HOMe}_2\text{Sn})\text{Ru}(\text{I})(\text{CO})(\text{CNR})(\text{PPh}_3)_2\), which in turn reacts with \(\text{H}_2\text{S}\) to form \((\text{HSMe}_2\text{Sn})\text{Ru}(\text{I})(\text{CO})(\text{CNR})(\text{PPh}_3)_2\) (254).

It is apparent from the above example that, once formed, the various Sn–halogen bonds in transition-metal stannanes are subject to the normal substitution chemistry of such
17. Transition metal complexes of germanium, tin and lead

species. Typical transformations are outlined in equations 160, 161 and 162.

\[
\begin{align*}
((\text{CO})_5\text{MnSnPh})_{n-1} \text{Cl}_3^{-} + \text{LiC}_6\text{F}_5 & \rightarrow ((\text{CO})_5\text{MnSnPh})_{n-1}(\text{C}_6\text{F}_5)_3^{-} \quad (160) \\
((\text{CO})_5\text{M}_2\text{SnCl}_2 + i-\text{Bu}_2\text{AlH} & \rightarrow ((\text{CO})_5\text{M}_2\text{SnH}_2 \quad (161) \\
\text{M} = \text{Mn, Re} \\
\text{Cp(L)}\text{NiSnCl}_3 + \text{PbEt}_4 & \rightarrow \text{Cp(L)}\text{NiSnEt}_3 \quad (162) \\
\text{L} = \text{PR}_3, \text{AsR}_3, \text{CyNC}
\end{align*}
\]

In equation 160, similar substitution by Ph groups may be effected using HgPh, and halogen substitution in \((\text{CpFe})_2\text{SnR}_2\text{X}\) \(\{\text{X} = \text{I, Br, R} = \text{CH_3(SiMe}_3\}_2\}\) occurs upon treatment with NaOMe, K[HBEt3] or [Bu4N]F to give [Cp2(MoSnR2)(OMe)], [Cp(CO)2FeSnR2H] and [Cp(CO)2FeSnR2F], respectively. The hydride reacts with benzoyl chloride to form [Cp2(MoSnR2)Cl].

6. Reactions at the transition metal center

There are many reactions of metal–tin complexes where the tin group is a spectator ligand. The majority of these reactions are simple ligand substitutions, typified by the chemistry outlined in equations 163, 164, 165.

\[
\begin{align*}
\text{Cp(CO)}_2\text{FeSnR}_3 + \text{L} & \rightarrow \text{Cp(CO)(L)FeSnMe}_3 + \text{CO} \quad (163) \\
\text{R} = \text{Me, Ph, Cl; L} = \text{PR}_3 \quad \{\text{R'} = \text{Ph, OPh}, \text{Ph}_2\text{C}_2\} \\
\text{[Cp}_2\text{(PhCH=CH}_2\text{)NbSnMe}_3 + \text{L} & \rightarrow \text{[Cp}_2\text{(L)NbSnMe}_3 + \text{PhCH=CH}_2 \quad (164) \\
\text{L} = \text{CO, MeCN, 1,3,5-Me}_2\text{C}_6\text{H}_3\text{CN}, \text{PMe}_3 \}
\end{align*}
\]

Hydride abstractions (equations 166 and 167) and oxidative additions to form mixed silyl/stannyl complexes are also reported.

\[
\begin{align*}
\text{[Cp}_2\text{(H)NbSnMe}_3 + \text{KH} & \rightarrow \text{[K(crown)][Cp}_2\text{(H)NbSnMe}_3 \quad (166) \\
\{(\eta^6-\text{arene})\text{(CO)}_2\text{Cr(H)SnPh}_3 + \text{KH} & \rightarrow \text{K(\eta^6-\text{arene})(CO)}_2\text{CrSnPh}_3 \quad (167) \\
\text{arene} = \text{C}_6\text{H}_6, 1,3,5-\text{Me}_3\text{C}_6\text{H}_3, 1,2,4,5-\text{Me}_4\text{C}_6\text{H}_2 \text{and Me}_4\text{C}_6 \\
\text{Cp(CO)}_2\text{FeSnPh}_3 + \text{HSiR}_3 & \rightarrow \text{Cp(CO)Fe(SnPh}_3)(\text{SiR}_3)\text{H} \quad (168) \\
\text{R}_3 = \text{Ph}_3, \text{MePh}_2, \text{P(OPh)}_3, \text{AsPh}_3 \text{and SbPh}_3, \text{PMe}_3 \\
\text{Photochemical reaction of Cp(CO)}_2\text{FeSnPh}_3 \text{with diphenylacetylene gave 39\% carbonyl substitution product Cp(CO)(PhC=CHPh)FeSnPh}_3 \text{and 10\% 2,3-diphenylindanone.} \quad (169)
\end{align*}
\]

Similarly, the CO groups in Ph3SnCo(CO)4, (CO)3SnCo(CO)4 and Bu2Sn[Co(CO)_4]2 can be replaced by both mono- and bidentate phosphines (L) and in the latter case can lead to new cluster. While the tin is usually unaffected by these substitutions, such chemistry can sometimes be used to synthesize further metal–tin complexes. Thus, the deprotonation of Cp2(H)MoSnPh3 with BuLi gives Li[Cp2MoSnPh3], which on further treatment with ClSnMe3 yields Cp2Mo(SnPh3)(SnMe3).
The formation of transition-metal carbene complexes containing tin substituents on the metal is another example where the tin group is a spectator ligand (equations 169–171) 395–401.

\[
\text{Cp(CO)}_3\text{MSnPh}_3 + (a)\text{LiPh}/(b)\text{Et}_3\text{O}^+ \rightarrow \text{Cp(CO)}_2[\text{Ph(ETO)}]\text{MSnPh}_3
\]

\[
M = \text{Mo, W; Cp = C}_5\text{H}_5, C_5\text{H}_4\text{Me and indenyl(η}_5\text{-C}_9\text{H}_7)\]

\[
[\text{CpM(SnPh}_3)(\text{CO})(\text{COCH}_2\text{R})]^− + \text{AcCl} \rightarrow [\text{CpM(SnPh}_3)(\text{CO})(\text{C(OCOMe)}\text{CH}_2\text{R})]^{-}
\]

\[
\text{CpM(SnPh}_3)(\text{CO})(\text{C = CHR}) + \text{AcOH}
\]

\[
M = \text{Fe, Ru; R = H, Me, Pr, Ph}
\]

\[
(\text{CO})_3\text{ReSnPh}_3 + (a)\text{LiR}/(b)[\text{Et}_3\text{O}]^+[\text{BF}_4]^{-} \rightarrow \text{cis-(CO)}_4\text{ReSnPh}_3[\text{C(OEt)}\text{R}]
\]

\[
R = \text{Ph, NEt}_2, \text{N(Pr-i)}_2, \text{C}_6\text{H}_4\text{NMe}_2-4
\]

Methylamine and \(\text{Cp(CO)(CS)FeSnPh}_3\) react to give \(\text{Cp(CO)(C = NMe)FeSnPh}_3\), without affecting the Sn−Fe bond; under similar conditions ethylenediamine also forms a carbene complex (equation 172) 402.

\[
\text{Fe CO SnPh}_3
\]

\[
\text{Fe C = NMe SnPh}_3
\]

An unusual carbyne complex \(\text{Ph}_3\text{SnM(CO)}_4(\text{CNMe}_2)\) was obtained from the reaction of \([\text{Et}_4\text{N}]_2(\text{CO})_4\text{M(SnPh}_3)_2\)] (\(M = \text{Cr, Mo}\)) with \([\text{Me}_2\text{NCCl}_2]\text{Cl}\) 187.

The reaction of \(\text{Cp(CO)}_3\text{MSnPh}_3\) (\(M = \text{Mo, W}\)) with organolithium reagents produced carbene complexes of the type \(\text{Cp(CO)}_2\text{MC(OR')R}\) (\(R = \text{Me, Ph, R'} = \text{Me, Et}\)) 395.

7. Stannyl group migrations

The treatment of \(\text{Cp(CO)}_3\text{MSnR}_3\) (\(M = \text{Mo, W}\)) with lithium diisopropylamide (LDA) results in deprotonation of the cyclopentadienyl ring, followed by migration of the SnR3 group to the organic ring; after quenching the metallate anion with methyl iodide the product \((\eta^5\text{-R}_3\text{SnC}_3\text{H}_4)\text{M(CO)}_3\text{Me}\) can be isolated (see, for example, equation 52 for the related germanium migration) 403. Treatment of \([\text{CpM(CO)}_3]_2\text{SnMe}_2\) (\(M = \text{Mo, W}\)) with LDA results in double migration products (equation 173), but with one equivalent of LDA a single migration product can be isolated 155. Similar single and double migrations occur from Fe to the cyclopentadienyl group when the analogous Fe complexes \(\text{CpFe(CO)}_2\text{SnR}_3\) (\(R = \text{Me, Ph}\)) are treated with LDA 404.
Triphenylstannyl group migration also occurs on treatment of ethoxy carbene complexes of the type Cp(CO)₂{PhC(OEt)}MSnPh₃ (M = Mo or W) with LDA/HMPA, with formation of carbyne complexes [(η⁵-Ph₃SnC₅H₄)(CO)₂CPh], after treatment with PhC(O)Cl₄⁰⁵.

8. Photolytic reactions

Several miscellaneous reactions involving photolysis of metal–tin complexes have been reported. In the presence of carbon dioxide the photolysis of [Cp₂(PhCH=CH₂)NbSnMe₃] yields a mixture of [Cp₂(CO)NbSnMe₃] and [(Cp₂NBnMe₃)₂(μ-O)] by cleavage of the CO₂ molecule. Photolysis of Cp(CO)₂FeSnMe₃ in a stream of butadiene in benzene solution gave [Me₃SnFe(CO)₂C₄H₆]. Similarly prepared was Cp(C₄H₆)FeSnPh₃. UV irradiation of [(η⁵-C₇H₈R)(CO)₃CrSnPh₃ (C₇H₈, cyclopentadienyl; R = H, CPh₂)] with two equivalents of 2-butyne or 3-hexyne gave tricyclic complex compounds, by reactions in the organic side groups, with loss of the Cr–SnPh₃ moieties.

9. Other reactions

The reaction of [Et₄N]₂[(CO)₄M(SnPh₃)₂] (M = Cr, Mo) with acetic acid gave a 40% yield of the protonated product [Et₄N][H(CO)₄M(SnPh₃)₂]¹⁶. Also, the complexes [(CO)₃M(SnPh₃)₃]⁻³ are protonated by Bronsted acids to form [H(CO)₃M(SnPh₃)₃]⁻² (M = Cr, Mo, W)¹⁹⁷.

Reaction of the anionic complexes [Cp₂MSnPh₃]⁻ (M = Mo, W) with HgX₂ (X = Br, I) in THF results in the formation of di- and trinuclear compounds Cp₂(M₃SnHgX or [Cp₂(P₃SnM)₂Hg, without M–Sn bond cleavage. Similarly, with ZnBr₂ and CdCl₂ the trinuclear complexes [Cp₂(P₃SnM)₂M']₂M' (M' = Zn, Cd) were formed.

The lability of the Sn–C bond in metal complexes is further illustrated by an interesting methyl group migration between osmium and tin. Treatment of Me₃SnOsCl(CO)(PPh₃)₂ with either pyridine or sodium acetate resulted in the formation of (ClMe₂SnOs(Me)(py)(CO)(PPh₃)₂ and (AcOMe₂SnOs(Me)(CO)(PPh₃)₂, respectively. Furthermore, the migration is reversible and treatment of (ClMe₂Sn)Os(Me)(py)(CO)(PPh₃)₂ with carbon monoxide yields Me₃SnOsCl(CO)(PPh₃)₂.

10. Synthetic utility of tin copper and tin zinc compounds

Trimethylstannyl cuprates are reactive toward unsaturated compounds and numerous organic syntheses involve their use as reagents, forming organotin derivatives which can be further converted into a broad variety of compounds. This topic is beyond the scope of this review, but the variety of reactions is briefly noted below. Thus, (R₃Sn)₂CuLi reacts with triple bonds of alkynes, acetylenic esters, acrylates (R = Bu), acetylene (R = Ph), with formation of vinylstannanes or allenes or with carbonylolefins (R = Me).
The reagents $\text{Me}_3\text{SnCu\cdot SMe}_2$ or $[\text{Me}_3\text{SnCuSPh}]\text{Li}$ react with alkynes to form stannylalkenes and related tin–copper reagents are also used for the stannylation of allenes.

The reagents $(\text{Bu}_3\text{Sn})_2\text{CuCNLi}_2$ and $(\text{Bu}_3\text{Sn})_2\text{CuCNLi}_2\cdot 2\text{LiCl}$ afford stannylcupration of terminal alkynes, acetylenes, allenes, enynes, propargylamines, enynols, enynals, acetylenic silyl ketones, propargylic sulfides, acetylenic ethers and aminoacetylenic ethers.

Organotin–zinc derivatives can be used as reagents in organic synthesis. Thus, the stannyl zincate complex $\text{Me}_3\text{Sn}()_2\text{Et}_2\text{ZnLi}$ reacts with alkoxy-unsaturated ketones to form five-membered ring heterocycles.

D. Reactivity of Metal Stannynes

The stannylene complexes $\text{CpR}(\eta^2\text{-C}_2\text{H}_4)\text{CoSn[CH(SiMe}_3\text{)]}_2$ ($\text{CpR = C}_5\text{H}_5$, $\text{C}_5\text{Me}_5$) react with 2-butyne to give different products. Thus, the $\text{C}_5\text{H}_5$ derivative affords hexamethylbenzene, the free stannylene and $\text{CpCo}(\eta^6\text{-C}_6\text{Me}_6)$ (equation 174) whereas in the similar reaction the $\text{C}_5\text{Me}_5\text{Co}$ derivative gives a stannacyclopentadiene complex (equation 175).

The hydroxo hydrido stannylene complex $\text{Co(\mu-OH)}(\text{H})\text{Co[Sn[CH(SiMe}_3\text{)]}_2\text{]}_2$ and its deuteriated analog were obtained by treating the ethylene complex $\text{Cp(\eta^2\text{-C}_2\text{H}_4)Co[Sn[CH(SiMe}_3\text{)]}_2\text{]}_2$ with $\text{H}_2\text{O}$ or $\text{D}_2\text{O}$.
### TABLE 11. X-ray crystal structures: compounds with M–Sn single bonds

<table>
<thead>
<tr>
<th>Compound</th>
<th>M–Sn bond length (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[K(15-crown-5)][(η⁵-C₅H₇CO)₂TiSnMe₃]⁺</td>
<td>2.868</td>
<td>237</td>
</tr>
<tr>
<td>[K(crypt-2.2.2)][C₅₃SnTi(CO)₆]</td>
<td>2.921</td>
<td>184</td>
</tr>
<tr>
<td>Cp₂Ti(SnPh₃)</td>
<td>2.843</td>
<td>439</td>
</tr>
<tr>
<td>[Pr₃N]₂[(CO₃)₂Zr(SnPh₃)₄]</td>
<td>3.086</td>
<td>234</td>
</tr>
<tr>
<td>[K(15-crown-5)][Zr(CO₃)₅(SnMe₃)₂]</td>
<td>3.012</td>
<td>328</td>
</tr>
<tr>
<td>[Pr₃N]₂[(CO₃)₄Hf(SnPh₃)₄]</td>
<td>3.063</td>
<td>234</td>
</tr>
<tr>
<td>Cp₂HNBn(SnMe₃)Cl₂</td>
<td>2.802–2.811</td>
<td>243</td>
</tr>
<tr>
<td>(Me₂SiC₅H₄)₂(H₂)Nb(SnPh₃)</td>
<td>2.830</td>
<td>440</td>
</tr>
<tr>
<td>(CO)₆V(SnMe₃)</td>
<td>2939</td>
<td>441</td>
</tr>
<tr>
<td>Cp(NBu-t)VSn(SiMe₃)₃Ph₃(NHBu-t)</td>
<td>2.767</td>
<td>442</td>
</tr>
<tr>
<td>[CP₅NB]₂(SnMe₃)₂(µ-µ-O)</td>
<td>2.862</td>
<td>387</td>
</tr>
<tr>
<td>[K(18-crown-6)][CP₂Nb(SnMe₃)₂]</td>
<td>2.817–2.830</td>
<td>190</td>
</tr>
<tr>
<td>(1,3,5-Me₂C₅H₄)₂(CO₂)₂Cr(SnPh₃)</td>
<td>2.703–2.720</td>
<td>247</td>
</tr>
<tr>
<td>(FC₅H₅)₂(CO₂)₂Cr(SnPh₃)</td>
<td>2.676–2.704</td>
<td>247</td>
</tr>
<tr>
<td>(1,4-F₂C₅H₄)₂(CO₂)₂Cr(SnPh₃)</td>
<td>2.700–2.714</td>
<td>247</td>
</tr>
<tr>
<td>[K(crypt)][Sn₆(Cr(CO)₅)₆]</td>
<td>2.604–2.611</td>
<td>443</td>
</tr>
<tr>
<td>[Ph₃P]₂[Sn(Cr(CO)₅)₅]</td>
<td>2.659–2.670</td>
<td>444</td>
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<tr>
<td>Sn[Cr(CO₃)₂(1,10-phen)-THF]</td>
<td>2.636; 2.647</td>
<td>445</td>
</tr>
<tr>
<td>Sn[Cr(CO₃)₂(bipy)]</td>
<td>2.619; 2.622</td>
<td>445</td>
</tr>
<tr>
<td>Sn[Cr(CO₃)₂Py₂]</td>
<td>2.603; 2.618</td>
<td>445</td>
</tr>
<tr>
<td>[Ph₃P]₂[2Br₂Sn(Cr(CO)₅)]</td>
<td>2.809</td>
<td>446</td>
</tr>
<tr>
<td>[Bu₄N]₂[Br₂Sn(Cr(CO)₅)]</td>
<td>2.640; 2.643</td>
<td>446</td>
</tr>
<tr>
<td>[Bu₄N]₂[Br₂Sn(Cr(CO)₅)]</td>
<td>2.560</td>
<td>446</td>
</tr>
<tr>
<td>[HPPH₃]₂[Cl₃SnCr(CO)₅]</td>
<td>2.583</td>
<td>446</td>
</tr>
<tr>
<td>(η⁶-C₆H₆)₂(CO)₂CrSnPh₂Cl</td>
<td>2.636; 2.647</td>
<td>200</td>
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<tr>
<td>[(MeO)₃P]₃(CO)₂ClMoSnBuCl₂</td>
<td>2.774</td>
<td>447</td>
</tr>
<tr>
<td>Cp₂Mo(SnPh₃)</td>
<td>2.754</td>
<td>394</td>
</tr>
<tr>
<td>Cp₂Mo(SnPh₃)(CH₂)₄OSiMe₃</td>
<td>2.769</td>
<td>394</td>
</tr>
<tr>
<td>(MeCOC₅H₅)₂(CO)₃MoSnBuCl₂</td>
<td>2.736</td>
<td>448</td>
</tr>
<tr>
<td>(MeCOC₅H₅)₂(CO)₃WSnCl₃</td>
<td>2.736</td>
<td>448</td>
</tr>
<tr>
<td>Cp₂W(SnPh₃)COPh</td>
<td>2.776</td>
<td>449</td>
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<tr>
<td>Cp₂W(SnPh₃)(Sn(Bu-t)₂Cl)</td>
<td>2.799; 2.811</td>
<td>449</td>
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<tr>
<td>Cp₂W(SnPh₃)(HgI)</td>
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<td>408</td>
</tr>
<tr>
<td>CH₂(3,5-Me₂Pz)₃(CO)₃ClWSnCl₃</td>
<td>2.741</td>
<td>448</td>
</tr>
<tr>
<td>(CO)₃(closo-C₂B₆H₆)₃W(SnPh₃)</td>
<td>2.825</td>
<td>450</td>
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<tr>
<td>O(SiMe₂O)₃SnBu-t(W(CO)₃Cp)</td>
<td>2.779</td>
<td>451</td>
</tr>
<tr>
<td>[Mn₂(μ-H)(μ-SnPh₃)₂]CO₆(μ-(EtO)₂)POP(OEt)₂]</td>
<td>2.605; 2.618</td>
<td>240</td>
</tr>
<tr>
<td>[(CO)₃(Ph₃Sn)Re(S₂CPC₅H₅)Mo(CO)₃]</td>
<td>2.762; 2.763</td>
<td>452</td>
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<tr>
<td>trans-(CO)₂CpRe(SnPh₃)</td>
<td>2.731; 2.734</td>
<td>257</td>
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<tr>
<td>[Cp(CO)₂Fe]₂SnOH</td>
<td>2.612–2.615</td>
<td>453</td>
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<tr>
<td>[Cp(CO)₂Fe]₂SnCl₂</td>
<td>2.505</td>
<td>454</td>
</tr>
<tr>
<td>[Cp(CO)₂Fe]₂Sn(N₃)₂</td>
<td>2.503</td>
<td>455</td>
</tr>
<tr>
<td>[Cp(CO)₂Fe]₂SnTePh₂</td>
<td>2.578; 2.582</td>
<td>454</td>
</tr>
<tr>
<td>(PhCH=CH)₂(CO)₂F(C₅H₅)SnPh₃</td>
<td>2.557</td>
<td>398</td>
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<tr>
<td>[Fe(CO)₂(dppm)(μ-SnBu₂)]</td>
<td>2.645; 2.674</td>
<td>456</td>
</tr>
<tr>
<td>mer-(PPh₃)₃(CO)₃Fe(SnMe₂Cl)</td>
<td>2.592</td>
<td>249</td>
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</table>

(continued overleaf)
**TABLE 11. (continued)**

<table>
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<tr>
<th>Compound</th>
<th>M—Sn bond length (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NO)(CO)(_3)FeSnPh(_2)Cl</td>
<td>2.576; 2.589</td>
<td>457</td>
</tr>
<tr>
<td>(NO)(CO)(_3)FeSnPh(_3)</td>
<td>2.620</td>
<td>457</td>
</tr>
<tr>
<td>mer, cis-[((CO)(_3)(dpmm)Fe(SnPh(_2)Cl)(_2)]</td>
<td>2.603; 2.608</td>
<td>458</td>
</tr>
<tr>
<td>(1-Me-3-Ph-allyl)(CO)(_3)FeSnMe(_3)</td>
<td>2.624</td>
<td>225</td>
</tr>
<tr>
<td>O(SiMe(_2)O)(_2)Sn(Fe(CO)(_2)Cp)(_2)</td>
<td>2.518</td>
<td>451</td>
</tr>
<tr>
<td>(PPh(_3))(_2)(CO)ClRuSnMe(_3)</td>
<td>2.603</td>
<td>280</td>
</tr>
<tr>
<td>(i-Pr-DAB)(CO)(_3)Ru(SnPh(_3))(_2)</td>
<td>2.686; 2.691</td>
<td>459</td>
</tr>
<tr>
<td>(i-Pr-DAB)(CO)(_2)(Cl)Ru(SnPh(_3))(_2)</td>
<td>2.652</td>
<td>459</td>
</tr>
<tr>
<td>(i-Pr-DAB)(CO)(_2)Ru(SnPh(_3))(_2)</td>
<td>2.658</td>
<td>460</td>
</tr>
<tr>
<td>(µ-CH(_2))(_2){(CO)CpRu}(_2)(SnMe(_3))(_2)</td>
<td>2.649</td>
<td>461</td>
</tr>
<tr>
<td>Ru(_3)(CO)(_9)(µ-Sn(C(_6)H(_2)(Pr-i)(_3)-2,4,6)(_2))(_3)</td>
<td>2.713–2.756</td>
<td>462</td>
</tr>
<tr>
<td>[(CO)(_4)OsSnMe(_2)](_2)</td>
<td>2.758; 2.677</td>
<td>211</td>
</tr>
<tr>
<td>O(_3)(SnMe(_2))(_2)(CO)(_9)</td>
<td>2.677–2.780</td>
<td>331</td>
</tr>
<tr>
<td>O(_4)(SnMe(_2))(_4)(CO)(_14)</td>
<td>2.666–2.673</td>
<td>331</td>
</tr>
<tr>
<td>O(_4)(µ(_3)-O)(_2)(SnMe(_2))(_4)(CO)(_14)</td>
<td>2.666–2.673</td>
<td>331</td>
</tr>
<tr>
<td>Sn[Co(CO)(_4)](_3)Cl</td>
<td>2.650; 2.671</td>
<td>467</td>
</tr>
<tr>
<td>[(PPh(_3))(_2)Cl]Sn[Co(CO)(_4)]</td>
<td>2.758; 2.677</td>
<td>211</td>
</tr>
<tr>
<td>[(PPh(_3))(_2)Cl]Sn[Co(CO)(_4)]</td>
<td>2.677–2.687</td>
<td>463</td>
</tr>
<tr>
<td>ClSn[Co(CO)(_4)]</td>
<td>2.602; 2.607</td>
<td>464</td>
</tr>
<tr>
<td>Cl(_2)Sn[Co(CO)(_4)]</td>
<td>2.531–2.534</td>
<td>465</td>
</tr>
<tr>
<td>(PPh(_3))(_2)(CO)(_2)CoSnMe(_3)</td>
<td>2.574</td>
<td>214</td>
</tr>
<tr>
<td>(AsPh(_3))(CO)(_3)CoSnMe(_3)</td>
<td>2.565</td>
<td>214</td>
</tr>
<tr>
<td>[(CO)(_4)Co](_2)Sn(µ-Sn)[Co(CO)(_4)]</td>
<td>2.591</td>
<td>466</td>
</tr>
<tr>
<td>[(CO)(_4)Co](_2)Sn(µ-Se)[Co(CO)(_4)]</td>
<td>2.593</td>
<td>466</td>
</tr>
<tr>
<td>Ph(_2)P(CH(_2))(_3)PPb(_2)(COD)RhSnCl(_3)</td>
<td>2.650; 2.671</td>
<td>467</td>
</tr>
<tr>
<td>(PCy(_3))(CO)(_3)IrSnPh(_3)</td>
<td>2.661</td>
<td>468</td>
</tr>
<tr>
<td>[P(Et(_2))CpNi](_2)SnCl(_2)</td>
<td>2.464</td>
<td>322</td>
</tr>
<tr>
<td>[(P(Et(_2))CpNi](_2)SnCl</td>
<td>2.519–2.529</td>
<td>322</td>
</tr>
<tr>
<td>cis-(PMe(_3))(_2)Pd(SnMe(_2))</td>
<td>2.604; 2.607</td>
<td>469</td>
</tr>
<tr>
<td>(i-Pr(_2))PCH(_2)CH(_2)(P-(Pr-i)(_2))PdSnR(_2)CHCH</td>
<td>2.670</td>
<td>470</td>
</tr>
<tr>
<td>(P(Tol-(_3))(_2))Pt(SnMe(_3))</td>
<td>2.629</td>
<td>471</td>
</tr>
<tr>
<td>(PPh(_3))(_2)ClPtSnCl(_3)</td>
<td>2.591</td>
<td>472</td>
</tr>
<tr>
<td>(HBPz(_3))Me(_2)PtSnMe(_3)</td>
<td>2.573</td>
<td>473</td>
</tr>
<tr>
<td>[Bu(_4)N][PtCl(_3)](_2)(Sn(Ph(_2))(_2)Sn)</td>
<td>2.703–2.744</td>
<td>474</td>
</tr>
<tr>
<td>Me(_2)Pt(SnMe(_2)SSnMe(_2)S)(t-Bu (_2) (_2) bipy)</td>
<td>2.552</td>
<td>475</td>
</tr>
<tr>
<td>[Me(_2)Pt(SnMe(_2)Cl)(t-Bu (_2) (_2) bipy)]BF(_4)</td>
<td>2.541</td>
<td>476</td>
</tr>
<tr>
<td>(Me(_2)phen)(CH(_2)CH(_2))Cl)PtSnPh(_3)Cl</td>
<td>2.534</td>
<td>477</td>
</tr>
<tr>
<td>[(C(_6)F(_5))(_3)GeHg][(PPh(_3))(_2)PtSn(C(_6)F(_3))(_3)]</td>
<td>2.518</td>
<td>346</td>
</tr>
<tr>
<td>cis-(PPh(_3))(_2)HPTsSnPh(_3)</td>
<td>2.564</td>
<td>478</td>
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</table>

![Diagram](image-url)
TABLE 11. (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>M–Sn bond length (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnMe2</td>
<td>2.596; 2.605</td>
<td>273</td>
</tr>
<tr>
<td>SnMe2</td>
<td>2.644; 2.645</td>
<td>274</td>
</tr>
<tr>
<td>SnMe2</td>
<td>2.597</td>
<td>480</td>
</tr>
</tbody>
</table>

\[ ^a \text{C}_{10}\text{H}_8 = \text{naphthalene.} \quad ^b \text{Pz} = \text{pyrazine.} \quad ^c \text{DAB} = 1,4\text{-diaza-1,3-butadiene.} \quad ^d \text{COD} = \text{cyclooctadiene.} \]

TABLE 12. X-ray crystal structures: stannylene complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>M–Sn bond length (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp₂Zr{[Sn(CH(SiMe₃)₂]₂}₂</td>
<td>2.871</td>
<td>481</td>
</tr>
<tr>
<td>cis-(CO)₂Cr{[Sn(N(SiMe₃)₂]₂}₂</td>
<td>2.5552; 2.566</td>
<td>482</td>
</tr>
<tr>
<td>(CO)₅Cr:SnRR'</td>
<td>2.614</td>
<td>300</td>
</tr>
<tr>
<td>(CO)₅Mo:SnRR'</td>
<td>2.755</td>
<td>300</td>
</tr>
<tr>
<td>R = 2, 4, 6-(t-Bu)₃C₆H₂, R' = CH₂CMe₃-3, 5-(t-Bu)₂C₆H₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cp₂HCl₂W:Sn{CH(SiMe₃)₂]₂}₂</td>
<td>2.706</td>
<td>483</td>
</tr>
<tr>
<td>{[η⁵-tol]₁(µ-OH)(H)Fe:Sn{CH(SiMe₃)₂]₂}₂</td>
<td>2.524</td>
<td>436</td>
</tr>
<tr>
<td>(t-Pr)₂PCH₂CH₂P(Pr-ι)₂Pd:Sn{CH(SiMe₃)₂]₂}₂</td>
<td>2.481(2)</td>
<td>470</td>
</tr>
</tbody>
</table>

Insertion of sulfur and selenium into the Co–Sn bonds of CpR(η²-C₂H₄)Co{Sn[CH(SiMe₃)₂]₂}₂ (CpR = C₅Me₅, C₅Me₄Et) give ternary Sn—Q—Co cluster compounds of the type Cp Co(µ-Q)₂Sn[CH(SiMe₃)₂]₂ (Q = S, Se), which can support reversibly either the removal or the addition of one electron (equation 176)³⁰¹,⁴³⁷.

\[
\begin{align*}
\text{Cp} & \text{Co(Sn(SiMe₃)₂)₂ + 2 S} \rightarrow \text{Cp} \text{Co(SnS(SiMe₃)₂)₂ (176)} \\
\end{align*}
\]
Some further reactions are of interest. Thus, the dimer \{\text{CpNiSn[CH(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{2}}\}\textsubscript{2} reacts with water to cleave a Ni−Sn bond with formation of \text{CpNiSn[CH(SiMe\textsubscript{3})\textsubscript{2}]OH}, which contains a Sn−OH−Sn bridge; the reaction with MeCN leads to cleavage of a Ni−Sn bond, elimination of a stannylene molecule and formation of \text{Cp(MeCN)NiSn[CH(SiMe\textsubscript{3})\textsubscript{3}]OH}\textsuperscript{20}.

The nickel stannylene complex \{(C\textsubscript{2}H\textsubscript{4})\textsubscript{2}NiSn[CH(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{2}\} reacts with 1,6-heptadiene with conservation of the Ni:Sn bond to form \(\eta^2,\eta^2\text{-C}_7\text{H}_{12}\text{NiSn[CH(SiMe\textsubscript{3})\textsubscript{2}]_2}\) in quantitative yield\textsuperscript{317,438}. Both compounds react with butadiene, isoprene, PMe\textsubscript{3} and BPh\textsubscript{3} to give a variety of compounds which preserve the Ni−Sn bond\textsuperscript{438}.

The structural aspects of tin–transition metal complexes are well studied. Some recent examples of metal–tin single and double bonded complexes are provided in Tables 11 and 12.

V. ORGANOLEAD TRANSITION METAL COMPLEXES

Although the first transition metal–lead compounds were reported in 1941, their chemistry is less explored compared to the −silicon, −germanium and −tin analogs. This is predominantly due to a lesser stability, since they are prone to decompose thermally and this process is accelerated in the presence of light. Secondarily, it is important to recognize that organolead hydrides are largely unknown, or very unstable. As noted in the previous sections, both germyl and stannyl hydrides are important reagents for the formation of transition-metal complexes, therefore it is not surprising that less chemistry is reported for lead systems. There appear to be no significant reviews of the chemistry of the metal–lead bond.

A. Synthesis of the Transition Metal Lead Single Bond

Table 13 gives information on the availability of spectroscopic and crystallographic data for selected mononuclear transition metal–lead compounds and Table 14 gives similar data for the binuclear/polynuclear compounds.

1. Salt-elimination reactions between transition metallates and lead halides

The salt-elimination reaction involving the use of a transition metallate and organolead halides has been widely used to form metal–lead complexes (equations 177–179) and a range of such derivatives have been prepared for many metals, i.e. Cr\textsuperscript{7,484,485}, Mo\textsuperscript{7,484,485}, W\textsuperscript{7,484,485}, Mn\textsuperscript{35,486,487}, Re\textsuperscript{35}, Fe\textsuperscript{3,485,488−494}, Os\textsuperscript{37}, Co\textsuperscript{22,492}, Rh\textsuperscript{495} and Ir\textsuperscript{495}. The reaction of \(\text{Na}_2\{\text{M}_2(\text{CO})\textsubscript{10}\}\) (\(\text{M}=\text{Cr, Mo, W}\)) with PbX\textsubscript{2} resulted in the isolation of mononuclear anions \[\text{M}(\text{CO})\textsubscript{5}PbX\textsubscript{3}\] along with the formation of binuclear dianions \[\text{M}(\text{CO})\textsubscript{5}PbX\textsubscript{2}\]\textsuperscript{2−}, stabilized as their Ph\textsubscript{4}P\textsuperscript{+} or Bu\textsubscript{4}N\textsuperscript{+} salts (equation 179)\textsuperscript{496}.

\[
\begin{align*}
\text{M}^-\text{Na}^+ + \text{ClPbR}_3 & \rightarrow \text{M}^+\text{PbR}_3 + \text{NaCl} \\
(M=\text{Cr, Mo, W}) & R=\text{Me, Et, Ph} \\
[(\text{CO})\textsubscript{5}\text{Mn}]^-\text{Na}^+ + \text{Me}_3\text{PbCl} & \rightarrow (\text{CO})\textsubscript{5}\text{MnPbMe}_3 + \text{NaCl} \\
[M_2(\text{CO})\textsubscript{10}]^{2−} & \rightarrow [M(\text{CO})\textsubscript{5}PbX\textsubscript{3}]^- + [(M(\text{CO})\textsubscript{5})_2PbX\textsubscript{2}]^{2−}
\end{align*}
\] (177) (178) (179)
TABLE 13. Selected mononuclear transition metal–lead compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Available data</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(CO)₆PbPh₃</td>
<td>IR, ⁵¹V NMR, X-ray</td>
<td>505, 526</td>
</tr>
<tr>
<td>CpCr(CO)₃PbMe₃</td>
<td>IR, NMR</td>
<td>484</td>
</tr>
<tr>
<td>CpCr(CO)₃PbEt₃</td>
<td>IR, NMR</td>
<td>484</td>
</tr>
<tr>
<td>CpCr(CO)₃PbPh₃</td>
<td>IR, NMR</td>
<td>35</td>
</tr>
<tr>
<td>CpMo(CO)₃PbMe₃</td>
<td>IR, NMR</td>
<td>7, 484</td>
</tr>
<tr>
<td>CpMo(CO)₃PbEt₃</td>
<td>IR, NMR</td>
<td>484</td>
</tr>
<tr>
<td>CpMo(CO)₃PbPh₃</td>
<td>IR, NMR</td>
<td>7</td>
</tr>
<tr>
<td>CpW(CO)₃PbMe₃</td>
<td>IR, NMR</td>
<td>484</td>
</tr>
<tr>
<td>CpW(CO)₃PbEt₃</td>
<td>IR, NMR</td>
<td>484</td>
</tr>
<tr>
<td>CpW(CO)₃PbPh₃</td>
<td>IR, NMR</td>
<td>7</td>
</tr>
<tr>
<td>Mn(CO)₅PbMe₃</td>
<td>IR</td>
<td>486</td>
</tr>
<tr>
<td>Mn(CO)₅PbEt₃</td>
<td>IR</td>
<td>486</td>
</tr>
<tr>
<td>Mn(CO)₅PbPh₃</td>
<td>IR, NMR</td>
<td>35, 486</td>
</tr>
<tr>
<td>[Et₄N][Mn(CO)₄(PbPh₃)₂]</td>
<td>IR</td>
<td>497</td>
</tr>
<tr>
<td>Re(CO)₅PbPh₃</td>
<td>IR, NMR</td>
<td>35</td>
</tr>
<tr>
<td>[Et₄N][Re(CO)₄(PbPh₃)₂]</td>
<td>IR</td>
<td>497</td>
</tr>
<tr>
<td>CpFe(CO)₂PbMe₃</td>
<td>IR, NMR</td>
<td>493, 494</td>
</tr>
<tr>
<td>CpFe(CO)₂PbEt₃</td>
<td>IR, NMR</td>
<td>493, 494</td>
</tr>
<tr>
<td>CpFe(CO)₂PbPh₃</td>
<td>IR, NMR</td>
<td>493, 494</td>
</tr>
<tr>
<td>[Fe(CO)₄(PbPh₃)₂]</td>
<td>IR, NMR</td>
<td>493</td>
</tr>
<tr>
<td>CpFe(CO)₃PbCH(SiMe₃)₂I</td>
<td>IR, NMR</td>
<td>512</td>
</tr>
<tr>
<td>[Fe(CO)₂(dppe)(PbMe₃)Si(OEt)₃]</td>
<td>IR, NMR</td>
<td>527</td>
</tr>
<tr>
<td>Os(CO)₄(PbMe₃)₂</td>
<td>IR, NMR</td>
<td>37</td>
</tr>
<tr>
<td>Co(CO)₄PbMe₃</td>
<td>IR</td>
<td>492, 525</td>
</tr>
<tr>
<td>Co(CO)₄PbEt₃</td>
<td>IR, NMR</td>
<td>492, 525</td>
</tr>
<tr>
<td>Co(CO)₄PbPh₃</td>
<td>IR</td>
<td>22</td>
</tr>
<tr>
<td>[Et₄N][Co(CO)₃(PbPh₃)₂]</td>
<td>IR</td>
<td>498</td>
</tr>
<tr>
<td>(PF₃)₄IrPbPh₃</td>
<td>IR, NMR</td>
<td>495</td>
</tr>
<tr>
<td>(PPh₃)₂Pd(PbPh₃)₂</td>
<td>IR</td>
<td>507</td>
</tr>
<tr>
<td>trans-(PBu₃)₂Pt(PbPh₃)₂</td>
<td>NMR</td>
<td>508</td>
</tr>
<tr>
<td>trans-(PPh₃)₂Pt(PbPh₃)₂</td>
<td>IR</td>
<td>507</td>
</tr>
<tr>
<td>trans-(PET₃)₂Pt(PbPh₃)₂</td>
<td>IR</td>
<td>506</td>
</tr>
<tr>
<td>cis-(PPh₃)₂Pt(PbPh₃)₂Ph</td>
<td>IR, NMR, X-ray</td>
<td>507, 508</td>
</tr>
<tr>
<td>cis-(PPh₃)₂Pt(PbMe₃)₂Me</td>
<td>IR</td>
<td>507</td>
</tr>
<tr>
<td>(PPh₃)₂PtCl(PbPh₃)₂</td>
<td>IR</td>
<td>507</td>
</tr>
</tbody>
</table>

Highly reduced metal anions [M(CO)ₙ]³⁻ (M = Mn, Re; n = 4; M = Co, n = 3) react with two equivalents of Pb₃PbCl to provide anionic complexes that were isolated as crystalline ammonium salts (equation 180)⁴⁹⁷,⁴⁹⁸.

\[
[\text{Co(CO)}₃]³⁻3\text{Na}⁺ + 2\text{Pb}_3\text{PbCl} + \text{NH}_4\text{Cl} \rightarrow (\text{NH}_4)[\text{Co(CO)}₃(\text{PbPh}_3)₂] \quad (180)
\]

The reaction of [Fe₃(CO)₁₁]²⁻ with Pb₃PbCl in THF produced a unique iron cluster ¹¹⁵, which contains triangular Fe₃ core and a terminal Ph₃Pb group bonded to one of the Fe atoms, forming a linear Fe–Fe–Pb arrangement⁴⁹⁹.

The reaction of [Co(CO)₄]⁻Na⁺ and Pb(O₂CCH₃)₂ resulted in the formation of the cluster [Co(CO)₄]Pb containing four Co–Pb single bonds. The same material was also formed directly using metallic lead⁵₀⁰,⁵₀¹. A variety of anionic lead-iron clusters of different stoichiometry were obtained from the reaction of PbX₂ (X = Cl, O₂CCH₃) with [HFe(CO)₄]⁻ and their redox chemistry investigated⁵₀₂–⁵₀₄.
TABLE 14. Binuclear/polynuclear transition metal–lead compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Available data</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ph₄P]₂[Cr(CO)₅]₂Pb(O₂CCH₃)₂</td>
<td>IR, UV, MS, NMR, X-ray</td>
<td>496</td>
</tr>
<tr>
<td>[CpMo(CO)₃]₂PbPb₂</td>
<td>IR</td>
<td>525</td>
</tr>
<tr>
<td>[CpW(CO)₅]₂PbEt₂</td>
<td>IR, NMR</td>
<td>484, 525</td>
</tr>
<tr>
<td>[CpW(CO)₅]₂PbPh₂</td>
<td>IR, NMR</td>
<td>525</td>
</tr>
<tr>
<td>[Mn(CO)₅]₂PbMe₂</td>
<td>IR</td>
<td>486, 487</td>
</tr>
<tr>
<td>[Mn(CO)₅]₂PbEt₂</td>
<td>IR</td>
<td>486</td>
</tr>
<tr>
<td>[Mn(CO)₅]₂PbPh₂</td>
<td>IR</td>
<td>487</td>
</tr>
<tr>
<td>[Mn(CO)₅]₂PbBr₂</td>
<td>IR</td>
<td>487</td>
</tr>
<tr>
<td>[CpFe(CO)₂]₂PbMe₂</td>
<td>IR, NMR</td>
<td>493</td>
</tr>
<tr>
<td>[CpFe(CO)₂]₂PbEt₂</td>
<td>IR, NMR</td>
<td>493</td>
</tr>
<tr>
<td>[Fe(CO)₄PbMe₂]₂</td>
<td>IR, NMR</td>
<td>493</td>
</tr>
<tr>
<td>[Fe(CO)₄PbEt₂]₂</td>
<td>IR, NMR</td>
<td>493</td>
</tr>
<tr>
<td>[Fe(CO)₄PbPh₂]₁₂</td>
<td>IR, NMR</td>
<td>492, 516</td>
</tr>
<tr>
<td>[Fe(CO)₄Pb]₄</td>
<td>IR, NMR, X-ray</td>
<td>493, 503</td>
</tr>
<tr>
<td>[Co(CO)₄]₂PbPh₂</td>
<td>IR</td>
<td>492</td>
</tr>
<tr>
<td>[Co(CO)₃(PEt₃)]₄Pb</td>
<td>UV/vis, IR, MS, X-ray</td>
<td>500, 501</td>
</tr>
<tr>
<td>[Co(CO)₃(PEt₃)]₄Pb</td>
<td>IR</td>
<td>528</td>
</tr>
</tbody>
</table>

Heptacoordinated vanadium complexes of Pb were obtained by the direct reaction of V(CO)₆ with Ph₃PbCl in high yields (equation 181)

\[
4 \text{V(CO)}_6 + 3 \text{Ph}_3\text{PbCl} \rightarrow 3\text{(CO)}_6\text{VPbPh}_3 + \text{VCl}_3 + 6 \text{CO}
\]  

(181)

2. Synthesis from transition metal halides and organoplumbates

Complexes of Pd and Pt were synthesized by the reaction of cis- or trans- [ML₂Cl₂] (M = Pd or Pt; L = PEt₃ or AsEt₃) with triphenyllead lithium in ether at low temperature (equation 182). The red solution produced yellow crystalline solids of trans- [ML₂(PbPh₃)₂] complexes. These complexes are thermally stable; however, attempts to prepare the corresponding triphenylphosphine derivatives were unsuccessful.

\[
[\text{Pt(PEt}_3)_2\text{Cl}_2] + 2[\text{Ph}_3\text{Pb}]^-\text{Li}^+ \rightarrow \text{trans-[Pt(PEt}_3)_2(\text{PbPh}_3)_2] + 2 \text{LiCl}
\]  

(182)

3. Oxidative addition of Pb—Pb, Pb—C and Pb—Cl bonds to metal centers

The thermodynamic stability of lead–lead, lead–carbon and related bonds are considerably lower than those of their group 14 analogs Ge and Sn. Thus, the direct cleavage of such bonds in the presence of coordinatively unsaturated metal complexes presents a convenient route to the formation of a variety of metal–lead complexes (equations 183 and 184).
17. Transition metal complexes of germanium, tin and lead

\[(\text{Ph}_3\text{P})_4\text{Pt} + \text{Ph}_3\text{Pb} \rightarrow ((\text{Ph}_3\text{P})_2\text{Pt}(\text{PbPh}_3)_2) + 2 \text{Ph}_3\text{P}\]  \hspace{1cm} (183)

\[(\text{Ph}_3\text{P})_4\text{Pt} + \text{Ph}_4\text{Pb} \rightarrow ((\text{Ph}_3\text{P})_2\text{Pt}(\text{PbPh}_3)(\text{Ph})) + 2 \text{Ph}_3\text{P}\]  \hspace{1cm} (184)

The \(\text{Pb}−\text{Cl}\) bond of \(\text{R}_2\text{PbCl}_2\) (\(\text{R} = \text{Me}, \text{Ph}\)) added to the three-coordinate Pt(0) complexes \([\text{Pt}(\text{N}−\text{N})(\text{olefin})]((\text{N}−\text{N}) = \text{chelating nitrogen})\) to produce five-coordinate Pt(II) complexes \([\text{Pt}(\text{N}−\text{N})\text{Cl}(\text{R}_2\text{ClPb})(\text{olefin})]\). The isolation of these complexes was dependent upon the structure of the nitrogen base and the olefin.\(^5\)

Air-stable ruthenium complexes \([\text{Ru}(\text{Cl})(\text{EPh}_3)(\text{CO})_2(L−L)](L−L = N,N′-\text{diisopropyl}-1,4-\text{diaza}-1,3-\text{butadiene}, E = \text{Ge}, \text{Sn}, \text{Pb})\) were obtained by the decarbonylation of \(\text{Ru}(\text{CO})_3(L−L)\) followed by the oxidative addition of E−Cl to the 16e\(^−\) ruthenium complex (equation 185)\(^5\).

\[
\begin{array}{c}
\text{L}−\text{L}−\text{Ru}−\text{CO}−\text{CO}−\text{L}−\text{L} + \text{Cl}−\text{PbPh}_3 \rightarrow \text{L}−\text{L}−\text{Ru}−\text{CO}−\text{CO}−\text{Cl} + \text{CO} \\
\end{array}
\]  \hspace{1cm} (185)

4. Insertion of plumbylenes into a metal halogen bond

Addition of \(\text{PbR}_2\) to a benzene solution of iron complexes \([\text{CpFe}(\text{CO})_2\text{X}] (\text{X} = \text{I}, \text{Br}\) or Cl) resulted in the formation of four-coordinated functionalized Fe−Pb complexes, \([\text{CpFe}(\text{CO})_2(\text{PbR}_2\text{X})]\).\(^5\)

Ruthenium–lead clusters \(^{116}\) and \(^{117}\) containing bridging Pb atoms were obtained from the reaction of the plumbylene \([\text{Pb}\{\text{CH}(\text{SiMe}_3)_2\}_2]\) with \(\text{Ru}_3(\text{CO})_{12}\) in hexane at 60°C. Both clusters have a planar Ru\(_3\) triangle with bridging Pb and carbonyl ligands.\(^5\)

\[
\begin{array}{c}
\text{R}_2−\text{Pb}−\text{OC}−\text{Ru}−(\text{CO})_3 \quad \text{R}_2−\text{Pb}−\text{OC}−\text{Ru}−(\text{CO})_3 \\
\quad \text{(116)} \quad \text{(117)}
\end{array}
\]

5. Elimination reactions

An interesting approach for the synthesis of transition metal–lead bonds which has not been extensively explored involves the reaction of metal hydrides with \(\text{R}_3\text{Pb}−\text{X}\). The interaction of the Nb–H bond of \([\text{Cp}_2\text{NbH}_3]\) and the Pb–Cl bond of \(\text{Me}_3\text{PbCl}\) resulted in the isolation of a niobium lead complex\(^5\) with the elimination of HCl. Mo and W complexes \([((\text{Cp}_2\text{MH})_2(\mu−\text{Pb}(\text{O}_2\text{CMe}))_2]\) were also synthesized from metallocene dihydrides and trimethyllead acetate with the elimination of methane, \(\text{Me}_4\text{Pb}\) and other products. The formation of \(\text{Me}_4\text{Pb}\) by the cleavage of Pb–C bonds in the reaction is an indication that the reaction may involve monomeric \([(\text{Cp}_2\text{MH})(\text{PbMe}_2(\text{O}_2\text{CMe}))]\) as an
intermediate (equations 186 and 187) \((M = Nb, n = 3; M = Mo, W, n = 2)^{515}\).

\[
\begin{align*}
\text{Me}_3\text{Pb(O}_2\text{CMe)}_2 & \quad \text{Me}_3\text{Pb(O}_2\text{CMe)M} \quad \text{Pb(O}_2\text{CMe)}_2 \\
\text{Me}_3\text{PbCl} & \quad \text{Et}_3\text{N} \quad \text{PbMe}_3 \quad \text{H}_2
\end{align*}
\]

\[(186)\]

\[
\begin{align*}
\text{R}_2\text{E} & \quad \text{Fe(CO)}_4 \quad \text{B} \\
\text{R}_2 & \quad \text{Fe(CO)}_4 \quad \text{B} \\
\text{R}_2 & \quad \text{Fe(CO)}_4 \quad \text{B} \\
\text{R}_2 & \quad \text{Fe(CO)}_4 \quad \text{B}
\end{align*}
\]

\[(187)\]

**B. Transition Metal Pb(II) Complexes**

The types of spectroscopic data available for these compounds are given in Table 15. Dimeric group 14 bridged complexes \([\text{R}_2\text{PbMC}\text{(CO)}_4]_2\) \((M = \text{Mn and Fe})\) were obtained from the reaction of \([\text{M(CO)}_4]_2 + 2\text{Na}^+ + \text{R}_2\text{PbX}_2\) in THF. \(^{486,487,492,493,516}\) In the presence of donor solvents (B) like pyridine, THF, DMF and acetonitrile (B), these complexes undergo reversible cleavage of the metal–group 14 element bond to yield base-stabilized plumbylene metal complexes (equation 188)\(^{516}\).

\[
\begin{align*}
\text{OC}_4\text{Fe} & \quad \text{Fe(CO)}_4 \quad +2\text{B} \quad -2\text{B} \\
\text{OC}_4\text{Fe} & \quad \text{Fe(CO)}_4 \quad \text{ER}_2 \quad \text{B}
\end{align*}
\]

\[(188)\]

A simple route to obtain Mo–Pb(II) complexes involves the elimination reaction between the lead amide \(\text{Pb}[\text{N(SiMe}_3)]_2\) and two equivalents of molybdenum hydride \([\text{Cp}^R\text{Mo(CO)}_3\text{H}]\) \((R = \text{H, Me}_5 \text{ or SiMe}_3)_2\) (equation 189)\(^{517}\).

\[
\begin{align*}
[\text{Cp}^R\text{Mo(CO)}_3\text{H}] + \text{Pb}[\text{N(SiMe}_3)]_2 & \quad \longrightarrow \quad [\text{Cp}^R\text{Mo(CO)}_3]_2\text{Pb}
\end{align*}
\]

\[(189)\]

The related three-coordinate complexes \(\text{Mo}[\{\text{Cp}^R\text{Mo(CO)}_3\}_2\text{Pb(thf)}]\) were obtained as green crystalline solids in fairly good yield. Changing the reaction solvent from THF to a hydrocarbon resulted in the formation of an unusual bridging carbonyl dimeric Mo–lead complex \((\text{Cp}^*\text{Mo(CO)}_3)_2\text{PbCp}^*\text{Mo(CO)}_2(\mu\text{-CO})_2\), \(^{118}\)\(^{4c,517}\).

<table>
<thead>
<tr>
<th>Table 15. Transition metal Pb(II) complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compound</strong></td>
</tr>
<tr>
<td>[CpMn(CO)]_2Pb</td>
</tr>
<tr>
<td>[(η^5-C_5H_4CH_3)Mn(CO)]_2Pb</td>
</tr>
<tr>
<td>[Cp^*Mo(CO)]_2Pb.THF</td>
</tr>
<tr>
<td>[Cp^*Mo(CO)]_2Pb</td>
</tr>
<tr>
<td>[(Cp^*Mo(CO)]_2PbCp^*Mo(CO)]_2</td>
</tr>
<tr>
<td>(Bu_4N)_2Pb[Pt(C_6F_5)]_2</td>
</tr>
</tbody>
</table>
The anionic platinum–lead(II) complex \([\text{Pb} \{\text{Pt}(\text{C}_6\text{F}_5)_4\}_2]^{2-}\) in which the Pb atom is linearly bonded to two Pt atoms was obtained in methanol (equation 190)\(^{518}\).

\[
2(\text{Bu}_4\text{N})_2[\text{Pt}(\text{C}_6\text{F}_5)_4] + \text{Pb(NO}_3)_2 \rightarrow (\text{Bu}_4\text{N})_2[\text{Pb} \{\text{Pt}(\text{C}_6\text{F}_5)_4\}_2] + 2(\text{Bu}_4\text{N})_2(\text{NO}_3)
\]

(190)

A lead allene analog of Mn, 119, was prepared from the reaction of the thermally labile Mn complex \(\text{CpMn} \{\text{CO}\}_2(\text{THF})\) with \(\text{PbCl}_2\) as a reddish-brown air and light sensitive complex (equation 192)\(^{4d,519}\).

\[
\text{PbCl}_2 + \text{Mn} \stackrel{\text{PbCl}_2}{\longrightarrow} \text{Pb} = \text{Mn}
\]

(191)

The same allene analog 119 was obtained from the reaction of hydrido manganese complex \([\text{Cp}'\text{Mn}(\text{CO})_2\text{H}]^+\) with \(\text{PbCl}_2\)\(^{520,521}\). Treatment of 119 with excess of
CpMn(CO)$_2$(THF) yielded black crystals of the air-sensitive planar Mn$_3$Pb complex noted above.

C. Reactivity of the Transition Metal Lead Single Bond

1. Transition metal lead bond cleavage

Platinum–lead complexes undergo a cleavage of Pt–Pb bond with halogens and halogen acids. These reactions are believed to occur through an electrophilic attack on Pt(II) leading to oxidative addition with the formation of a hexa-coordinated Pt(IV) complex. Reductive elimination of a plumbane results in the observed products (equation 193).

\[
\text{Ph}_3\text{P} \begin{array}{c} \text{Pt} \end{array} \text{Et}_3\text{P} \begin{array}{c} \text{PbPh}_3 \end{array} + \text{HCl} \rightarrow \text{Ph}_3\text{P} \begin{array}{c} \text{Pt} \end{array} \begin{array}{c} \text{PEt}_3 \end{array} \begin{array}{c} \text{H} \end{array} \text{Cl} \begin{array}{c} \text{PbPh}_3 \end{array} \rightarrow \text{Ph}_3\text{P} \begin{array}{c} \text{Pt} \end{array} \begin{array}{c} \text{PEt}_3 \end{array} + \text{HPbPh}_3
\]

Hydrogen chloride attacks the Mn–Pb bonds to form lead chloride. To compare the reactivity of the M–H bond with the M–Pb bond in the [Cp$_2$MH$_2$(µ-Pb(O$_2$CMe)$_2$)] (M=Mo, W), the complexes were reacted with cyanoalkyne, HC≡C–CN; however, the only isolated product was Cp$_2$M[C(CN)=CH$_2]$.

2. Cleavage of the lead carbon bond

Halogenation of the binuclear Mn complex [Mn(CO)$_5$]$_2$PbPh$_2$ with Cl$_2$ or Br$_2$ cleaves the Pb–C bond rather than the Mn–Pb bond to produce halogenated Mn–Pb derivatives (equation 194, X = Cl, Br).

\[
[(\text{CO})_5\text{Mn}]_2\text{PbPh}_2 + 2\text{X}_2 \rightarrow [(\text{CO})_5\text{Mn}]_2\text{PbX}_2 + 2\text{PhX}
\]

No cleavage of the Mn–Pb bond was observed in these reactions and monohalogenated intermediates, [Mn(CO)$_5$]$_2$PbPhX, were not isolated.

3. Thermal and photochemical Studies

There are several reports concerning the thermal and photochemical reactivity of triorganolead metal complexes. In general they eliminate plumbylenes, R$_2$Pb, with a concurrent transfer of the organic radical to the metal center. Such chemistry is reported for platinum, iron and molybdenum inter alia. A typical reaction is outlined in equation 195.

\[
\begin{array}{c}
\text{OC} \begin{array}{c} \text{Fe} \end{array} \text{OC} \begin{array}{c} \text{PbMe}_3 \end{array} \rightarrow \text{OC} \begin{array}{c} \text{Fe} \end{array} \begin{array}{c} \text{Me} \end{array} + \text{PbMe}_2 \rightarrow 1/2 \text{Pb} + 1/2 \text{PbMe}_4
\end{array}
\]

The plumbylene species described, PbMe$_2$, disproportionated into metallic lead and Me$_4$Pb. This is analogous to the proposed mechanism involving 1,2-alkyl migrations from
Pb to Zn for the decomposition of alkyl lead chlorides in aqueous zinc slurry which are used for the removal of organolead compounds in industrial effluents. The disproportionation of the Pt complex \([\text{Pt(PPh}_3\text{)}_2(\text{PbPh}_3\text{)}_2]\) to \(\text{cis-}[\text{Pt(PPh}_3\text{)}_2(\text{PbPh}_3\text{)}\text{Ph}]\) is also believed to proceed through 1,2-phenyl migration from Pb to the Pt metal\(^{507,509}\). Upon photochemical treatment, the related lead complexes of group 6, \(\text{CpM(CO)}_3\text{PbMe}_3\) (\(\text{M} = \text{Cr, Mo and W}\)), behave in the same manner. However, the triethyllead complexes \(\text{CpM(CO)}_3\text{PbEt}_3\) (\(\text{M} = \text{Mo, W}\)) exhibit a different behavior and undergo disproportionation into bis-metal complexes (equation 196). Similar disproportionations were also observed in Mn\(^{486}\) and Fe\(^{492}\) complexes; e.g. the \(\text{Mn(CO)}_5\text{PbMe}_3\) complex in THF gave the bis-Mn complex, \([\text{Mn(CO)}_5]_2\text{PbMe}_2\).

\[\begin{align*}
\text{M-PbEt}_3 & \rightarrow \text{M-PbEt}_2
\end{align*}\]

(196)

The mechanistic details for these disproportionation reactions are not clear. It is possible that \(\alpha\)-elimination chemistry as outlined in equation 197 is involved, resulting in transient plumbylene metal complexes; however, no definitive data are available to substantiate such intermediates.

\[\begin{align*}
\text{M-PbR}_3 & \rightarrow \text{M-PbR}_2
\end{align*}\]

(197)

\[\text{4. Substitutions at the transition metal center}\]

Few examples of chemistry at the metal center, while maintaining the metal–lead bond, are reported. Usually, the reaction conditions are such that rupture of the metal–lead bond occurs. Nucleophilic substitution at Ru occurs when the product from the chemistry in equation 185 is reacted with Grignard reagents (equation 198)\(^{511}\).

\[\begin{align*}
\text{Ph}_3\text{Pb} & + \text{RMgX} \rightarrow \text{Ph}_3\text{Pb}
\end{align*}\]

(198)
Simple CO substitution by phosphine ligands has been observed for \([\text{(CO)}_4\text{Co}]_4\text{Pb}\) to produce a variety of phosphine-substituted clusters\(^{500,501}\). It is noteworthy that this compound does not contain organic substituents on lead.

**D. Reactivity of the Transition Metal Lead Double Bond**

There are few reports on the reactivity of the transition metal—plumbylene complexes. The allene analog of the Mn derivative \(119\) underwent oxidative addition of thiolate \(t\)-BuS\(^-\) to yield the trigonal-planar \(121\) (equation 199)\(^{521,523}\). The Pb—Mn bond length of 2.574(3) Å in \(121\) is longer than the bond length of 2.463(1) Å in \(119\) and the Mn—Pb—Mn bond angle is reduced to 135.5(1)° from the almost linear angle of 177.2(1)° found in \(119\). Changing the thiolate group to mesityl results in the isolation of anionic tetrahedral complex \(122\). The Mn—Pb bond in \(122\) undergoes further elongation to 2.617(3) Å and the angles around Pb atom are reduced to 118.2(1)—129.3(2)°. The Pb—S bond length of 2.594(6)—2.617(3) Å is also longer in comparison to the Pb—S bond length of 2.574(4) Å in \(121\).

Complex \(119\) also reacted with neutral nitrogen-containing ligands, bipyridine, 1,10-phenanthroline and TMEDA to form neutral complexes in which the Pb atom has a distorted tetrahedral geometry. The Pb—Mn bonds are longer (2.510—2.528 Å) than in the starting allene analog \(119\) but are shorter than the normal Mn—Pb single bonds. The Mn—Pb—Mn angles (146.9—149.4°) are also reduced from that of \(119\) and this, coupled to the elongation of the Pb—N bonds (2.535—2.559 Å), indicates the dative interactions of nitrogen\(^{520,523}\).

**E. Solid State Structures**

There are a limited number of structures reported for Fe—Pb complexes and these are recorded in Tables 16—18. For a series of iron carbonyl lead clusters, the Fe—Pb bond lengths vary from 2.624 Å for an electron-deficient three-coordinate planar Pb cluster \([\text{Fe(CO)}_4]_3\text{Pb}\) to 2.828 Å for a tetrahedral bridging anionic Pb cluster
TABLE 16. Selected X-ray structural data of transition metal Pb(IV) complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond</th>
<th>Bond length (Å)</th>
<th>L–M–Pb angle (deg)</th>
<th>M–Pb–X angle (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp₂NbH₂PbMe₃</td>
<td>Nb–Pb</td>
<td>2.8991(4)</td>
<td></td>
<td></td>
<td>514</td>
</tr>
<tr>
<td>[{Cr(CO)₅}₂Pb(O₂CMe)₂]²⁻</td>
<td>Cr–Pb</td>
<td>2.722(2)</td>
<td>147.85(5)</td>
<td>496</td>
<td></td>
</tr>
<tr>
<td>CpMo(CO)₃PbPh₃</td>
<td>Mo–Pb</td>
<td>2.90</td>
<td></td>
<td></td>
<td>515b</td>
</tr>
<tr>
<td>(Cp₂MoH₂)₂Pb(O₂CMe)₂</td>
<td>Mo–Pb</td>
<td>2.808(1)</td>
<td>76.3</td>
<td>141.4(1)</td>
<td>515</td>
</tr>
<tr>
<td>Cp₆W(SnPh₃)₃PbMe₂Cl</td>
<td>W–Pb</td>
<td>2.7662(8)</td>
<td>83.37(3)</td>
<td>100.3(1)</td>
<td>529</td>
</tr>
<tr>
<td>[(η⁵-C₅H₄CH₃)Mn(CO)₂Pb(SMes)₃]⁻</td>
<td>Mn–Pb</td>
<td>2.617(3)</td>
<td>94.8(8)</td>
<td></td>
<td>523</td>
</tr>
<tr>
<td>[PPh₄][Fe₃(CO)₉(μ-CO)₂(PbPh₃)]</td>
<td>Fe–Pb</td>
<td>2.651(1)</td>
<td>164.3(1)</td>
<td>117.2(1) (av)</td>
<td>499</td>
</tr>
<tr>
<td>[Et₄N]₂[Fe(CO)₄]₃</td>
<td>Fe–Pb</td>
<td>2.624 (4) (av)</td>
<td></td>
<td>118.6(1)–122.0(1)</td>
<td>504</td>
</tr>
<tr>
<td>[Et₄N]₂[Fe(CO)₄(PbPh₃)₂(Fe₂(CO)₈)]</td>
<td>Fe–Pb</td>
<td>2.655(5) (av)</td>
<td>177.8(12)</td>
<td>115.95(14)</td>
<td>502</td>
</tr>
<tr>
<td>[Fe(CO)₄]₄Pb</td>
<td>Fe–Pb</td>
<td>2.606(3)–2.635(3)</td>
<td></td>
<td>57.49(9)</td>
<td>503</td>
</tr>
<tr>
<td>[CpFe(CO)₂]₂PbMe₂</td>
<td>Fe–Pb</td>
<td>2.71 (av)</td>
<td>83.8</td>
<td>123.8</td>
<td>530</td>
</tr>
<tr>
<td>Ru(Cl)(PbPh₃)(CO)₂(i-Pr-DAB)²⁻</td>
<td>Ru–Pb</td>
<td>2.7028(8)</td>
<td>176.71(7)</td>
<td></td>
<td>511</td>
</tr>
<tr>
<td>cis–(PPPh₃)₂Pt(PbPh₃)₃Ph</td>
<td>Pt–Pb</td>
<td>2.698(1)</td>
<td></td>
<td>127.8, 112.1, 116.1</td>
<td>507</td>
</tr>
<tr>
<td>(dimethylmaleate)(dmphen) PtCl(PbPh₂Cl)</td>
<td>Pt–Pb</td>
<td>2.642(1)</td>
<td>178.7(1)</td>
<td></td>
<td>510</td>
</tr>
<tr>
<td>[MeCO₂]₂Pb(crown-P₂)₂Pt(CN)₂(O₂CMe)²⁻</td>
<td>Pt–Pb</td>
<td>3.313(2)</td>
<td></td>
<td></td>
<td>531</td>
</tr>
<tr>
<td>(Ph₃P)(S)CH₂₄PbAu₂</td>
<td>Au–Pb</td>
<td>2.896(1)</td>
<td>90.1(5)</td>
<td>180.0</td>
<td>532</td>
</tr>
</tbody>
</table>

* DAB = 1,4-Diaza-1,3-butadiene.
* Crown-P₂ = Pb₂PCH₂N((CH₂)₂O(CH₂)₂OCH₂)NCH₂PPh₂.
TABLE 17. X-ray structural data for transition metal lead complexes containing-bridging lead ligands

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond</th>
<th>Bond length (Å)</th>
<th>L–M–Pb angle (deg)</th>
<th>M–Pb–X angle (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>([t-(t-BuO)_3Fe(CO)_4]_2Pb)</td>
<td>Fe–Pb</td>
<td>2.939(2)</td>
<td>80.0(1)</td>
<td>112.9(1)</td>
<td>533</td>
</tr>
<tr>
<td>([Fe_2(CO)_8{\mu-Pb(C_2H_5)_2}_2])</td>
<td>Fe–Pb</td>
<td>2.718(4)</td>
<td>77.6(1)</td>
<td>102.4(2)</td>
<td>493, 534</td>
</tr>
<tr>
<td>([Ru_3((\mu-Pb)CH(SiMe_3)_2{\mu-CO})(CO)_9])</td>
<td>Ru–Pb</td>
<td>2.765(2)–2.790(2)</td>
<td>58.15(4)</td>
<td>64.12(4)</td>
<td>513</td>
</tr>
<tr>
<td>([Os_2(CO)_8{\mu-Pb(CH_3)_2}_2])</td>
<td>Os–Pb</td>
<td>2.835 (av)</td>
<td></td>
<td></td>
<td>535</td>
</tr>
<tr>
<td>([Pb{Co(CO)_4}_4])</td>
<td>Co–Pb</td>
<td>2.761(5)</td>
<td></td>
<td></td>
<td>501</td>
</tr>
<tr>
<td>([Ir_2(PbI)(CO)_2I_2{\mu-dmpa}_2])((PF_6)^a)</td>
<td>Ir–Pb</td>
<td>2.855(2)</td>
<td>89.7(1)–100.6(5)</td>
<td>146.4(1)</td>
<td>536, 537</td>
</tr>
<tr>
<td>([Bu_4N]{[(C_6F_5)_3Pt}_2{\mu-Pb}(\mu-Cl)}])</td>
<td>Pt–Pb</td>
<td>2.721(1)</td>
<td></td>
<td></td>
<td>538</td>
</tr>
<tr>
<td>([Bu_4N]{[(C_6F_5)_3Pt}_2{\mu-Pb}(\mu-OH)}])</td>
<td>Pt–Pb</td>
<td>2.701(1)</td>
<td></td>
<td></td>
<td>538</td>
</tr>
</tbody>
</table>

\(dmpa = \text{bis(diphenylphosphinomethyl)phenylarsine.}\)
TABLE 18. X-ray structural data for transition metal Pb-(II) complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond</th>
<th>Bond length (Å)</th>
<th>L−M−Pb angle (deg)</th>
<th>M−Pb−X angle (deg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(η⁵-C₅Me₅)Mo(CO)₃]₂Pb·THF</td>
<td>Mo−Pb</td>
<td>2.989(2)</td>
<td>118.35(5)</td>
<td>517</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.019(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[((η⁵-C₅Me₅)Mo(CO)₃]_{Pb}</td>
<td>Mo−Pb</td>
<td>2.935(1)</td>
<td>120.71(2)</td>
<td>517</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.989(1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(η⁵-C₅H₅)Mn(CO)₂]₂Pb</td>
<td>Mn−Pb</td>
<td>2.463(1)</td>
<td>89.9(2)</td>
<td>519</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>91.3(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(η⁵-C₅H₅CH₃)Mn(CO)₂]₃Pb</td>
<td>Mn−Pb</td>
<td>2.611(1)</td>
<td>72.97(4)</td>
<td>522</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.620(1)</td>
<td>143.41(4)</td>
<td>522</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.490(1)</td>
<td>143.56(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(η⁵-C₅H₅CH₃)Mn(CO)₂]₂Pb</td>
<td>Mn−Pb</td>
<td>2.574(3)</td>
<td>135.5(1)</td>
<td>520</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>149.4(1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbSBu-t⁻</td>
<td>Mn−Pb</td>
<td>2.510(3)</td>
<td></td>
<td>520, 523</td>
<td></td>
</tr>
<tr>
<td>[(η⁵-C₅H₅CH₃)Mn(CO)₂]₂Pb</td>
<td>Mn−Pb</td>
<td>2.769(2)</td>
<td>178.6(1)</td>
<td>518</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.793(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

²⁰⁷Pb NMR Spectroscopy

²⁰⁷Pb NMR spectroscopy is a valuable method for studying the transition metal–lead bond in solution and selected data are provided in Table 19. It is evident that the variations in chemical shift values with respect to the transition metal are large. Among all the transition metal–lead complexes, the lowest chemical shift value was observed for [Fe(CO)₄]₄Pb at 3587 ppm⁴⁹₃. Most of the data are available for metal carbonyl and metal phosphine complexes⁴⁹₃,5₂₄,5₂₅. The trends in chemical shift values are consistent with the trends observed in ²⁹Si and ¹¹⁹Sn NMR spectra of the corresponding transition-metal complexes where a comparison is possible. From the data available, it appears that the third-row transition metals exert a high field which has been interpreted as due to the higher polarizability of the transition metal and decreased capacity of the π-bonding between the transition metal and lead. Interestingly, the Pb chemical shift values are not dependent upon the concentration and the nature of the solvent, indicating a distinct lack of Lewis acidity for the Pb atom. The transition metal has a strong influence on the variation of chemical shift values due to the organic R group bonded to the lead. For example, in the iron series CpFe(CO)₅PbR₃, [CpFe(CO)₂]₂PbR₂ and [Fe(CO)₄(µ-PbR₂)]₂, introduction...
TABLE 19. $^{207}$Pb NMR data for transition metal lead complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{207}$Pb NMR, $\delta$(ppm)</th>
<th>$^1J$(M–Pb) $\delta$(ppm)</th>
<th>M NMR, $\delta$(ppm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpCr(CO)$_3$PbMe$_3$</td>
<td>360.2</td>
<td></td>
<td></td>
<td>524</td>
</tr>
<tr>
<td>CpCr(CO)$_3$PbEt$_3$</td>
<td>423.1</td>
<td></td>
<td></td>
<td>524</td>
</tr>
<tr>
<td>CpCr(CO)$_3$PbPh$_3$</td>
<td>210.1</td>
<td></td>
<td></td>
<td>524</td>
</tr>
<tr>
<td>CpMo(CO)$_3$PbMe$_3$</td>
<td>220.5 (229)</td>
<td>−1989</td>
<td>524, 525</td>
<td></td>
</tr>
<tr>
<td>CpMo(CO)$_3$PbEt$_3$</td>
<td>311.8 (301)</td>
<td>−2007</td>
<td>524, 525</td>
<td></td>
</tr>
<tr>
<td>CpMo(CO)$_3$PbPh$_3$</td>
<td>115.6 (125)</td>
<td>−1927</td>
<td>524, 525</td>
<td></td>
</tr>
<tr>
<td>[CpMo(CO)$_3$]$_2$PbPh$_2$</td>
<td>421</td>
<td>−1838</td>
<td>524, 525</td>
<td></td>
</tr>
<tr>
<td>[CpW(CO)$_3$]$_2$PbEt$_2$</td>
<td>−130.7 (−128)</td>
<td>135</td>
<td>524, 525</td>
<td></td>
</tr>
<tr>
<td>CpW(CO)$_3$PbMe$_3$</td>
<td>−100.7 (−87)</td>
<td>170</td>
<td>524, 525</td>
<td></td>
</tr>
<tr>
<td>CpW(CO)$_3$PbEt$_3$</td>
<td>29.2 (25)</td>
<td>115</td>
<td>524, 525</td>
<td></td>
</tr>
<tr>
<td>CpW(CO)$_3$PbPh$_3$</td>
<td>−221.0 (−217)</td>
<td>390</td>
<td>524, 525</td>
<td></td>
</tr>
<tr>
<td>[CpW(CO)$_3$]$_2$PbPh$_2$</td>
<td>−375</td>
<td>270</td>
<td>524, 525</td>
<td></td>
</tr>
<tr>
<td>Mn(CO)$_5$PbMe$_3$</td>
<td>140.0</td>
<td></td>
<td></td>
<td>525</td>
</tr>
<tr>
<td>Mn(CO)$_5$PbEt$_3$</td>
<td>230.6</td>
<td></td>
<td></td>
<td>525</td>
</tr>
<tr>
<td>Mn(CO)$_5$PbPh$_3$</td>
<td>55.0</td>
<td></td>
<td></td>
<td>525</td>
</tr>
<tr>
<td>CpFe(CO)$_2$PbMe$_3$</td>
<td>245.6 (243.1)</td>
<td>89.1</td>
<td>493, 525</td>
<td></td>
</tr>
<tr>
<td>CpFe(CO)$_2$PbEt$_3$</td>
<td>398.9 (397.4)</td>
<td>82.0</td>
<td>493, 525</td>
<td></td>
</tr>
<tr>
<td>CpFe(CO)$_2$PbPh$_3$</td>
<td>125.1</td>
<td></td>
<td>525</td>
<td></td>
</tr>
<tr>
<td>CpFe(CO)$_2$Pb(Pr-i)$_3$</td>
<td>469.8</td>
<td></td>
<td>493</td>
<td></td>
</tr>
<tr>
<td>CpFe(CO)$_2$Pb(Bu-t)$_3$</td>
<td>632.1</td>
<td>104.3</td>
<td>493</td>
<td></td>
</tr>
<tr>
<td>CpFe(CO)$_2$PbBr(Pr-i)$_2$</td>
<td>1087.3</td>
<td></td>
<td>493</td>
<td></td>
</tr>
<tr>
<td>[Fe(CO)$_4$]PbMe$_2$</td>
<td>692.8</td>
<td></td>
<td>493</td>
<td></td>
</tr>
<tr>
<td>[Fe(CO)$_4$]PbEt$_2$</td>
<td>886.6</td>
<td></td>
<td>493</td>
<td></td>
</tr>
<tr>
<td>[Fe(CO)$_4$]$_2$Pb</td>
<td>457.1</td>
<td></td>
<td>525</td>
<td></td>
</tr>
<tr>
<td>[Fe(CO)$_4$]PbMe$_2$</td>
<td>293.4</td>
<td></td>
<td>493</td>
<td></td>
</tr>
<tr>
<td>[Fe(CO)$_4$]PbEt$_2$</td>
<td>411.8</td>
<td></td>
<td>493</td>
<td></td>
</tr>
<tr>
<td>[Fe(CO)$_4$]$_2$(µ-PbMe$_2$)</td>
<td>293.4</td>
<td>117.0</td>
<td>493</td>
<td></td>
</tr>
<tr>
<td>[Fe(CO)$_4$]$_2$(µ-PbEt$_2$)</td>
<td>411.8</td>
<td>100.2</td>
<td>493</td>
<td></td>
</tr>
<tr>
<td>[Fe(CO)$_4$]$_2$(µ-Pb(Pr-i)$_2$)</td>
<td>460.9</td>
<td>83.7</td>
<td>493</td>
<td></td>
</tr>
<tr>
<td>[Fe(CO)$_4$]$_4$Pb</td>
<td>3586.6</td>
<td>33.5</td>
<td>493</td>
<td></td>
</tr>
<tr>
<td>Co(CO)$_4$PbMe$_3$</td>
<td>348.9</td>
<td></td>
<td>525</td>
<td></td>
</tr>
<tr>
<td>Co(CO)$_4$PbEt$_3$</td>
<td>478.3</td>
<td></td>
<td>525</td>
<td></td>
</tr>
<tr>
<td>Co(CO)$_4$PbPh$_3$</td>
<td>132.6</td>
<td></td>
<td>525</td>
<td></td>
</tr>
<tr>
<td>CpFe(CO)(PPh$_3$)PbEt$_3$</td>
<td>207.4</td>
<td>4432J(P–Pb)</td>
<td>525</td>
<td></td>
</tr>
<tr>
<td>Co(CO)$_3$(PPh$_3$)PbEt$_3$</td>
<td>438.4</td>
<td>1782J(P–Pb)</td>
<td>525</td>
<td></td>
</tr>
<tr>
<td>cis-(PPh$_3$)$_2$Pt(PbPb$_3$)Ph</td>
<td>−100</td>
<td>18380</td>
<td>−4610</td>
<td>508</td>
</tr>
<tr>
<td>cis-(PPh$_3$)$_2$Pt(PbPb$_2$Br)Ph</td>
<td>530</td>
<td>17195</td>
<td>−4548</td>
<td>508</td>
</tr>
<tr>
<td>cis-(PPh$_3$)$_2$Pt(PbPb$_2$I)Ph</td>
<td>515</td>
<td>16855</td>
<td>−4568</td>
<td>508</td>
</tr>
<tr>
<td>trans-(PBU$_3$)$_2$Pt(PbPb$_3$)$_2$</td>
<td>76</td>
<td>14395</td>
<td>−4915</td>
<td>508</td>
</tr>
</tbody>
</table>

of Me, Et, and i-Pr produces a gradual low field shift$^{493}$. However, a different trend is observed in the Mo and W complexes of the type CpM(CO)$_3$PbR$_3$, where shielding increases in the sequence Et < Me < Ph, analogous to the trend observed in R$_3$PbX (R = Me, Et, Ph; X = Cl, Br, I).

Substitution of a carbonyl group by a phosphine ligand produces a high frequency shift. The extent of this shift is dependent upon the transition metal and organic group R. In Pt–Pb complexes, Pt(PPh$_3$)$_2$R(PbR$_3$) (R = C$_6$H$_4$X-4, X = H, Me, MeO, Cl, F), coupling constants $^1J$(Pb–$^{195}$Pt) range from 145 kHz to 18.5 kHz, the trans Pt–Pb compounds having the smaller coupling constants. Variation of the substituents on the phenyl groups had no apparent effect on the Pb chemical shift values$^{508}$. 

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17. Transition metal complexes of germanium, tin and lead


17. Transition metal complexes of germanium, tin and lead

1330  Hemant K. Sharma, Ionel Haiduc and Keith H. Pannell


17. Transition metal complexes of germanium, tin and lead

Synthetic applications of organic germanium, tin and lead compounds (excluding \( R_3MH \))

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I. ABBREVIATIONS

AIBN 2,2’-azobisisobutyronitrile
BINAP 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
BINOL 1,1’-binaphthalene-2,2’-diol
BOM benzylxoyethyl
DME 1,2-dimethoxyethane
DMF N,N-dimethylformamide
DMSO dimethyl sulphoxide
MCPBA m-chloroperbenzoic acid
MOM methoxymethyl
NBS N-bromosuccinimide
NMP N-methyl-2-pyrrolidone
PMP p-methoxyphenyl
Phebox 2,6-bis(oxazolinyl)phenyl
SEM 2-(trimethylsilyl)ethoxymethyl
tetrahydrofuran
TBAF tetrabutylammonium fluoride
TBDPS t-butyldiphenylsilyl
TBS t-butyldimethylsilyl
TES triethylsilyl
TMS trimethylsilyl

II. INTRODUCTION

The use of organometallic compounds of group 14 elements for organic synthesis is undoubtedly overwhelmed by organotin chemistry, and in spite of increasing environmental considerations, the chemistry of organotins and its applications for organic synthesis continues to flourish during the years. In contrast, organogermanium and organolead applications decreased over the last decades up to the point of appearing anecdotic. Consequently, this chapter deals almost exclusively with organotin chemistry, reference being made to organogermanium or organolead chemistry when necessary.

However, it should be noted that all the applications of tin chemistry for organic synthesis cannot be covered comprehensively in this chapter, which is devoted to organotin compounds and to the reactivity of the metal–carbon bond. Tin hydride chemistry, which is of major importance in this field, is, for instance, treated in a separate chapter. For the same reasons, the numerous uses of tin(II) and tin(IV) reagents as Lewis acid or chirality inducers are not reported here as long as these reagents do not possess any tin–carbon bonds. Finally, the reactivity of the tin–oxygen bond (as a catalyst, or a protecting group) will not be mentioned in the following.
III. NUCLEOPHILIC ADDITION

A. Nucleophilic Addition to Carbonyl Compounds

1. Background

The addition of organotin reagents to carbonyl compounds remains a quite recent reaction compared to other organometallic reagents. This was presumably due to a lack of reactivity of the organotin, which necessitated thermal activation or high-pressure conditions. Consequently, the activation of the carbonyl partner by a Lewis acid, first reported in 1979, appeared to be the key factor in the increasing use of organotin reagents. The versatility of allyltin reagents enables one to achieve various orientations in the regio- and stereo-control of the addition and is regularly reviewed. Such selectivity depends on different mechanisms and transition states, which are closely related to the experimental conditions employed.

2. Lewis acid activation of the electrophile

a. Mechanisms and diastereoselectivities induced by γ-substituted allyltins. In contrast to the thermal or high-pressure activated reactions, which adopt a chair-like transition state, the Lewis acid promoted reaction proceeds via an open transition state, as the tin does not compete with the Lewis acid in the coordination to the carbonyl compound. The reaction leads to an excellent syn diastereoselectivity, first reported by Maruyama and coworkers, which was explained by proposing an antiperiplanar transition state. This proposal was completed by introducing a syn-clinal transition state to account for the syn selectivity, whatever the nature (E or Z) of the crotyl reagent (equation 1).
In contrast, it was reported that $\gamma$, $\gamma$-disubstituted allyltins reacted stereospecifically, the ($E$)-reagent giving a syn adduct and the ($Z$)-reagent giving an anti adduct. In such a case the reaction is assumed to proceed essentially via the syn-clinal acyclic transition state. It is noteworthy that $\alpha$-substitution on the allyltin reagent may affect dramatically the syn selectivity as well. This reaction was successfully extended to various $\gamma$-substituted allyltins, and applied in the total synthesis of complex frameworks achieved with excellent diastereoselections. The access to optically active $\alpha$-oxygenated allyltins and their subsequent rearrangement to $\gamma$-alkoxyallyltins allowed easy access to stereo-controlled 1,2 syn diols which were further applied for a synthetic purpose. Iterative use of allyltins enabled a rapid and efficient synthesis of a carbon chain containing several contiguous asymmetric centres (equation 2).

\[ \text{PMP} = p\text{-methoxyphenyl} \]

*b. Diastereoselectivity induced by chiral aldehydes.* The substrate plays an important role in the facial diastereoselection, particularly when there is an asymmetric centre
adjacent to the carbonyl group. In the general case, the approach of the allyltin is believed to follow the Felkin–Anh model giving the syn adduct 1 preferentially (equation 3)

\[ \begin{align*}
\text{anti (minor)} & \quad \text{syn (major) (1)} \\
\text{Nu:} & = \text{nucleophilic}
\end{align*} \]

However, a reversal of the diastereofacial selectivity may arise when the substrate has, in \( \alpha \) or \( \beta \) position of the side chain, a group prone to complexation with the Lewis acid. Then, the use of bidentate Lewis acids such as MgBr\(_2\), TiCl\(_4\) or ZnCl\(_2\) allows the reaction to proceed under a 'chelation control' model, providing preferentially the syn adduct for a 1,4-chelation and the anti adduct for a 1,5-chelation. This was exploited in the stereoselective synthesis of both diastereomers, simply by changing the chelation conditions on the substrate\(^{18}\). An impressive amount of work was done with various \( \alpha \)-alkoxy aldehydes\(^{19–23}\) as a route to carbohydrate chemistry. Similarly, \( \alpha \)-amino aldehydes were used as substrates for \( \beta \)-amino alcohol synthesis\(^{24,25}\).

It should be noted that when the reaction is conducted with a chiral aldehyde and a chiral \( \gamma \)-substituted allyltins, a ‘matching effect’ when both partners impose a convergent selectivity, or a ‘mismatching effect’ when the facial selectivity is divergent, may happen\(^{26}\). Such a stereoconvergent effect was used in the synthesis of the antitumour agent azinomycin\(^{27}\) (equation 4).

3. Activation of the allyltin reagent

a. In situ transmetallation. The activation of the allyltin may be performed by its transmetallation with the Lewis acid prior to the addition to the carbonyl. The first example was reported with SnCl\(_4\)\(^{28}\), but other Lewis acids such as TiCl\(_4\), AlCl\(_3\) or InCl\(_3\) may be used for the transmetallation. The main difference lies in the fact that the transient allyl metal has a stronger acid character than the starting allyltin, favouring the cyclic 6-membered transition state introduced by Zimmerman and Traxler\(^{29}\). Thus the diastereoselectivity of the reaction is different from that observed with an open transition state, with (\(E\))-crotyltin giving an anti selectivity, when (\(Z\))-crotyltin leads to a syn selectivity. We note
that the transmetallation proceeds via the allylmetal 2, which gives the thermodynamically favoured crotyltin 3 (equation 5). Then, under kinetic conditions, it remains possible to direct the reaction towards the formation of the ‘kinetic’ homoallylic alcohol.

\[
\begin{align*}
&\text{[Drawings and equations for reactions and structures]} \\
&\text{syn : anti} \geq 10 : 1
\end{align*}
\]

Under thermodynamic control, the homoallylic alcohol is obtained with an anti/syn selectivity up to 95 : 5.\(^3\) In order to prevent competition between the transmetallation and the complexation of the aldehyde, it is important that the allyltin reagent is added first to the Lewis acid. This is termed a ‘reverse addition’.

\[
\begin{align*}
&\text{[Drawings and equations for reactions and structures]} \\
&\text{‘Kinetic’} \\
&\text{‘Thermodynamic’}
\end{align*}
\]
b. Stereochemical outcomes.  

i. α-substituted allyltins. The easy and efficient access to enantiopure α-substituted allyltins associated to the transmetallation process is at the origin of impressive progress in the field of enantioselective synthesis. This is due to the ‘chirality transfer’ which occurs in the two steps of the reaction (equation 6).

\[
\begin{align*}
\text{SnBu}_3 \xrightarrow{\text{InCl}_3} \text{Cl}_2\ln \xrightarrow{\text{R}_2\text{CHO}} \text{InCl} \xrightarrow{\text{H}} \text{R}_1\text{Me(S)} \xrightarrow{\text{OH}} \text{R}_1\text{R}_2\text{H}
\end{align*}
\]

Thus efficient enantioselective synthesis of 1,2 diols can be achieved starting from enantio-enriched α-alkoxytins. However, in that case the use of a strong Lewis acid, such as TiCl₄, AlCl₃, SnCl₄ or ZnCl₂, causes a premature decomposition of the allyltin. Marshall and Hinkle circumvented this by using InCl₃ and applied it to the enantioselective synthesis of sugar-related compounds.

ii. γ-substituted allyltins. The enantiocontrolled preparation of δ-substituted allyltins has been used as well for the enantioselective synthesis of functionalized homoallylic alcohols. A major contribution is represented by a comprehensive study on various alkoxylated allyltins which, upon transmetallation with SnCl₄, gave intramolecularly coordinated trihalogenotins. This coordination appears to be essential either for its stabilization via a rigid cyclic structure, and for the transfer of the chirality by directing the addition on the less hindered face of the trihalogenotin. Interestingly, when using α-chiral aldehydes, the stereochemical induction of the tin reagent prevails over the substrate effect (equation 7). Efficient 1,4-, 1,5-, 1,6- and 1,7-asymmetric inductions were achieved in that way and have found application in the total synthesis of macrolides or a complex tetrahydrofuran.

4. Catalytic use of Lewis acid

Recent studies have been engaged in finding a catalytic version of the Lewis acid activated reaction. Bulky aluminium reagents may be used (5 to 10 mol%), for which the development of unfavourable interactions with the resulting tributyltin alkoxide moiety accounts for the decomplexation reaction. The method offers a good chemoselectivity, depending on the steric hindrance of the considered carbonyl compound. The catalytic effect of B(C₆F₅)₃ has been also evidenced, again with a good chemoselectivity, for which the reason is still under discussion. Lanthanide triflates (2 mol%) have been used as well, in the presence of stoichiometric amounts of benzoic acid in order to regenerate the Yb(OTf)₃ catalyst, ensuring a good turnover for the reaction. InCl₃ can perform allylation and alkynylation addition reactions catalytically, when associated to trimethylsilyl chloride as regenerating reagent. In that case, however, the nature of the solvent plays a role in the reaction efficiency.
an important role in favouring the transmetallation even with the ‘normal addition’ process. The transmetallation of allyltributyltin with catalytic quantities of dialkyldichlorotin leads to a more reactive allyldialkylchlorotin. The turnover of the catalytic system is maintained by HCl or Me₃SiCl. Finally, an association of triaryl methyl chloride as a Lewis acid and chlorosilane as the regenerating agent was described, giving promising results.

\[
\begin{align*}
\text{Bu}_3\text{Sn} & \quad \text{(4)} \\
\text{Me} & \\
\text{OBn} & \\
\begin{array}{c}
\text{SnCl}_4 \\
\text{Me} \\
\text{OBn}
\end{array} \\
\rightarrow \\
\begin{array}{c}
\text{Cl}_3\text{Sn} \\
\text{OBn}
\end{array} \\
\begin{array}{c}
\text{Me} \\
\text{OBn}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{RCHO} & \\
\rightarrow \\
\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{BnO} \\
\text{H} \\
\text{R}
\end{array} \\
\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{H} \\
\text{Me} \\
\text{RCHO}
\end{array} \\
\begin{array}{c}
\text{Me} \\
\text{CHO} \\
\text{OBn}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{Me} & \\
\text{OH} \\
\text{OBn} \\
\text{Me} & \\
\text{OBn} \\
\rightarrow \\
\begin{array}{c}
\text{Me} \\
\text{CHO} \\
\text{OBn}
\end{array} \\
\begin{array}{c}
\text{Me} \\
\text{OBn}
\end{array}
\end{align*}
\]

5. Enantioselectivity

In parallel with the search for catalytic systems, an impressive amount of results in the field of enantioselective allylation has emerged (equation 8). The pioneering work of Marshall and Tang, using a chiral (acyloxy)borane 6 (CAB) system, was followed by titanium-based catalysts 7 and 8 leading to various homoallylic alcohols with enantiomeric excess up to 98%. Several variations of this system were reported replacing, for instance, Ti(OPr-i)₄ by Zr(OPr-i)₄ or ZrCl₄, leading to a more reactive catalyst, particularly suitable for the allylation of aromatic aldehydes. The use of activators, such as i-PrSSiMe₃, i-PrSBEt₂, i-PrSAEt₂ or B(OMe)₃, was realized for both systems. They are believed to accelerate the reaction by regenerating the Ti or Zr catalysts. Finally, one of the more active catalysts seems to be the zirconium–BINOL system associated with 4-t-butylcalix[4]arene,
which remains active with only 2% of the chiral inductor. It is noteworthy that the BINOL-Ti catalysed allylation was extended to ketones in good yields but with varied ee. In general, BINOL catalysts enable the replacement of the allyltin by crotyltin without lowering the yield or the enantioselectivity. β-Functionalized allyltin reagents were added with high levels of enantioselection, and such a strategy has been used in the total syntheses of macrolides.

Silver BINAP complex was used as well by Yanagisawa and coworkers. The particular feature of this catalyst is the marked anti selectivity when using crotyltins, regardless of whether the double bond is (E) or (Z). This selectivity is explained by a fast transmetallation step between the chiral complex and the organotin reagent, followed by the addition on the carbonyl group via a cyclic transition state. This reaction has been extended to other organometallics such as 2,4-pentadienylstannanes.

Catalysts with nitrogen ligands such as bisoxazolines have been introduced as Lewis acids. Recently, air-stable and water-resistant (Phebox)rhodium(III) complexes gave up to 80% ee.

6. Other organotin reagents

a. Activated allyltins. Replacing the butyl units by electron-withdrawing groups in order to activate the allyltin has been known for a long time and the replacement of allyltributyltin by tetraallyltin provided interesting results without any added Lewis acid. Some activation by alcoholic solvents or intramolecular participation of hydroxyl...
groups allowed the preparation of homoallylic alcohols under particularly mild conditions. However, most efforts have been focused on allyltin halide reagents. The first evidence of their reactivity dates back to 1978 and a scale of reactivity was established according to the Lewis acidity of the tin atom. They can be used in the presence of water, and when the allyltin halide is a transient reagent, electrochemically generated in situ, the allylation reaction can become catalytic in tin. Allyltin trihalides can be prepared easily and represent interesting reagents in the sense that the tin side products of the reaction are inorganic, allowing an easy purification. Moreover, they offer a solution to the problem caused by the toxicity of tributyltin residues. They have been largely used for the preparation of homoallylic alcohols in Barbier-type allylation reactions, and for the synthesis of α-methylene-γ-butyrolactones when starting from β-functionalized allyltins. The anti/syn selectivity is about 90:10 and is consistent with a cyclic transition state. Adjacent groups to the carbonyl may participate in the reaction by hexacoordinating the tin atom (equation 9) and creating a chelation control to determine the stereochemistry of the adduct.

The ability of allyltin halides to extend their coordination sphere allowed the preparation of chiral hypervalent complexes with diamine ligands, which have been efficient in the asymmetric synthesis of homoallylic alcohols with up to 82% ee. Similarly, a chiral hypervalent allyltin was prepared from a low valent tin (II) catecholate, chiral dialkyl tartrate and allylic halide. The allylation of aldehydes and activated ketones proceeded with high enantiomeric excess. Allyltins prepared from Lappert’s stannylene and allylic halides were shown to be efficient as well, although the Lewis acid character of the tin atom is much less marked in that case.

b. Allenyl- and propargyltins. Allenyl- and propargyltins are peculiar reagents in the sense that a possible interconversion between the two forms may occur, thus leading to a mixture of homopropargylic and homoallenic alcohols (equation 10). This isomerization is activated by Lewis acids, and may represent a serious drawback when
using a terminal alkyne as the organometallic reagent; however, it remains possible to obtain selectively both alcohols 12 and 13.

Complementary studies showed that it is possible to obtain selectively homoallenyl alcohols\textsuperscript{104} and homopropargyl alcohols\textsuperscript{105} when preparing \textit{in situ} the organotin reagent. The chemoselectivity remains outstanding with propargyl bromides leading exclusively to the homopropargylic alcohols 14 (equation 11).

The asymmetric approaches include the preparation of the configurationally stable chiral allenyltin starting from enantio-enriched propargylic precursors. When submitted to transmetallation with Sn, Bi or In Lewis acids before addition to the aldehyde, the homopropargyl alcohol is obtained in a 95 : 5 \textit{anti/syn} ratio and in a 90\% ee\textsuperscript{106}. On the other hand, the use of a chiral allenyltin reagent, without prior transmetallation, gives the \textit{syn} adduct selectively (95 : 5) (equation 12)\textsuperscript{107}. However, the use of chiral allenyltin and chiral aldehydes may lead to the same ‘match/mismatch’ effect that was observed with allyltins\textsuperscript{108,109}. Both approaches were applied to the synthesis of macrolides subunits\textsuperscript{110,111}.

The catalytic asymmetric allenylation has been explored with a BINOL/Ti system, giving selectively the homoallenyl alcohol with up to 95\% ee\textsuperscript{112}. Nevertheless, the lower reactivity of allenyltin compared to allylvin necessitated a nearly stoichiometric amount of 8. Recently, an improvement of the reaction by using \textit{i}-PrSBEt\textsubscript{2} overcame that limitation, making the system truly catalytic, with ee in the range of 81 to 97\%\textsuperscript{113,114}. Interestingly, this reaction showed an unexpected equilibration phenomenon, thus producing exclusively
the allenylation adduct irrespective of the propargyl or allenyl structure of the organotin reagent\textsuperscript{115}.

\[ \text{TBSO} \quad \text{Me} \quad \text{H} \quad + \quad \text{H} \quad \text{Me} \quad \text{SnBu}_3 \quad \text{OPiv} \]

\[ \text{BF}_3 \cdot \text{OEt}_2 \]

\[ \text{TBSO} \quad \text{Me} \quad \text{Me} \quad \text{OH} \quad \text{Me} \quad \text{SnBu}_3 \quad \text{OPiv} \]

\[ 97\% \quad \text{syn} : \text{anti} 95 : 5 \]

\[ 12 \]

\[ \text{TBSO} \quad \text{Me} \quad \text{H} \quad + \quad \text{Me} \quad \text{SnBu}_3 \quad \text{OPiv} \]

\[ \text{InBr}_3, \text{EtOAc} \]

\[ \text{TBSO} \quad \text{Me} \quad \text{Me} \quad \text{OH} \quad \text{SnBu}_3 \quad \text{OPiv} \]

\[ 78\% \quad \text{anti} : \text{syn} >99 : 1 \]

\[ \text{Piv} = \text{Me}_3\text{CO} \]

c. Buta-2,3-dienyltins. Recent studies on the synthesis and reactivity of buta-2,3-dienyltins showed their reactivity either with aldehydes or acetals when activated by BF\textsubscript{3} \cdot \text{Et}_2\text{O}, in producing butadien-2-yl methanol derivatives in good yields\textsuperscript{116}. In the same way, buta-2,3-dienyltins generated \textit{in situ} by the transmetallation of 1,3-butadien-2-yl tin with SnCl\textsubscript{4} reacted with various aldehydes to give the butadienyl adduct in 65 to 98\% yields\textsuperscript{117}. The asymmetric catalysed version with the BINOL/Ti/i-PrSBE\textsubscript{2} system was achieved with up to 98\% ee\textsuperscript{118}. 

\[ \text{Piv} = \text{Me}_3\text{CO} \]
d. Alkynyltins. The catalytic InCl$_3$ promoted allylation of aldehydes was extended to various alkynyltins, which were found to be highly reactive after a transmetallation reaction$^{119}$. The choice of solvent was found to be critical for ensuring that transmetallation occurs rather than complexation of the carbonyl substrate. The addition of alkynyltins to $\beta$-alkoxy aldehydes is reported to proceed with a 1,3-anti/syn selectivity reaching a ratio of 64 : 6 when using MeAlCl$_2$ as the Lewis acid$^{120}$.

e. Tin cyanide. Tin cyanide reacts even better than its silicon congener with $\alpha$-chiral aldehydes to give the cyanohydrins with excellent diastereoselectivities$^{121}$. A system using tin cyanide as catalyst and acetyl cyanide gives access to the acetylated cyanohydrins$^{122}$.

7. Conclusion

The allylation of carbonyl compounds with allyltin reagents is still an active area of organotin chemistry from the methodological point of view, and also for synthetic applications. For completeness we should add several alternative techniques, such as the development of trifluoromethanesulphonic acid as a Brønsted acid catalyst for the allylation of aldehydes in water$^{123}$, or the design of fluorous allyltin reagents for the platinum-catalysed allylation of aldehydes$^{124}$.

B. Nucleophilic Addition to Imines and Related Compounds

1. Reactions with imines

a. Introduction. In spite of the fact that the reactivity of allylmagnesium bromide towards imines was observed in 1957, the development of the addition reaction of allylmetals to imines remains quite recent. In contrast to more reactive allylmetals (e.g. M = Li, Mg, Zn), allyltins need the assistance of Lewis acid in order to react with imines. This was reported simultaneously by Trost and Bonk$^{125}$ with TiCl$_4$, and by Keck and Enholm$^{126}$ with TiCl$_4$ and BF$_3$·Et$_2$O. It was then demonstrated that TiCl$_4$ participated exclusively by activating the imine. Contrary to what was observed with aldehydes, a ‘reverse addition’ to favour the transmetallation reaction failed to give any homoallylic amine. Importantly, the transmetallation route remained effective with SnCl$_4$, so that Thomas and coworkers were able to extend the 1,5-asymmetric induction concept to the allylation of imines$^{127-129}$. Similarly to what has been observed with carbonyl compounds, the activation of the iminyl group can be achieved catalytically by using Ln(OTf)$_3$ as a Lewis acid$^{130}$.

b. Mechanisms and diastereoselectivity. It should be noted that allyborons and allyltins are the only allylmetals to add regioselectively to imines, providing exclusively $\gamma$-adducts$^{131}$. The stereochemistry of the addition was explained by Yamamoto and coworkers$^{132}$, using two sets of models to predict the syn/anti selectivity. One possibility could be a reaction via a cyclic transition state with the tin atom interacting with the lone pair of the nitrogen, giving four possible conformations depending on the position of the substituents. An alternative proposal suggested anti-periplanar or syn-clinal open transition states. The main difference between the two models lies in the fact that changing the $E/Z$ stereochemistry of the imine would result in a reversal of the syn/anti selectivity by applying the cyclic model, but it would give the same result with the open model. All the models presented for the diastereofacial selectivity in the case of carbonyl compounds are still valid for the imines. However, it has to be kept in mind that, due to the substitution on the nitrogen atom, imines can possess an additional chiral auxiliary which
can influence the diastereoselectivity. For instance, the use of carbohydrates as chiral templates orientated the SnCl$_4$ activated reaction of allyltributyltin with $N$-galactosylimines to give high asymmetric induction$^{133}$. Consequently, the introduction of chiral centres on both the carbonyl and the amine moiety of the substrate may cause match or mismatch effects$^{134}$.

The first example of 1,2-asymmetric induction was reported by Yamamoto and coworkers with $N$-propylaldimines derived from $\alpha$-phenylpropionaldehyde (equation 13). The reaction gave mainly the $anti$ product$^{135}$, consistent with a Felkin–Ahn addition. A 1,3-asymmetric induction took place with the imine prepared from 1-phenylethylamine and isovaleraldehyde, giving a somewhat lower 7 : 1 diastereoselectivity.

\[
\begin{align*}
\text{Ph} & \quad \text{H} \quad \text{SnBu}_3, \text{Et}_2\text{O} \\
\text{N} & \quad \text{Pr} \quad \text{TiCl}_4 \\
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & \quad \text{NHPr} \\
93 & \quad + \\
\text{Ph} & \quad \text{ NHPr} \\
7 & \quad \\
\end{align*}
\]

\[
\begin{align*}
\text{RH} & \quad \text{NP h} \\
\text{RH} & \quad \text{NPh} \\
\text{Cl}_4\text{Ti} & \quad \text{TiCl}_4 \\
\end{align*}
\]

\[
\begin{align*}
\text{kinetic} & \quad \text{thermodynamic} \\
\end{align*}
\]

\[
\begin{align*}
\end{align*}
\]

Crotyltins react regioselectively with $\alpha$-alkylimines to give exclusively branched products with an excellent $syn/anti$ selectivity up to 30 : 1, when the imine activation is conducted at $-78^\circ$C prior to the addition of the crotyltin. This selectivity which is consistent with an acyclic transition state is rapidly fading when operating at a higher temperature. This would be the result of an equilibrium between the two imine/Lewis acid complexes (equation 14). There are very few examples with $\alpha$, $\beta$-unsaturated aldimines, but it has to be noted that under TiCl$_4$ activation, they are able to undergo a double nucleophilic addition of ketene silyl acetal and allyltributyltin to give the homoallylic amine in a reasonable yield$^{136}$.

\[
\begin{align*}
\end{align*}
\]

2. Other imino substrates

a. Reactions with $N$-heterosubstituted imines. These reagents may be used as ‘protected’ imines which, upon allylation and deprotection, give an access to primary homoallylic amines. For instance, the use of benzoyl- and acylhydrazones as stable surrogates of
imines was exploited in allylation reaction with tetraallyltin\textsuperscript{137,138}. Finally, nitrones can be used as substrates for the allylation reaction, giving access to homoallylic hydroxylamines\textsuperscript{139,140}.

\textit{b. Reactions with iminium salts.} Iminium salts are widely used substrates in order to overcome the lack of reactivity of imines. Thus, the reaction of allyltins with iminium salts, prepared from primary amines and formaldehyde, in protic media give access to bis(homoallyl)amines\textsuperscript{141,142}. Most of the iminium salts are prepared \textit{in situ}. Examples are acyliminium salts, generated from the corresponding \(\alpha\)-ethoxycarbamates which were shown to react with \(\gamma\)-alkoxyallyltins to give \(\alpha\)-amino alcohols in good yields. The \textit{syn/anti} selectivity depends on the nature of the iminium substituents\textsuperscript{143}. This reaction has been extended to various cyclic \(\alpha\)-alkoxycarbamates with high diastereoselectivities\textsuperscript{144}. Chiral acyliminium salts were used for the preparation of enantiopure piperidines\textsuperscript{145}. Lately, the addition of enantio-enriched \(\gamma\)-alkoxyallyltins to chiral acyl iminium salts\textsuperscript{146} provided a new entry to the synthesis of products 15, which are potential precursors of \(\alpha\)-amino-\(\beta\)-hydroxy acids or of aminosugars, with a total control of the stereochemistry (equation 15). Imines can be activated as well by Me\textsubscript{3}SiCl to give the corresponding iminium salts, which are reactive enough to undergo the allylation reaction with allylttributyltin\textsuperscript{147}.

\begin{equation}
\text{EtO}_2\text{C}^+\text{N}^+\text{CH}_2\text{Ar}^+ \text{MeOBDPS}(R) \begin{array}{c} \text{MOMOM} \text{SnBu}_3^- \end{array} \begin{array}{c} \text{BF}_3\cdot\text{OEt}_2, \text{CH}_2\text{Cl}_2, -78 \text{ °C} \end{array} \rightarrow \text{EtO}_2\text{C}^-\text{N}^-\text{CH}_2\text{Ar}^- \text{MeOBDPS} \text{OMOM} \text{BDPS} = t\text{-Bu(Ph}_2\text{)Si} \end{equation}

\textit{c. Reactions with pyridines and pyridinium salts.} Allyltins react as well with substrates such as pyridines or pyridinium salts selectively at the \(\alpha\) position\textsuperscript{148}. The \(\alpha\)- and \(\delta\)-regioselectivity of the addition is closely related to the substitution of the allylmetal reagent. An enantioselective approach was applied with a chiral acyl chloride as activator and an enantioselectivity inductor\textsuperscript{149}. Similarly, oxazolidinones were used as chiral auxiliaries, to promote the synthesis of chiral 1,4-dihydropyridines\textsuperscript{150}.

3. \textit{Catalytic enantioselective addition}

Among the increasing amount of work related to the catalytic enantioselective addition to imines, which appeared in the last 5 years\textsuperscript{151}, some papers were associated with organotin reagents. The first example of catalytic enantioselective allylation of imines was reported by Yamamoto and coworkers, by using 5\% of a bis \(\pi\) allyl palladium complex\textsuperscript{152–154}. Contrary to the BINAP ligand which was found to be totally ineffective under these conditions, \(\beta\)-pinene ligands used as non-transferable allyl ligands gave up to 81\% ee. An extension to the intramolecular reaction of \(\gamma\)-alkoxystannane was applied to prepare \(\beta\)-amino cyclic ethers, for which the \textit{trans} preference in the cyclization is
consistent with an acyclic transition state\textsuperscript{155}. A recent contribution showed that TolBINAP-CuX catalysts were also efficient for the allylation of $N$-tosyl imines\textsuperscript{156}, giving access to $\alpha$-amino acids with up to 98\% ee (equation 16). A polymer-supported version of Yamamoto’s catalyst has been recently prepared, giving moderate ee (13–47\%), but showing promising results in terms of stability and reusability\textsuperscript{157}.

![Image of reaction](image)

\textbf{4. Other organotin reagents}

The use of transition metals to increase the reactivity of allyltins towards imines or related substrates permitted the extension of the reaction to various other organotin reagents. Thus, a recent rhodium-catalysed arylation and alkenylation of imines was described by using 2\% molar of a $[\text{Rh(cod)(MeCN)}_2]\text{BF}_4$ catalyst, affording the corresponding amines in good yields\textsuperscript{158}. An asymmetric version was developed for the rhodium catalysed arylation of $N$-alkylidene sulphonamides, with the chiral monodentate phosphine ligand $(R)$-MeO-MOP giving the amines with ee in the range of 75 to 96\%\textsuperscript{159}. The enantioselective synthesis of an $\alpha$-aminonitrile was achieved in up to 86\% ee, by a zirconium-catalysed asymmetric cyanation reaction\textsuperscript{160}.

\section*{IV. METAL-CATALYSED COUPLING REACTIONS}

\textbf{A. The Stille Coupling Reaction}

\textit{1. Historical background}

\textit{a. Introduction}. The coupling reactions involving organotin reagents catalysed by transition metals are without any doubt the most prolific reactions in the literature. The very first example of this reaction dates back to 1977 with the pioneering work of Kosugi, Shimizu and Migita\textsuperscript{161,162}. However, the reaction is known as the Stille coupling, due to its mechanistic studies and synthetic applications by Stille and coworkers which definitely popularized this reaction\textsuperscript{163,164}. Nowadays, the versatility of tetraorganotins in terms of synthesis and reactivity render this reaction by far the most popular pallado-catalysed coupling along with the Suzuki reaction, involving organoborons. It has been regularly
reviewed\textsuperscript{165–168} and to be strictly correct it would be more accurate to talk about several Stille couplings, due to the impressive mass of different substrates, catalysts, ligands and experimental conditions which were used.

\textit{b. Mechanism.} A deliberately oversimplified catalytic cycle could be represented as shown in equation 17: (i) Formation of the active Pd(0) species, (ii) oxidative addition, (iii) transmetallation step, (iv) reductive elimination.

\[
\text{Pd(II)} \xrightarrow{(i)} \text{R}^1\text{Sn(R}^2\text{)}_3 \xrightarrow{(ii)} \text{R}^1\text{-R}^1 \xrightarrow{(iii)} \text{R}^3\text{-Pd(II)L}_n \xrightarrow{(iv)} \text{R}^3\text{-Pd(II)L}_n^\circ - \text{X} \xrightarrow{(17)} \text{R}^3\text{-Pd(II)L}_n^\circ - \text{R}^1 \xrightarrow{\text{transmetallation}} \text{XSn(R}^2\text{)}_3 \xrightarrow{\text{reductive}} \text{elimination} \xrightarrow{\text{oxidative}} \text{addition} \]

The active palladium catalyst is likely to be a coordinatively unsaturated Pd(0) species such as Pd(PPh\textsubscript{3})\textsubscript{2}\textsuperscript{169}. It can be obtained (i) either by reduction of a Pd(II) precatalyst\textsuperscript{170} or by the \textit{in situ} loss of ligands from a Pd(0) species\textsuperscript{171}. In the latter case the ratio Pd versus ligand is often found to be critical for the kinetic of the reaction. The first step of the catalytic cycle is the addition of the electrophilic substrate R\textsuperscript{1}-X to the palladium catalyst (ii), which goes up to a Pd(II) oxidation state and is favoured by σ-donor ligands\textsuperscript{172}. The mechanism of the oxidative addition depends on the nature of the electrophile. With an aromatic, alkenyl or alkynyl substrate, the catalyst would insert into the carbon–halogen bond via a three-centre mechanism\textsuperscript{173}, preserving the olefin stereochemistry. With substrates possessing an sp\textsuperscript{3} carbon–halogen bond, the mechanism would account for an S\textsubscript{N}2 reaction with inversion of asymmetric centres\textsuperscript{174,175}. This oxidative addition is believed to form primarily the \textit{cis} complex, which readily isomerizes to the thermodynamically favoured \textit{trans} complex\textsuperscript{176–178}. With the allylic substrates, the intermediacy of η\textsuperscript{3}-complexes is postulated\textsuperscript{179}. However, the reaction appears to be ligand and solvent dependent as well\textsuperscript{180}. In addition to this, recent results showed that the nucleophile itself could intervene in the kinetics of the oxidative addition step\textsuperscript{181}. 
The transmetallation step (iii) is certainly the most enigmatic part of the catalytic cycle. Generally, it is assumed to be rate limiting, and several mechanisms are proposed depending on the solvent. An ‘open’ transition state with inversion of the stereochemistry would arise with polar solvents which are able to stabilize the transient partial charges\textsuperscript{182,183}, whereas a cyclic transition state with retention of the stereochemistry would arise in less polar solvents\textsuperscript{184}. It should be noted that the nature of the ligands on the palladium may influence dramatically the kinetics of the transmetallation step. A 1000-fold rate enhancement was observed when replacing triphenylphosphine by tri(2-furyl)phosphine\textsuperscript{185}. However, the dissociative or associative nature of the substitution on the palladium is still under discussion\textsuperscript{186,187}.

The reductive elimination step (iv) is a three-centre mechanism, which creates the carbon–carbon bond, regenerates the catalyst and needs the R\textsuperscript{1} and R\textsuperscript{3} groups to be cis on the palladium. This may be the case when cis bidentate ligands are used\textsuperscript{188}. On the other hand, a trans to cis isomerization may precede the reductive elimination, which operates through T-shaped Pd(II)\textsuperscript{189,190} or Pd(IV)\textsuperscript{191–193} intermediates. Finally, recent studies argued that a T-shaped three-coordinate species cis-[PdR\textsuperscript{1}R\textsuperscript{2}L] may be formed directly by an associative transmetallation step.

2. Scope and limitations

a. Organotins. i. Alkynyltins. Alkynyltins are considered to be the most reactive organotins\textsuperscript{194}, so that the coupling reaction with alkynyltins operates smoothly and offers an elegant solution to the synthesis of several conjugated systems. The reaction takes generally a few minutes at room temperatures\textsuperscript{195}; however, this high reactivity is not a limitation to their use in tandem reactions such as that shown for the dienyne in equation 18\textsuperscript{196}. The only limitation lies in the fact that alkynes themselves are able to couple with electrophiles in the Sonogashira coupling, simply by adding an amine as a base and copper salts\textsuperscript{197}.
ii. Alkenyltins. The use of alkenyltins has been thoroughly explored for both intermolecular and intramolecular reactions. The reaction tolerates a wide range of functionalities such as aldehydes, ketones, esters, unprotected alcohols, ethers and amines. Importantly, the transfer of alkene operates with a retention of the double-bond stereochemistry. Indeed, most of the observed isomerizations occurred after the coupling reaction\(^\text{198}\). Moreover, the reaction is not affected by the steric hindrance of the electrophile\(^\text{199}\). Nevertheless, a substitution in \(\alpha\) or \(\beta\) position of the tin atom may lower in some cases the yield of the reaction\(^\text{200}\). Allenyltins may be used as well, leading to allenyl\(^\text{201},\text{202}\) or propargyl\(^\text{203}\) transfer products, depending on the nature of the substrate.

iii. Aryl- and heteroaryltins. Their reactivities are in the same range as those observed for vinyltins\(^\text{204}\). Both electron-poor or electron-rich groups are tolerated on the aromatic group without altering the reactivity, but an \(\text{ortho}\) substitution may exert an influence on it\(^\text{205},\text{206}\). Consequently, an \(\text{ortho}\) substitution on the organotin and/or the substrate appears to be the main limitation of the reaction\(^\text{207}\). This reaction was rapidly extended with success to heteroaromatic chemistry, to organic synthesis and to supramolecular chemistry. For instance, iterative Stille coupling reactions of substituted pyridines were used to prepare polydentate ligands\(^\text{208}\) (equation 19).

iv. Allyl- and benzyltins. The transfer of allyl and benzyl groups is possible, but their reactivity appears to be lower than with organotins possessing an Sn-Csp\(^2\) bond. Furthermore, when reacting with olefinic or aromatic substrates, the coupling products are prone to reconjugate under Stille coupling conditions\(^\text{209},\text{210}\). Another limitation consists in the loss of the regioselectivity when operating with \(\gamma\)-substituted allyltins, the results being strongly dependent on the nature of the substitution\(^\text{211–213}\).

v. Alkyltins. The transfer of an alkyl group by using organotins remains exceptional and necessitates harsh conditions\(^\text{214}\) (equation 20). As a consequence, methyl and butyl groups, which are considered as non-transferable ligands, do not usually interfere with the transfer of the aforementioned groups. However, some examples of methyl, ethyl and butyl transfers\(^\text{215–218}\) from the corresponding tetraalkyltins are known. The transfer of an alkyl substituent is nevertheless possible when the electrophile is \(\beta\)-substituted by a heteroatom to the tin, thus improving the nucleophilicity of the carbon to be transferred\(^\text{219}\). Interestingly, the transfer of the hydroxymethyl group from Bu\(_3\)SnCH\(_2\)OH does not require protection of the alcohol function\(^\text{220}\).

b. Substrates. i. Halide. Alkenyl and aryl halides are the most commonly used substrates for the Stille coupling reaction. The stereochemistry of the double bond is usually preserved, and the reaction takes place even with a tetra-substituted olefinic electrophile. Furthermore, functionalized substrates such as \(\beta\)-halo-\(\alpha,\beta\)-unsaturated ketones, esters\(^\text{221–223}\) or sulphoxides\(^\text{224,225}\), \(\alpha\)-halo-\(\alpha,\beta\)-unsaturated ketones\(^\text{226,227}\) or haloquinones\(^\text{228–231}\) are reactive.

Aryl iodides and bromides couple with most of the organotins, and the reaction is compatible with poly-substitution on the aromatic ring. As the insertion of the palladium into the C–Br bond requires more drastic conditions, the oxidative addition may become the rate-limiting step, so that the reaction can be accelerated by electron-withdrawing groups in the \(\text{para}\) position. Similarly to alkenyl chlorides, aryl chlorides do not generally react, due to their lack of reactivity in the oxidative addition to the Pd(0) catalyst. However, very recent results established that the cooperative effect of an electron-rich sterically hindered \((t\text{-Bu})_3\text{P}\) associated to a fluorne source results in the coupling of various organotins with aryl chlorides (equation 21)\(^\text{232}\).
18. Synthetic applications of organic germanium, tin and lead compounds

```
N  | SnBu₃ + Br- N  | Br
    |              |     
    | Pd(PPh₃)₄    | THF, 65 °C
    |               | 93%

Cl- N  | N- Cl
    | N- N
    | Cl Cl
    | SnBu₃
    | BuLi
    | Bu₃SnCl

Pd(PPh₃)₂Cl₂
DMF, 90 °C

N  | N  | N  | N  | N
    |   |   |   |   

67%

DMF, 90 °C
Pd(PPh₃)₂Cl₂
Bu₃Sn

N  | N  | N  | N  | N
    |   |   |   |   

45%
```
Heteroaryl halides such as halopyridines\(^{233}\), bromoquinolines\(^{234,235}\), furyl halides\(^{236}\), thienyl halides\(^{237−241}\) and imidazoyl bromides\(^{242}\) were found to be reactive. A particularly interesting application concerns nucleoside chemistry, since 2-iodopurine\(^{243−246}\), 5-iodouridine\(^{247−249}\), 5-halouracil\(^{250−252}\) and 5-iodocytosine\(^{253}\) were used successfully. When the reactivity of the carbon–halogen bond is exalted, the coupling reaction can be extended to chloro derivatives, such as 6-chloropurines\(^{254}\), 4- and 5-chloropyrimidines\(^{255−259}\) and 2-chloropyrazines\(^{260}\).

In the same way, the coupling reaction of acyl chlorides and organotins is particularly efficient and general\(^{261}\). This represents an alternative to the ‘carbonylative’ three-component coupling reaction, and gives access to various aldehydes, ketones and \(\alpha, \beta\)-unsaturated ketones. A similar reaction is feasible with chloroformates, carbamoyl chlorides and sulphonyl chlorides, giving respectively \(\alpha, \beta\)-unsaturated esters, amides\(^{262}\) and sulphones\(^{263}\).

\(\text{ii. Sulphonates}\). The use of sulphonates was first observed in 1984\(^{264}\) and concerned essentially with organic triflates, which appear as the substrates of choice for the Stille coupling reactions. The rapid development in the field is due to the ready preparation of vinylic triflates from ketones and of aromatic triflates from phenols. However, triflates gave poor yields under usual Stille coupling conditions, presumably due to the formation of an unstable ionic palladium species\(^{265}\). In order to avoid the premature decomposition of the catalyst, it appeared necessary to add halide salts such as LiCl, to form the classical
Pd(II) intermediate. Another approach stated that LiCl was unnecessary when operating in polar solvents (DMF, NMP) which formed a solvated reactive Pd intermediate. As the solvent is believed to displace ligands out of the coordination sphere of the metal, the system was finally optimized by replacing the strong donating phosphine ligands by a softer triphenylarsine ligand. The overall understanding of the mechanism involving triflates is still under discussion.

In addition to the triflates, it can be noted that some attempts were made with mesylates, tosylates, p-fluorophenyl sulphonates, nonaflates and other polyfluorinated sulphonates and fluorosulphonates.

iii. Miscellaneous. The use of various salts, highly reactive towards nucleophiles, was applied in the Stille coupling. Trivalent iodonium salts such as phenyliodonium tetrafluoroborate or triflate were introduced in 1992. They undergo facile coupling reactions, under particularly mild conditions. Various vinyl-, aryl- and heteroaryl iodonium salts were prepared, and their use can be illustrated by the preparation of a potent antiviral uracil analogue (equation 22). A similar approach involves the use of aryldiazonium salts, and quite recently the efficiency of sulphonium hexafluorophosphates was established. In the particular case of allylic electrophiles, and due to their peculiar reactivity towards oxidative addition to the palladium, some unusual leaving groups such as chlorides, acetates or phosphates were found to be quite reactive. Interestingly, whereas propargyl acetates failed to react, allenyl acetates underwent the coupling reaction efficiently. The extension to vinyl phosphates was recently achieved and applied to the total synthesis of Brevetoxin A.

\[
\begin{align*}
\text{H}_3\text{C} & \text{N} & \text{O} & + \text{IPhOTf} & + \text{PhSnBu}_3 \\
                   & \text{O} & \text{N} & \text{CH}_3
\end{align*}
\]

\[
\text{Pd(OAc)}_2(5 \text{ mol\%})
\]

\[
\text{AsPh}_3(10 \text{ mol\%})
\]

\[
\text{THF, 45 °C, 180 min.}
\]

\[
\text{95%}
\]

\[\text{c. Catalysts. Pd(PPh}_3)_4 \text{ is a widely used catalyst for palladium coupling reactions, but several studies demonstrated that it is not the best catalyst. However, there is no clear rule to point out what will be the ‘good’ catalyst for a given reaction, and several factors are}]

to be considered in order to optimize the coupling conditions. Farina demonstrated that an excess of ligand would inhibit the coupling by slowing the formation of the supposed coordinatively unsaturated PdL2 active species. The optimum ratio can be easily attained by replacing Pd(PPPh3)4 with the stable Pd2dba3 and the correct quantity of the phosphine ligand. Another possibility implies the use of the Pd(II)(PPh3)2Cl2 complex which is in situ reduced to the active PdPPPh32.

The nature of the ligand itself is of paramount importance for both the oxidative addition and the transmetallation steps. The replacement of a strong donating ligand such as PPh3 by softer ligands such as tri(2-furyl)phosphine125,185 or phosphites generally results in a great enhancement of the reaction rate. This is the case in coupling reactions involving triflates, in which triphenylarsine was shown to be particularly efficient. It is also possible to change the bulk of the ligand, e.g. by using P(Bu-t)3 in order to favour the ligand dissociation step232. Finally, it is noteworthy that several Stille couplings were conducted under ‘ligandless’ conditions without altering the stability of the catalyst294,295.

Cocatalysis with copper salts has proven its efficiency in the enhancement of the reaction rate, particularly in polar solvents. Discovered by Liebeskind and Feng296, and largely exploited, the cocatalytic effect of Cu(I) depends on the reaction conditions in two ways297,298 (equation 23). The copper acts as a ligand scavenger in polar solvents, thus enhancing the ligand/solvent exchange. It is also able to transmetalate with the organotin to produce an active organocopper reagent299. This interesting event was highlighted by the success of coupling reactions between organotins and halides conducted without palladium, and with CuCN as a catalyst300,301 or when mediated by CuCl302–304.

3. Synthetic applications

a. Intermolecular couplings. i. Vinyl–Vinyl couplings. Use of the Stille coupling reaction has found applications in several domains such as heteroaromatic chemistry, supramolecular chemistry, polymers and total synthesis. The major contribution of
Stille coupling to organic synthesis is the preparation of polyconjugated systems via the vinyl–vinyl coupling reactions. This methodology was used in carbohydrate chemistry, terpenoids chemistry and in preparing polyconjugated dienes. The enone functionalization can be performed either in α, β or γ position, and this was applied to leucotrienes synthesis. There were several uses in steroid chemistry and for the synthesis of complex natural molecules such as onnamide A, avermectin, calyculin, lepicidin, ratjadone, amphidinolide B and brevetoxin A. Interestingly, the synthesis of polyconjugated dienes involved frequently the use of (E,Z)- or (E,E)-dienyltins, and was applied to the synthesis of natural products such as Pateamine A, Nisamycin (equation 24) or Polycavernoside A.

The reaction has been extended to alkynyltin reagents due to the particularly smooth conditions allowed in these couplings. Various substrates such as enynes, vinyl ethers, α, β unsaturated esters, cyclobutenediones, quinones or chiral vinyl sulphoxides were reacted successfully. All the combinations are possible, so that ynynyltin, enynyltin and diynyltin reagents were used. Finally, distannylated reagents such as 1,2-vinylditin, 1,4-dienylditin or 1,2-ethynylditin were prepared in order to obtain double Stille coupling reactions.

**ii. Aryl–aryl couplings.** This reaction is particularly useful for different types of reactions, such as the preparation of ligands or cryptands, the design of materials with optical and electronic properties such as polythiophenes, the functionalization of more complex aromatic structures such as porphyrins and even the total synthesis of natural products or peptide receptors analogues. All types of aromatic systems were used including benzenes, pyridines, pyrroles, furans, thiophenes, pyrimidines and others. Furthermore, the reaction is particularly tolerant to functional groups or moieties such as fluorine or chlorine, trifluoromethyl, acetylenes, nitriles, ethers and thioethers, esters and amides, ketones and aldehydes, ketals, nitro, unprotected amines, hydroxyls or carboxylic acids. As outlined above, an ortho disubstitution may alter the reaction. However, there are several examples of couplings with o,o'-disubstitution either on the aromatic substrate or on both reaction partners. An interesting possibility of this reaction is related to the poly-substitution of aromatic systems, thus allowing 1,2-, 1,3-, 1,4- and 1,3,5-triple coupling reactions in one pot. Moreover, it is possible to conceive sequential couplings, depending on the intrinsic reactivity of each functionality of the substrate under a given experimental condition.

**b. Intramolecular coupling.** The intramolecular version of the Stille coupling, first reported in 1985, is a particularly attractive way to get rings ranging from four to thirty-two members. It is noteworthy that, contrary to the classical macrocyclization processes, the intramolecular Stille coupling does not require high dilution techniques to operate.

**i. Alkenyl–alkenyl cyclizations.** The elaboration of conjugated polyenic cyclic structures remains a major tool in the total synthesis of natural products. The retention of the stereochemistry of both the alkene electrophile and the alkenyltin, coupled with the mildness of the coupling conditions led to the advantageous use of the Stille coupling at the very end of the macrocycles synthesis. The alkenyl–alkenyl coupling permits the synthesis of small rings such as four, five, six-membered rings with exocyclic dienic system or with one internal double bond. Medium-sized rings from seven to fifteen members were also formed. It should be noted that ten-membered...
cycles with internal triple bonds can be obtained in good yields\textsuperscript{406,407}. The high potential of the intramolecular coupling was realized by several syntheses of macrocycles having, from fourteen- to twenty-nine-membered\textsuperscript{408} rings. In this series, either $Z/E$ dienes were prepared for the synthesis of leynamicyn\textsuperscript{409}, $Z/Z$ dienes were used for the synthesis of papuamine\textsuperscript{410} or an $E/E/E$ triene was used for the famous Nicolaou’s total synthesis of rapamycin using the aforementioned 1,2-vinylditin reagent\textsuperscript{411}. One of the most impressive examples for the potential of Stille coupling reaction is certainly the recent total synthesis
of Sanglifehrin A\textsuperscript{412}, for which the two key steps are an intramolecular vinyl–vinyl coupling to form the 22-membered ring, followed by an intermolecular vinyl–vinyl coupling to connect the spirolactamic side chain (equation 25).

\begin{align*}
\text{ii. Alkenyl–aryl cyclizations.} \text{ Cyclizations involving an alkenyl–aryl coupling reaction gave four–} & 413 \text{ to fifteen-membered} \text{ rings. The olefinic moiety can be extracyclic} & 415 \text{ or intracyclic with } Z \text{ or } E \text{ stereochemistry, depending on the substrate and the size of the ring to be formed} & 416 \text{ (equation 26). Other examples of heteroaryl–vinyl couplings can be found in the recent literature. An example is the approach to the synthesis of lophotoxin,}
\end{align*}
using a vinyl iodide and a 2-(tributylstannyl)furan coupling reaction.  

\[ \text{SEM} \quad \text{SnBu}_3 \]

\[ Z:E = 1:1 \]

ThF, reflux $\text{Pd}_2(\text{dba})_3, \text{P(2-furyl)}_3$ 1%  

SEM = Me$_3$Si(EtO)CH

iii. Aryl–aryl cyclizations. Aryl–aryl couplings gave cyclizations from six- to thirty-two-member rings, giving access to polyaromatic compounds, cryptands and heterocycles. A particularly interesting version is represented by the Stille–Kelly cyclization, which implies primarily a coupling between Bu$_6$Sn$_2$ or Me$_6$Sn$_2$ with an aryl halide to form \textit{in situ} the ArSnR$_3$ reagent ($R = \text{Me, Bu}$) which subsequently reacts with another Ar-X function to give the cyclized product (equation 27).

iv. Miscellaneous reactions. Advantage of the high reactivities of acyl chlorides and chloroformates was taken in order to obtain macrocycles having from seven to twenty-two members. This represents an interesting access to various cyclic ketones, lactones, $\alpha$-methylene lactones and $\alpha, \beta$-unsaturated esters. The carbonylative macrocyclization has been targeted as well to prepare $\alpha$-methylene lactones containing twelve- to sixteen-member rings. For such reactions, Pd catalysts supported on polymers were shown to be more selective than the classical homogeneous systems.

4. New trends in the Stille coupling reaction

a. Solid-phase supported reactions. The development of solid-phase chemistry and combinatorial chemistry in the last ten years has offered new fields of investigation to the Stille coupling reactions. The main advantage of the method is obviously related to the purification step, which allows one to free the product from tin residues. There are three different possible ways to employ the coupling reaction (equation 28):
18. Synthetic applications of organic germanium, tin and lead compounds

\[
\text{Bu}_6\text{Sn}_2 + \text{Toluene, reflux, 12 h} \rightarrow \text{Pd(PPh}_3\text{)}_2\text{Cl}_2 \ 5\%, \text{Et}_4\text{NCl} \rightarrow \text{68%}
\]

\begin{align*}
(i) & \quad \text{Sn} - R^2 + R^1 - X \\
(ii) & \quad R^2 - \text{Sn} + R^1 - X \\
(iii) & \quad R^1 - X + R^2 - \text{Sn} \\
\end{align*}

(28)
(i) The substrate is in solution and the organotin is bonded to the polymer via the tin atom.
(ii) The substrate is in solution and the organotin is bound to the polymer via the organic moiety.
(iii) The substrate is grafted to the solid phase and the organotin is in solution.

**i. Organotin grafted on polymers.** The first approach is derived from the chemistry developed by Neumann’s and Pereyre’s groups among others, to get tin hydrides supported on polymers (see the preceding section). The organotin reagent is grafted on a polystyrene resin and the product is released into the organic phase and purified by filtration. The method was recently extended to an intramolecular coupling reaction used for the synthesis of the antibiotic zearalenone. The second approach was used for the synthesis of various benzodiazepines via an aryl–acyl chloride coupling already in 1995, and was further extended to the biaryl synthesis. The product, which is bound to the polymer, is purified from the tin residues by successive washings, before its cleavage from the resin. It is noteworthy that the reaction is believed to work better when the aryltin nucleophile is the one on the solid support (method ii versus method iii).

**ii. Substrate grafted on polymers.** The third method was first reported in 1994 for aryl–aryl and aryl–alkenyl couplings, and then extended to aryl–heteroaryl couplings and used for a phenyl–furan coupling on various supports frequently used in peptide chemistry, giving up to 90% yield. An extension of the method consists in developing sequential halogenation–Stille coupling reactions to get oligothiophenes, up to the pentamer, in 89% yield and excellent purity.

A general tendency for the three methods lies in the need to raise the Pd ratio up to 5–10% in order to avoid a too long reaction time. Nevertheless, the continuing search for new solid supports, linkers or palladium catalysts will ensure the development of the ‘supported Stille coupling reaction’.

**b. Unusual media.** In comparison with heterogeneous solid supported methods, the fluorous synthesis technique offers the advantage of the non-miscibility at room temperature and the homogeneity under heating. First developed by Curran and coworkers for tin-mediated radical chemistry (see the preceding section), the method was extended to the Stille coupling reaction in 1996. The method was recently improved by using microwave activation which enabled one to get coupling products in six minutes and up to 78% yield. The Stille reaction is easily adaptable to the emerging techniques, as shown by its successful use in aryl–vinyl couplings using supercritical carbon dioxide as the reaction medium. Likewise, the Stille coupling can be conducted in aqueous medium by using a Pd(II) catalyst and water-soluble phosphines, or a palladium complex supported on silica.

**c. Hypervalent organotin reagents.** The activating effect caused by an additional coordination to the tin atom was established in the early 1990s by Vedejs and coworkers and by Van Koten and coworkers. The formation of a hypervalent organotin is supposed to accelerate the limiting transmetallation step by increasing the nucleophilicity of the organic group to be transferred. Thus, the α-heteroalkyl-enol triflate coupling was used for the synthesis of carbapenem derivatives (equation 29) by means of Vedejs’ stannatrane. The affinity of a fluorine atom for the tin, the ease of halogen–fluorine exchange and the production of easily removable fluorotin side products encouraged several investigators to synthesize various fluorostannates as activated organotin reagents. However, in contrast with their silicon and boron counterparts, the use of fluorostannates...
for the Stille coupling remained limited until recently. The transfer of a phenyl group to vinylic triflates by using triphenyldifluorostannate was reported only in 1994, followed by an extension to various aryltins by using tetraorganofluorostannates. A promising approach using monoorganotins and TBAF as a fluorinating agent revealed the generality of the reaction to all kinds of organic moieties, including alkyl transfer which occurred in up to 76% yield. Furthermore, these reagents exhibited a specific reactivity compared to classical organotin reagents, such as a total γ-stereocontrol for the transfer of substituted allyltins (equation 30). This methodology was finally applied to vinyl and aryl triflates as substrates.

\[
\begin{align*}
&\text{PMB = } p\text{-MeOC}_6\text{H}_4\text{CH}_2 \\
&\text{SN(TMS)}_2 \quad \text{Sn} \quad \text{SN(TMS)}_2 \\
&\text{Br} \quad + \quad \text{I} \\
&\text{Pd(PPh}_3)_4 \quad \text{THF} \\
&\text{Bu}_4\text{NF, 3 eq} \\
&81\%
\end{align*}
\]
**d. Conclusion.** Despite the established toxicity of organotins, the Stille reaction remains particularly attractive due to the mild and neutral conditions required for the coupling. There is no doubt that the aforementioned recent techniques will be used to further develop the application of organotins. In addition, the forthcoming efforts to create a real Stille coupling catalytic in tin hold great promise for the future.

**B. Metal Catalysed Coupling Reactions**

1. **Palladium-mediated coupling reactions**

   **a. Carbon–carbon coupling reactions.** There are some reactions involving organotins and palladium catalysis which are not related to the Stille coupling reaction. Whereas the reactivity of organotin was reported as early as 1969 for a Heck-type reaction, the coupling of aryltin with electron-poor olefin or in the presence of a palladium(II) catalyst is quite a recent reaction. Similarly, the difunctionalization of alkenes or alkynes is poorly documented. Interesting results were obtained for the carbostannylation of alkenes by alkynyltin in the presence of an iminophosphine–palladium complex, leading to the corresponding functionalized stannyl enynes (equation 31) in up to 82% yield. Finally, the allylation of pronucleophiles can be achieved as an alternative to the radical or carbanionic processes, with allyltins in the presence of Pd\(_2\)(dba)\(_3\) as a catalyst.

   \[
   \begin{align*}
   \text{Ph} & \quad \text{SnBu}_3 \\
   + & \\
   \text{Me} & \quad \text{CO}_2\text{Et} \\
   \text{Ph} & \quad \text{PPh}_2 \\
   \text{THF} & \quad \text{Bu}_3\text{Sn} \\
   \text{EtO}_2\text{C} & \quad \text{Me} \\
   \text{57%} & \quad (31)
   \end{align*}
   \]

   **b. Carbon–heteroatom coupling reactions.** In addition to the Stille reaction, several carbon–heteroatom coupling reactions can be achieved with organotins and palladium catalysis.

   i. **Carbon–nitrogen bonds.** This reaction was first reported in 1983 by Migita and coworkers, who described the amination of aryl bromides with \(\text{N, N-diethylaminotributyltin}\) (equation 32). The scope of this reaction was studied since 1994 by Hartwig’s and Buchwald’s groups and still represents an advantageous alternative to the classical coupling strategy employing a free amine which necessitates the use of stoichiometric amounts of bases such as NaOBu-t.

   ii. **Carbon–sulfur and carbon–selenium bonds.** The reactivity of the tin–sulfur bond comprises an easy access to aryl,

   heteroaryl, and vinyl sulphides.

   Both unsymmetrical and symmetrical sulphides can be obtained by using trialkyltin sulphides or \(\text{R}_3\text{Sn–S–SnR}_3\) (equation 33). The reaction has been extended to the preparation of alkylaryl selenides with alkylselenotin or PhSeSnBu\(_3\) reagents in up to 88% yield.

   iii. **Carbon–silicon bonds.** Following the earlier reports mentioning the palladium-catalysed addition of organosilylstannanes to alkynes or isonitriles, Mori and coworkers realized tandem transmetallation–cyclization reactions with bifunctional halogeno triflates and Bu\(_3\)SnSiMe\(_3\). The reactivity of 18 under palladium catalysis was used for the silylstannylation of alkenes or the synthesis of allylic silanes via a three-component (aryl iodide + diene + 18) coupling reaction. Recently, a similar
approach to substituted allylic silanes used a three-component coupling reaction involving 18, a substituted allene and various halides as electrophiles (equation 34)\(^4\).

\[
\begin{align*}
R = \text{H, Me, MeO, Cl, Br, MeCO, NMe}_2 \\
\text{Tolune, 100 °C, 3 h} \\
\text{PdCl}_2[\text{P(o-tolyl)}_3]_2 \\
\end{align*}
\]

iv. Carbon–tin bonds. The potential of distannanes to undergo a coupling reaction under palladium catalysis has long been known\(^4\) and represents an easy access to various organotin reagents. Various substrates such as aryl halides\(^4\), aryl acetates\(^4\), vinyl triflates\(^4\), or vinyl chlorides\(^4\) can be used.

2. Copper-mediated coupling reactions

It is established that the addition of copper(I) salts could accelerate the Stille coupling by transmetallating the organotin reagent. Following the pioneering study of Tanaka and coworkers\(^4\), who used the tin-to-copper transmetallation to add various vinyltins to allenes, further work established that the resulting organocopper intermediate could achieve the coupling without any palladium catalysis. Most of the studies were conducted with stoichiometric amounts of copper(I) salts. The air-stable Cu(I)thiophene-2-carboxylate allowed rapid reactions at room temperature between iodides and vinyl or aryltins\(^4\). The reaction was extended to vinylic triflates for the synthesis of cepheums\(^4\). The total synthesis of the sixteen-membered macrolide Elaiolide was achieved via a double coupling reaction (equation 35) as a key step\(^4\). Bis stannyalted compounds undergo five to seven ring closures when subjected to five equivalents of CuCl\(^4\), with yields ranging from 62 to 97%.
Interestingly, it was established that α-substituted organotins were able to couple with electrophiles with catalytic amounts of copper\(^{495,496}\). This exalted reactivity was explained by an intramolecular complexation of the copper atom (equation 36).

Recently, the catalytic use of Cu(I) salts was applied to the aryl–aryl and aryl–vinyl couplings\(^{497}\) and to the allylation of furans and thiophenes\(^{498}\), even without the benefit of such activation. In parallel with the use of Cu(I) salts, the reactivity of stoichiometric amounts of Cu(II) was established for the homocoupling of vinyltins\(^{499,500}\). Copper nitrate was found to be particularly efficient, leading to the cyclotrimerization of 1-bromo-2-stannylalkenes\(^{501,502}\). Lately, the use of catalytic amounts of CuCl\(_2\) was shown to be superior to the use of Cu(I) salts for achieving these homocoupling reactions\(^{503}\).

\[
\text{PMB} = p\text{-MeOC}_6\text{H}_4\text{CH}_2
\]

(Reference 495) (Reference 496)
3. Nickel-mediated coupling reactions

Replacing the palladium catalyst in coupling reactions by a nickel catalyst would broaden the scope of the reaction, since non-activated chlorides would become suitable substrates. However, organotins are much less reactive with such catalysts than their corresponding magnesium or zinc congeners. The first example of nickel-based catalysis concerned the coupling reaction of organic halides with tetramethyltin in the presence of carbon monoxide\(^{504}\). However, synthetic applications dealt essentially with the addition reactions of organotins, such as the addition of alkenyltins to enoxysilanes derived from aldehydes, in the presence of Ni(cod)\(^2\)^{505}. Further extension of this reaction was the Ni(0) catalysed synthesis of stereo-defined enynes by a three-component coupling reaction of alkylnyltins, alkynes and enones (equation 37)^{506}. The reaction is believed to proceed via a \(\eta^3\)-allylnickel complex and was successfully extended to allyl halides as substrates\(^{507,508}\). Other substrates such as aryl mesylates were envisaged, but they lead to the coupling products in only moderate yields\(^{509}\). An intramolecular eight-membered cyclization between an aryl bromide and an aryltin was recently used to prepare the biaryl portion of vancomycin antibiotic\(^{510}\). The corresponding Stille coupling surprisingly failed in that case, and the NiCl\(_2\)(PPh\(_3\))\(_2\) had to be used stoichiometrically in order to raise the yield up to 50%.

![Equation 37]

4. Rhodium-mediated coupling reactions

The use of organotins in conjunction with rhodium catalysis is an emerging reaction which holds great promise due to the potential of these catalysts to activate C—H bonds. For instance, the ortho arylation of 2-arylpuridines has been directly realized with tetraphenyltin in the presence of a rhodium(I)phosphine complex\(^{511}\). A cationic rhodium complex allowed the conjugate addition of arylstannanes to \(\alpha,\beta\)-unsaturated ketones or esters in good yields under neutral conditions\(^{512}\). Finally, alkynylnyltins are able to undergo \([C_2 + C_1 + C_1]\) couplings in the presence of carbon monoxide, giving highly unsaturated cyclobutenone derivatives\(^{513}\).
V. FREE RADICAL REACTIONS

A. Allyltins

1. Background

The radical chemistry of organotins is undoubtedly dominated by tin hydride chemistry, which has been at the source of radical chain reactions of valuable interest for organic synthesis. However, the demonstration of the ability of allyltin reagents to undergo homolytic cleavage of the carbon–tin bond goes back to the early 1970s, and only ten years later Keck and coworkers established the synthetic potential of this reaction. Nowadays this is a particularly useful way of introducing various functionalized allyl groups into a system under mild and neutral conditions.

2. Mechanism and reactivity

The radical chain mechanism involving allytin belongs to the ‘fragmentation method’ family and can be schematically presented as in equation 38, which involves five steps: (i) initiation step, (ii) reaction with the substrate, forming the carbon-centred radical, (iii) a possible evolution of this radical, (iv) addition of the newly formed radical to the allylic double bond and (v) β-scission, regenerating the chain-carrying tin radical.

\[
\begin{align*}
\text{SnBu}_3 & \quad \text{Bu}_3\text{Sn}^- \\
\text{R}^2 & \quad \text{R}^1-\text{X} \\
\text{SnBu}_3 & \quad \text{Bu}_3\text{SnX} \\
\text{SnBu}_3 & \quad \text{SnBu}_3 \\
\end{align*}
\]

The initiation step (i) producing the tributyltin radical can be performed by thermolysis of radical initiators such as AIBN. Complementarily, the use of a Et_3B/O_2 system or of photochemical irradiation allows the reactions to proceed at low temperature. The reaction (ii) with the substrate forming the carbon radical applies the same substrates as those used in tin hydride chemistry, such as iodides, bromides, selenides, xanthates and even thiocarbonates. Furthermore, the possible competitive addition of tributyltin radicals to the allyltin reagent is of no consequence due to the rapid β-fragmentation of the resulting carbon-centred radical, which renders this reaction a degenerate one. It is noteworthy that less reactive radical precursors such as chlorides or phenyl thioethers can be used efficiently. The evolution of the radical (iii) via several intra- or intermolecular elementary
steps before trapping with allyltins is possible, without using any slow addition or high dilution techniques. Indeed, the main difference from tin hydride chemistry lies in the fact that the addition of radicals to the allyltin reagent (iv) is not so fast\(^{524}\) \((k_{\text{add}}\) being only \(10^4-10^5\text{M}^{-1}\text{s}^{-1}\) at 60°C), avoiding a premature quenching of the carbon radicals. This can be illustrated by various three-component intermolecular coupling reactions, involving activated olefins\(^ {525,526}\), or carbon monoxide (equation 39)\(^ {527}\). It is important to note that the electrophillic radicals attack the allyltin \(\pi\) bond more easily than do nucleophilic alkyl radicals\(^ {528}\), whereas the addition of carbon radicals to allyltin is not severely affected by their nature, thus enabling a wide range of substrates to react. For instance, \(N\)-acyl radicals are able to add efficiently to allyltin before their decarbonylation\(^ {529}\). Finally, a rapid \(\beta\)-scission (v) with a rate constant likely over \(10^6\text{s}^{-1}\) occurs to regenerate the tributyltin radical. The efficiency of that step avoids the undesired addition of 19 to the precursor allyltin.

The allylic radical transfer has been applied to the synthesis of complex structures such as \(\beta\)-lactams\(^ {530,531}\), steroids\(^ {532}\), alkaloids\(^ {533}\) or C-glycosides\(^ {534,535}\).

3. Functionalized allyltins

The synthesis and use of functionalized allyltins has been thoroughly explored, especially when functionalized at \(\beta\)-position. The use of allyltins \(\beta\)-substituted by an electron-withdrawing group represents a particularly attractive option, due to their enhanced reactivity towards nucleophilic carbon radicals. For that purpose several allyltins substituted with amide or ester\(^ {536}\), chloride or nitrile\(^ {537,538}\), trimethylsilyl\(^ {539}\) and sulphones\(^ {540}\) as substituents were prepared. They have been used for the synthesis of 1,4-dienes\(^ {541}\), and in amino acids\(^ {542}\) or carbohydrate chemistry\(^ {543}\). The ester functionality may be used afterwards for intramolecular endo-cyclizations leading to 10–15-membered \(\alpha\)-methylene lactones\(^ {544}\). The functionalization by non-activating alkyl groups, such as methyl or hydroxymethyl, is tolerated and more complex organotin reagents, such as 20, were used in the synthesis of prostaglandins\(^ {545,546}\) (equation 40), and \(\beta\)-lactams\(^ {547}\).

Unfortunately, substitution in the \(\gamma\)-position, such as in crotyltin, led to poorly reactive allyltins, due to the decrease in the addition rate of the radicals to the double bond. It has been established that, generally, the competitive allylic hydrogen abstraction became predominant, destroying the crotyltin reagent\(^ {548}\). The use of \(\gamma\)-substituted allyltins for the photo-induced radical allylation of carbonyl compounds represents an interesting
The limitation can then be overcome as well in intramolecular processes such as 5-exo trig cyclizations (equation 41). In a similar way, Baldwin has shown that the substitution at the $\alpha$-position has to be avoided. In that case the competitive tin radical addition to the double bond is not degenerate and isomerization to the non-reactive $\gamma$-substituted counterpart occurs.

\[ \text{Equation 40} \]

\[ \text{Equation 41} \]

4. **The stereoselective approach**

Albeit radical chemistry was regarded for a long time as being unable to achieve stereoselective reactions, there is growing interest in finding new systems which will enable the radical reactions to proceed with a high level of stereoselectivity. Most of the work done with allyltributyltin is relevant to the 1,2-asymmetric induction. The stereocontrol by an adjacent asymmetric centre, of the addition of the radical to the allyltributyltin, proved to be efficient especially with cyclic systems such as $\gamma$-lactones, either under photochemical or thermal activation. The induction of chirality involving acyclic substrates, for which the control is much less obvious, was explored as well. The elegant
study of Hanessian and coworkers\textsuperscript{554}, in which the intervention of a hydrogen bonding rigidified the structure to give diastereoselectivities up to 98 : 2, should be noted.

Another way to fix the substrate structure was to use bidentate Lewis acids, which enabled work to be conducted under chelation control. The use of MgBr\textsubscript{2} \cdot OEt\textsubscript{2} for the allylation of \(\alpha\)-iodo-\(\beta\)-alkoxyesters at \(-78^\circ\text{C}\) gave diastereoselectivities of over 100 : 1 (equation 42)\textsuperscript{555}. Lanthanide triflates were also used and gave de up to 10 : 1 diastereoselectivities at refluxing dichloromethane\textsuperscript{556}. Importantly, this methodology can be extended to achiral substrates by using chiral Lewis acids, prepared from Zn(OTf)\textsubscript{2} and chiral C\textsubscript{2}-symmetric bis(oxazoline) ligands, reaching up to 90% ee\textsuperscript{557,558}.

In addition to the Lewis acid protocols, the stereo-controlled introduction of the allyl group was studied with various chirality inductors. The allylic substitution was realized with a 1,2-asymmetric induction using substrates possessing chiral sulphoxide moieties\textsuperscript{559}. This strategy can be coupled with the use of Lewis acids to enhance the stereo-selection up to 50 : 1\textsuperscript{560,561}. Similarly, the use of arylurea acting as a protic Lewis acid and complexing the sulphoxide is reported to give stereoselectivities of up to 14 : 1\textsuperscript{562}. The use of chiral auxiliaries such as oxazolidinones was reported to act efficiently when the allylation is performed on the oxazolidinone ring\textsuperscript{563,564}. The selectivity was somewhat lower when the reaction was conducted on the tethering chain of the oxazolidinyl nitrogen, due to the unfavourable position of the radical, which is too far away from the stereogenic centre\textsuperscript{565}. This was overcome by using a Lewis acid in order to proceed under chelation control and the selectivity was raised up to 100 : 1\textsuperscript{566}. A recent example of C-centred radical generated in the \(\alpha\)-position to the nitrogen showed a good diastereoselectivity in the absence of any Lewis acid. The de, up to 98 : 2, remained however strongly dependent on the radical nature\textsuperscript{567}. Other auxiliaries, such as oxazolidines\textsuperscript{568} which were used, were shown to be insensitive to Lewis acid additives.

**B. Other Organotins**

1. **Propargyl- and allenyltins**

Propargyltin was equally found to be efficient for transferring an allene group\textsuperscript{569}. A larger excess of propargyltin is needed, however, due to its isomerization to more stable
allenyl tin under the radical conditions (equation 43). This was used in the synthesis of modified nucleosides. Finally, the use of phenylmenthyl esters as chiral inductors proved its efficiency in the synthesis of various stereo-controlled α-amino acids with allyl-, methallyl-, crotyl-, propargyl- and allenyltins. Nevertheless, regarding the unconventional outcome of the reaction, it is not clear if the mechanism is a radical chain process.

\[ \begin{align*}
\text{NHCO}_2\text{Bu}^- & \quad \text{PMBO}_2\text{C} \\
\text{SnMe}_3 & \quad \text{SO}_2\text{Ph}
\end{align*} \]

2. Vinyltins

Vinyltins were used for synthetic purposes in radical addition–elimination sequences. The main limitation comes from the necessity to functionalize the olefin by groups such as esters able to stabilize the transient carbon-centred radical. Phenyl-substituted systems proved to be reactive as well, whereas methyl- and cyclohexenyl-substituted ones failed to react. An intramolecular version was developed giving access to methylene cyclopentane units (equation 44).
3. Miscellaneous

In addition to the use of Bu$_6$Sn$_2$ as initiator for radical reactions, this reagent can be used stoichiometrically to ensure that reactions take place whenever classical organotins failed to react. For instance, it was described that an association of Bu$_6$Sn$_2$ and $\gamma$-substituted allyl sulphides were able to give allylation reactions (equation 45) whereas the corresponding $\gamma$-substituted allyltins were inefficient. Other reagents such as 2,4-pentadienylin were shown to be reactive. In some case alkyltins can participate in radical chemistry when the $\beta$-elimination is thermodynamically favoured, leading for instance to carbocyclic ring expansions. In a similar way radical reactions involving a 1,3-stannyl shift could afford 5-exo cyclizations.

\[ \text{O} \quad \text{O} \]
\[ \quad \text{SPh} \quad \text{Bu}_6\text{Sn}_2 \quad (1.0 \text{ eq}) \]
\[ \quad \text{h} \nu \]
\[ \text{O} \quad \text{O} \]
\[ \quad \text{60\%} \]

C. New Trends in Allyltin Transfer

Most of the radical reactions are conducted with an excess of the allyltin reagent, so that problems of purification may arise from and combine with the established toxicity of triorganotin side products. This represents the main drawback of the radical organotin methodology. In addition to the development of efficient purification processes, different ways of circumventing these problems are being continuously studied and can be divided into three different classes: (i) the search for catalytic systems which will regenerate in situ the organotin, (ii) the design of new organotin reagents, supported on polymers or leading to easily removable side products and (iii) the invention of alternative free organotin radical systems. The essential part of this work has so far been devoted to optimizing or replacing the tin-hydride chemistry, and very little attention has been paid to the allyl transfer process.

A silicon-based approach, in which various allyltris(trimethylsilyl)silanes were prepared and used for radical allylic transfer, was published, but in contrast to its silicon hydride homologues, these reagents exhibited too much sensitivity towards polar effects which required an adaptation of the nature of the substrate with the allylic moieties, and consequently restricted the scope of their use. Such restrictions are often encountered with all the ‘tin-free’ radical allylation methods in the recent literature. Recently, a new allyloganotin, bearing a ‘polar tail’ to allow an easy purification step, was described. For the same purpose an alternative, using monoallyltin, which gives after hydrolysis of the reaction mixture, inorganic tin side products, was developed. In contrast with electrophilic SnX$_3^*$ radicals, they were able to transfer efficiently the functionalized allyl group via a radical chain mechanism using XSn[N(TMS)$_2$]$_2$ as a chain carrier agent. Allyltin reagents supported on polymer underwent free radical allylic transfer with a marked preference for electron-poor carbon radicals. The fluorous method developed by Curran and coworkers has recently been successfully extended to four-component radical reactions using fluorinated allyltin reagents.

\[ \text{O} \quad \text{O} \]
\[ \quad \text{I} \]
\[ \quad \text{SPh} \quad \text{Bu}_6\text{Sn}_2 \quad (1.0 \text{ eq}) \]
\[ \quad \text{h} \nu \]
\[ \text{O} \quad \text{O} \]
\[ \quad \text{60\%} \]
VI. TRANSMETALLATION REACTIONS

A. Historical Background and General Features

The transmetallation reaction consists of the replacement of the tin atom by another metal and was discovered by Seyferth and Weiner in 1959\textsuperscript{600,601}. In fact, it has already been dealt with in this chapter in connection with some aspects of the transmetallation process: for instance, the activation of allyltins by Lewis acids (Ti, Al, In) for the nucleophilic addition reaction, or some coupling reactions mediated by copper are also relevant to the subject. The favourable driving force renders this reaction general with lithium as a metal and popularized it for various uses in organic synthesis. Indeed, the reactivity of the tin–carbon bond, which is compatible with a high level of functionality, makes organotins much better candidates than organosilicon reagents for this reaction. Other metals, such as copper or boron, were employed later in similar reactions.

B. Tin to Lithium Exchange

1. Alkenyltins

The main feature of tin to lithium exchange is the preservation of the alkene stereochemistry, which was already demonstrated in 1964\textsuperscript{602}. In conjunction with the easy access to stereodefined alkenyltins, this feature has been extensively exploited for synthetic purposes such as the construction of prostaglandins side chains\textsuperscript{603,604} and unsaturated fatty acids\textsuperscript{605,606}, the syntheses of a macrocyclic lactone\textsuperscript{607}, brefeldin A\textsuperscript{608}, cerulenin and aplasmomycin antibiotics\textsuperscript{609–611}. Furthermore, the reaction is compatible with several functionalities on the alkene moieties like unprotected hydroxy\textsuperscript{612–616}, amino\textsuperscript{617}, or esters groups\textsuperscript{618}. The presence of halides is also tolerated\textsuperscript{619}, leading to bifunctional reagents which are further engaged in various annulation reactions\textsuperscript{620–623}. This strategy was extended to the formation of cyclobutenes with tosylates on the tethering chain of the alkene (equation 46)\textsuperscript{624,625}. It should be noted that the tin–lithium exchange occurs faster than the nucleophilic attack to the carbon bearing the tosylate.

\[ \text{BuLi, THF} \stackrel{-20^\circ C}{\longrightarrow} 0^\circ C \]

\[ \text{Ph} \quad \text{TsO} \quad \text{SnBu}_3 \quad \text{BuLi, THF} \quad \text{Ph} \]

\[ \quad \text{61\%} \]

Cis and trans vinyltins exhibited a dramatic difference in terms of the reactivity of the tin to lithium exchange\textsuperscript{626,627}. This enabled an interesting regioselectivity when the substrate possesses several vinyltins functionalities. Also, 1,1- or 1,2-distannylalkenes were successively lithiated\textsuperscript{628}. Additional effects can intervene in the regiocontrol of the lithiation, such as steric effects which favour the terminal lithiation\textsuperscript{629}, or the stabilization of the lithium species by an intramolecular lithium–oxygen complexation\textsuperscript{630}. An interesting reagent is the 1-stannacyclohexa-2,5-diene \( \text{21} \), which is the formal equivalent of the (Z,Z)-1,5-dilithiated penta-1,4-diene (equation 47)\textsuperscript{631,632}.

\[ \begin{array}{c}
\text{Sn} \\
\text{(21)}
\end{array} \]
The reaction was extended to 1,3-dienyltins, giving the corresponding lithiated reagents, both in terminal\textsuperscript{633–635} or internal\textsuperscript{636} position, which can be substituted by alkoxy groups\textsuperscript{637}. Recently, a 1,3,5-triienyl lithium carbanion was prepared in a similar way from 22 and used for a further synthesis (equation 48)\textsuperscript{638}.

2. $\alpha$-Heterosubstituted organotins

The importance of carbanions $\alpha$-substituted by heteroatoms in organic synthesis explains the vast amount of literature concerning the use of $\alpha$-heterosubstituted organotins in transmetallation reactions. As the tin–lithium exchange is assumed to occur with a complete retention of configuration at the carbanion centre\textsuperscript{639}, the enantioselective approach of such stabilized carbanions for synthesis has been the subject of recent developments.

a. Oxygen-substituted organotins. A general route to alkyl-ox-, aryloxy- and allyloxy-methyltins and their subsequent transformation into their lithiated equivalents was proposed more than twenty years ago\textsuperscript{640,641} and is still used for the total synthesis of
complex targets such as Taxusin or aspidospermin alkaloids. The allyloxymethyl lithium intermediate can either react intermolecularly with an appropriate substrate or intramolecularly by way of a [2,3]-sigmatropic rearrangement (equation 49) which has been exploited for numerous syntheses of natural products.

\[
\text{OH} \quad \text{1. KH, THF, 18-Cr-6} \quad \text{2. Bu}_3\text{SnCH}_2\text{I} \quad \text{3. BuLi} \quad \text{OBn} \\
\] \\
\text{75%}

(49)

The extension of the reaction to the preparation of an $\alpha$-substituted alkoxymethyl lithium holds great promise in terms of chirality induction and was investigated by Still already in 1978. The advantage lies in the stabilization of the carbanion formed by the oxygen atom, but it is known that substitution at the carbon bearing the tin atom may render the exchange by the lithium more difficult. This was overcome by changing the aryl tributyltins to more activated trimethyltin reagents, and by conducting the reactions in DME as solvent instead of in THF.

b. Nitrogen-substituted organotins. The preparation of aminomethyllithium species proved its efficiency for the preparation of $\beta$-aminoalcohols a long time ago. However, these reagents remained much less developed till recently, presumably due to their lower configurational stability compared to the alkoxymethyllithium equivalents. Nevertheless, intramolecular ring closures leading to substituted pyrrolidines or azabicyclic structures were achieved. Alternatively, the generation of 2-azaallyl anions by tin–lithium exchange of stannylated imines led to the formation of pyrrolines and bridged azabicyclic compounds by a [3 + 2] cycloaddition approach (equation 50).

\[
\text{SnBu}_3 \quad \text{R}^1 \quad \text{X} \quad \text{R}_2 \quad \text{R}_3 \quad \text{Li} \quad \text{R}_2 \quad \text{R}_3 \quad \text{X} \quad \text{R}_1 \quad \text{Li} \\
\] \\
\text{(50)}

An interesting application concerns the generation of carbanions bearing chiral auxiliaries tethered to the nitrogen. In this case, a rapid equilibration follows the transmetallation step, so that the formation of the more stable aminomethyllithium intermediate is ensured, depending on the stereochemistry of the auxiliary. It then appears possible to take advantage of the configurational instability of the aminomethyl lithium to prepare stereo-defined organolithium and organocopper reagents starting from racemic organotin compounds.
c. Sulphur-substituted organotins. $\alpha$-Thioalkoxymethyl lithiums are readily prepared from the corresponding thiomethyl ethers. Their configurational instability causes a rapid racemization even at low temperature, but the tin to lithium exchange may occur with retention of configuration when starting from some $\alpha$-arylthioalkyltins and $\alpha$-arylthioalkenyltins. Further transmetallation from lithium to zinc was also exemplified. Recently, the tin to lithium exchange, in the presence of the chiral bis (oxazoline) bidentate ligand to complex the transient organolithium followed by trapping with a carbonyl compound as an electrophile furnished the thioalcohol with a high level of enantioselectivity. Interestingly, lithiated carbanions prepared from $\alpha$-arylthioalkyltins appeared to undergo carbon–carbon bond fragmentation as well when a carbonyl group was suitably placed in the $\gamma$-position.

\[ \text{Ph} \text{S} \text{SnBu}_3 \xrightarrow{n-\text{BuLi}} \text{Ph} \text{S} \text{Li} \]

(51)

3. Other organotins

The organotins mentioned below are used much less for generating organolithium reagents, because there are alternative procedures which can efficiently replace the tin–lithium exchange reactions. Allyltins were the first organotins to be transmetallated, and the methodology was rapidly extended to related compounds such as methallyl, crotyl, and prenyltins. With such reagents, a competition between the $\alpha$- and $\gamma$-reaction sites of the lithiated intermediate may occur. It should be kept in mind that the nature of the substituents may affect the regiochemistry either by steric or by electronic effects. In some cases the addition of $\text{Ti(OPr-i)}_4$ prior to the addition of the electrophile may reverse the regioselectivity. Nevertheless, the transmetallation of allyltins for synthetic purposes has scarcely been used, due (i) to the sufficient reactivity of the allyltin itself and (ii) to the easy preparation of allyllithium by the deprotonation method. For the same reasons there are very few examples of transmetallation with benzyltins, although this reaction is easily carried out. Although the tin–lithium
exchange is assumed to be easier than the bromine–lithium exchange, aryl and heteroaryltins are rarely used due to the fact that the corresponding lithiated reagents are commonly prepared by deprotonation reactions or by halogen–lithium exchange reactions.

The applications of tin to lithium transmetallation involving alkyltins remain uncommon, with the exception of cyclopropyllithium reagents. They were primarily used by Corey and coworkers for the synthesis of hybridolactone with a total retention of configuration at the carbon bearing the metal. This stereoselectivity was further investigated and shown to be unaffected by the functionalization of the cyclopropyl moiety. Recent results on dichlorodialkyltin showed a marked contrast in its reactivity compared with the parent teraalkyltin (equation 52). This was explained by an intramolecular complexation of the tin atom, which is responsible for the activation of and predisposes the system to obtain selectively the Z-form enolate. Finally, we note the synthesis of fluoroolefins via the transmetallation of a bis(trimethylsilyl)fluoromethyltin reagent, followed by the addition of the resulting organolithium to carbonyl compounds.

\[ \text{LiO} _{-\text{Bu}} \text{Li} (4 \text{ eq}) \quad \text{THF} \quad \text{Me}_3\text{SiO} \quad \text{SiMe}_3 \]

\[ \begin{array}{c}
\text{O} \quad \text{SnBuCl}_2 \\
\text{t-Bu} \\
(23)
\end{array} \quad \text{LiO} _{-\text{Bu}} \text{Li} (4 \text{ eq}) \quad \text{THF} \quad \text{Me}_3\text{SiCl} \\
\text{t-Bu} \\
\text{Me}_3\text{SiO} \quad \text{SiMe}_3 \\
\text{t-Bu} \\
90\% \quad E/Z = 0/100
\]

C. Other Transmetallations

1. Tin to copper exchange

Although there were numerous examples in the literature of tin to copper transmetallations, the exchange reactions involved a transient organolithium until recently. There is no doubt that, during the last decade, the main advance for organic synthesis in tin–metal exchange reactions is related to the tin to copper direct transmetallation. The first example, reported by Behling and coworkers in 1988, was the formation of mixed cuprate upon treatment of an alkenytin with \( R_2\text{Cu(CN)}\text{Li}_2 \) without prior lithiation. The reaction was shown to be general with alkenyltins, and was readily extended to the formation of allylic cuprates.

The reaction was applied to the formation of arylcopper used for homocoupling and coupling reactions, which have already been described in Section IV.B.2. In addition, it was established that the simple use of copper(I) salts in polar solvents permitted the transmetallation from tin to copper. The transient vinylcopper reagent was subjected to various intramolecular reactions such as coupling with vinyl halides, addition to \( \alpha, \beta \)-unsaturated ketones, to \( \alpha, \beta \)-unsaturated esters and addition to \( \alpha, \beta \)-alkynic esters. In addition to copper(I) halides, the reaction can be mediated by copper(I) cyanide and
applied to the synthesis of fused bi- and tricyclic structures (equation 53).

2. Tin to boron exchange

The transmetallation process was extended to the preparation of vinylboranes, and the superior reactivity of organotins over organosilicons was elegantly demonstrated by Williams and coworkers for the preparation of the optically active allylborane from the corresponding allylic stannane in the total synthesis of \((-\)-Hennoxazole A \(^{\text{711}}\) (equation 54).
VII. SUBSTITUTION REACTIONS

A. Halodestannylations

1. Introduction

The halodestannylation of organotins is a long-known reaction established for vinyltins by Seyferth in 1957\(^ {712} \). The reaction has been widely applied to aryl-, heteroaryl- and vinyltins, and to a lesser extent to benzyl- and allyltins. Its popularity is due to the easy cleavage of the tin–carbon bond in reactions with electrophiles, which allows a great reactivity, and a high level of chemo- and regioselectivity, under particularly smooth conditions. The reactivity in the Sn–C halodestannylation follows the following order: Ph > PhCH\(_2\) > CH\(_2\)=CH > Me > Alk. A striking application of the halodestannylation reaction is represented by the widening use of organotin precursors for the synthesis of labelled bioactive molecules used as radiotracers in nuclear medicine.

2. Iododestannylation

The iododestannylation reaction is a commonly used reaction due to the high reactivity of the formed vinyl iodides, which can be used for further transformations. The stannylated precursors are easily prepared by hydrostannation of alkynes, and the iodide–tin exchange proceeds with an excellent regio- and stereocontrol. Furthermore, the reaction is compatible with the presence of several functionalities such as ethers\(^ {713,714} \), alcohols\(^ {715–718} \), ketones\(^ {719,720} \), esters\(^ {721,722} \) and amines\(^ {723} \). Functionalized dienyltins were also used for the preparation of 1-iodo-1,3-dienes\(^ {724} \), and the reaction was even extended to the preparation of fully stereo-determined iodo tetraenes\(^ {725} \).

Aryl- and heteroaryltins\(^ {726,727} \) are similarly used for the synthesis of the corresponding iodides, and they also allow the presence of functional groups such as alcohols\(^ {728} \), esters and amides\(^ {729} \) and amines\(^ {730} \). It is noteworthy that with substrates such as allyltins or propargyltins the iododestannylation occurs with rearrangement of the unsaturation\(^ {731,732} \).

The main application of this reaction in the last twenty years is undoubtedly the preparation of various radiotracers labelled with iodide 131, 125 or 123 (I\(^ * \)) for SPECT medical imaging. For such radiosynthesis, NaI\(^ * \) associated to an oxidant is preferred over the usual I\(_2\)-mediated iododestannylation. Among several examples of bioactive molecules synthesized in recent years, the iodopyridine\(^ {25} \) (a radioligand for nicotinic receptors)\(^ {733} \) or iodopyridine bisphosphonate\(^ {26} \) (a bone disease related tracer)\(^ {734} \) was prepared in high radiochemical yields. Similarly, iodoaromatic derivatives such as 4-iodosipperone\(^ {27} \) (a selective antagonist for 5-HT\(_2\) serotonin receptors)\(^ {735} \), deoxy-nojirimycin derivative\(^ {28} \) (a glucose analog)\(^ {736} \), benzodiazepine\(^ {29} \)\(^ {737} \), the vesamicol analog\(^ {30} \) (an acetylcholine transport inhibitor)\(^ {738} \) or methoxybenzamide\(^ {31} \) (a breast cancer imaging agent)\(^ {739} \) were prepared via the iododestannylation procedure.
In order to facilitate the purification step, organotin precursors supported on polymers were also used for the iododestannylation reaction. The reaction occurred in reasonable reaction times, which are compatible with the use of short half-life radioactive elements, thus allowing the preparation of iodolisuride (a dopamine D2 receptor
imaging agent\textsuperscript{743} or the oestrogenic derivative 33\textsuperscript{744}.

![Chemical structures](image)

3. Bromodestannylation

This reaction can be similarly applied to bromination with \( \text{Br}_2 \textsuperscript{745} \), \( \text{CuBr}_2 \textsuperscript{746} \) or \( \text{BrCN} \textsuperscript{747} \) as the halogenating reagents. Alternatively, in the total synthesis of Calyculin, a vinyl bromide synthon was prepared from the corresponding vinyl stannane by reaction with NBS\textsuperscript{748}. Radiotracers for medical imaging can be synthesized by using short-lived isotopes such as \( ^{75}\text{Br} \left( t_{0.5} = 97 \text{ min} \right) \) or \( ^{76}\text{Br} \left( t_{0.5} = 16.2 \text{ h} \right) \). In addition to the classical NaBr\textsuperscript{–}/oxidant couple, the labelled targets can be prepared with \( \text{NH}_4\text{Br} \) and chloramine-T\textsuperscript{749–751} or peracetic acid\textsuperscript{752} as oxidizing agent.

4. Fluorodestannylation

There are several reagents applicable for the fluorodestannylation. In addition to \( \text{F}_2 \textsuperscript{753,754} \) and acetyl hypofluorite\textsuperscript{755}, xenon difluoride\textsuperscript{756} was able to replace the organotin moiety by a fluorine under mild conditions. In the same way caesium fluorooxysulphate is able to give an electrophilic fluorination on aryltins\textsuperscript{757} as well as on alkenyl- and heteroaryltins\textsuperscript{758}. Finally, the difluorotriphenylstannate\textsuperscript{759} has to be mentioned, although it is not relevant to the fluorodestannylation. This hypervalent tin reagent is an anhydrous nucleophilic fluorinating agent for benzylic and aliphatic substrates\textsuperscript{760}. The radiosyntheses of bioactive molecules were achieved with sources of \( ^{18}\text{F} \left( t_{0.5} = 120 \text{ min} \right) \)\textsuperscript{761–763}.

B. Tin to Oxygen Substitution

Benzy1- and allyltins possess a relatively weak tin–carbon bond enabling an easy oxidation with \( m \)-chloroperbenzoic acid. The corresponding alcohols are obtained\textsuperscript{764,765} with rearrangement in the particular case of allyltins\textsuperscript{766}. The oxidation of vinyltins by \( m \)-chloroperbenzoic acid (MCPBA) gives the corresponding epoxide\textsuperscript{767,768}. Interestingly, the oxidation of vinyltins by lead tetraacetate does not follow the same route and gives the corresponding alkyne\textsuperscript{769,770}.

With non-activated tin–carbon bonds such as allyltins, strong oxidizing agents like chromium trioxide are usually required\textsuperscript{771}. The reactions lead to the corresponding alcohols or ketones, depending on the substitution of the carbon bonded to the tin atom.
Iodosylbenzene can oxidize the tin–carbon bond as well. This reaction is followed by a stereospecific ring opening when operating with γ-stannyl cycloalkanols. An m-chloroperbenzoic acid may be used, giving selectively the alcohols with retention of configuration. A two-step procedure involving the initial cleavage of an alkyl substituent by bromine, followed by an oxidation of the resulting trialkyltin halides with ammoniacal MCPBA was described. An alternative method using ceric ammonium nitrate was also developed to transform selectively primary alkyltins into aldehydes and applied to the total synthesis of the antibiotic Burseran. Recently, fluorinated organotins were subjected to a mild oxidation system (alkaline H₂O₂) giving the alcohols with retention of configuration (equation 55).

\[ \text{SnBu}_2(Rf) \rightarrow \text{MeOH/THF, 14 h} \rightarrow \text{H}_2\text{O}_2/\text{KHCO}_3 \rightarrow \text{alcohols, 73%} \] (55)

C. Tin to Sulphur Substitution

Sulphonyl chloride reacts with aryl- and vinyltins to give the corresponding sulphones. In conjunction with secondary amines, the reaction with sulphonyl chloride gives access to sulphonamides. In addition, the reaction of aryltins with arenésulphonyl halides gives the dissymmetric sulphones. Dithiocyanogen reacts as well with aryl-, vinyl- and allyltins to form the thiocyanates. When different types of tin–carbon bonds are present, the reaction is chemoselective showing the following selectivity order: benzyl > aryl > alkyl.

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18. Synthetic applications of organic germanium, tin and lead compounds


CHAPTER 19

Synthetic uses of $R_3 MH$ ($M = \text{Ge, Sn, Pb}$)

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I. INTRODUCTION

The chemistry of $R_3 MH$ ($M = \text{Ge, Sn, Pb}$) is highlighted firstly by the dominance of trialkyltin hydrides in synthesis, and secondly by the prevalence of free-radical chemistry in the large majority of transformations of synthetic significance reported in the literature.
There is no doubt that free-radical chemistry has benefited enormously through the invention of tin-based chain-carrying reagents\textsuperscript{1–5}. Of these, tributyltin hydride and, to a lesser extent, triphenyltin hydride have been the reagents of choice\textsuperscript{1}. Their ready availability and favourable rate constants for attack of the corresponding tin-centred radicals at a variety of radical precursors\textsuperscript{6}, coupled with useful rate constants for hydrogen transfer\textsuperscript{7} to alkyl and other radicals, provide for reagents superior to their silicon counterparts\textsuperscript{8}; only tris(trimethylsilyl)silane rivals tributyltin hydride in its synthetic utility\textsuperscript{9}.

A knowledge of rate constants is crucial to the successful design of synthetic procedures involving these reagents. Giese points out that stannane chain-carrying reagents are useful because a knowledge of the important rate constants allow, through control of substrate concentration, necessary selectivity criteria to be met\textsuperscript{1}.

Toxicity\textsuperscript{10} and product purification\textsuperscript{11} concerns have led to the development of ‘friendlier’ reagents. Improvements in synthetic flexibility resulting from the use of germanes as hydrogen donors has resulted in extensions of free-radical methodology to systems in which the primary bond-forming reaction (e.g. intramolecular addition) lies outside the range acceptable for stannane chemistry\textsuperscript{1}. The use of trialkylgermanes, for example, with their lower rate constants for the delivery of hydrogen atom to alkyl radicals can often lead to increased reaction yields when slow C–C bond-forming reactions are crucial in the overall synthetic strategy\textsuperscript{12–14}.

Hydrostannylation represents another class of important reaction that often gives rise to interesting polymeric materials as well as precursors for transition metal mediated coupling transformations such as the Stille coupling protocol\textsuperscript{15}.

Davies provides a comprehensive account of the state of organotin hydride chemistry up to the end of 1995 in his recent book\textsuperscript{15}, while Gielen and coworkers detail methods for the preparation of organo-germanium, tin and lead compounds in their 1995 contribution to this series\textsuperscript{16}; the reader is referred to these works for chemistry which precedes that found in this chapter. The purpose of this account is to consolidate developments since the work of Davies and Gielen. Consequently, the preparation and synthetic uses of R\textsubscript{3}MH (M = Ge, Sn, Pb) from the beginning of 1996 until the end of 2000 are documented in this chapter.

New methods for the preparation of germanes and stannanes reported since 1995 are dealt with in Section II. In Section III, radical chain chemistry involving trialkyltin hydrides is examined. In particular, the synthetic utility of tributyltin hydride will be reviewed, as well as that of other stannanes. Recent advances in the area of asymmetric radical chemistry involving chiral non-racemic stannanes are also included. Section IV details a limited number of examples of non-radical stannane chemistry, while Section V covers recent advances in germane and plumbane chemistry. While we have restricted ourselves largely to the literature since the beginning of 1996, some salient features of earlier work are included when relevant to the discussion.

II. THE PREPARATION OF NOVEL TRIALKYLMERMANES AND STANNANES

A. Trialkygermanium Hydrides (R\textsubscript{3}\text{Ge}H)

Work describing procedures for the preparation of trialkygermanium and tin hydrides is well documented\textsuperscript{16}. Since 1996, to the best of our knowledge, there have appeared few papers detailing novel preparations or methods for the preparation of new trialkygermanium hydrides. Of those few, Colacot describes a one-pot preparation of tributylgermanium hydride by reaction of GeCl\textsubscript{4} with butyllithium chloride in the presence of a catalytic amount of titanocene dichloride (equation 1)\textsuperscript{17}, while Takeuchi and his colleagues report the synthesis of tris[2-alkoxyphenyl]germanes (1) and
related compounds by standard methods (equation 2\textsuperscript{18}). Oshima and coworkers report the preparation of tri-2-furanylgermane (2) by reaction of 2-furanyl lithium with GeCl\textsubscript{4} followed by lithium metal (equation 3\textsuperscript{19}), while Tacke and coworkers describe methods for the synthesis and enzymatic separation (porcine pancreas lipase, PPL) of chiral germanes (3) (equation 4\textsuperscript{20,21}).

\begin{align*}
\text{GeCl}_4 + \text{BuMgCl} \xrightarrow{\text{ether}} \text{GeCl}_4 + \text{Bu}_3\text{GeH} \quad (69\%) \quad (1)
\end{align*}

\begin{align*}
\text{MgBr} \xrightarrow{\text{Th}} \text{GeCl} \xrightarrow{\text{LiAlH}_4} \text{GeH} \quad R = \text{Me, Et, t-Bu} \quad (2)
\end{align*}

\begin{align*}
\text{i. BuLi} \quad \text{ii. GeCl}_4 \xrightarrow{\text{i. Li} \quad \text{ii. H}^+} \text{GeH} \quad (3)
\end{align*}

\begin{align*}
\begin{array}{c}
\text{EtOAc or CH}_2\text{CHOAc} \xrightarrow{\text{PPL (E.C. 3.1.1.3)}} \text{PPL} \\
\text{R} = \text{H, F}
\end{array}
\end{align*}

Esteruelas and his associates report the preparation of OsH(\eta^5-C_5H_5)Cl(GeHPH_2)(i-Pr_3P) (4) by treatment of 5 with Ph_2GeH_2 and describe interesting exchange
chemistry en route to 5 (equation 5)\textsuperscript{22}. Jutzi and coworkers describe the conversion of bis(2,4,6-tri-tert-butyl)germylene, a \(-30^\circ\text{C}\) stable orange-red crystalline solid, into germaindane (6) through the use of Lewis acid catalysed C–H bond insertion chemistry (equation 6)\textsuperscript{23}. Unno and coworkers describe the preparation and reactions of hepta-tert-butylcyclotetragermane (7) which is conveniently prepared by the reductive coupling of 1,2-dichloro-1,1,2,2-tetra-tert-butylgermane (equation 7)\textsuperscript{24}. 

\[
\begin{align*}
\text{Ph}_2\text{GeH}_2 & \xrightarrow{\text{THF Lewis acid}} i-\text{Pr}_3\text{P}\text{GeHPh}_2 & & i-\text{Pr}_3\text{P}\text{GePh}_3 \\
\text{(4)} & \quad & \text{(5)}
\end{align*}
\]

\[
\begin{align*}
\text{THF} \quad \text{Lewis acid} & \quad \xrightarrow{\text{Li THFCl(t-Bu)2GeGe(Bu-t)2Cl}} \quad t-\text{Bu} & \quad t-\text{Bu} \quad \text{Bu-t} \quad \text{Bu-t}
\end{align*}
\]

\[
\begin{align*}
\text{(6)} & \quad \text{(7)}
\end{align*}
\]
Polymer-supported germanium hydrides have been investigated by Mochida and co-workers who report the preparation of poly(4-diethylhydrogermane)styrene and related polymers and examine their reactivity as free-radical reducing agents (equation 8)\(^\text{25}\).

Very recently, Gualtieri reported the preparation of chiral, \(C_2\)-symmetric binaphthyl-substituted germanes (8, 9) containing \(S\--\text{Ge}\) bonds (equation 9) and their application to enantioselective radical chemistry\(^\text{26}\). These compounds are reported to exhibit superior stability properties than the corresponding tin compounds which could not be isolated (see later)\(^\text{26}\).

**B. Trialkyltin Hydrides (\(R_3\text{SnH}\))**

The past five years have witnessed several advances in stannane technology with direct application to organic synthesis. Significantly, the introduction of fluororous
reagents, chiral, non-racemic stannanes and the development of more robust polymer-supported tin hydrides will be seen in the future as major advances with direct application to many areas of synthesis, including the regulation-intensive pharmaceutical industry.

In a series of papers, Curran and coworkers introduce several fluorous stannanes with distinct separation (extraction and chromatography) and combinatorial chemistry advantages over traditional trialkyltin hydrides. These perfluorinated stannanes (10) are conveniently prepared by the reaction of the appropriate fluorous Grignard reagent with phenyltrichlorotin followed by standard manipulation (equation 10)\(^{27-30}\) and have the advantage of having limited solubility, depending on fluorine content, in both organic and aqueous media. Purification can often be facilitated by extraction of the fluorinated tin by-products into a fluorous solvent in which the reaction products are insoluble.

\[
\text{PhSnCl}_3 + \text{Rf(CH}_2\text{)}_n\text{Mgl} \rightarrow (\text{Rf(CH}_2\text{)}_n\text{)}_3\text{SnPh} \quad \text{i. Br}_2 \quad \text{ii. LiAlH}_4 \rightarrow (\text{Rf(CH}_2\text{)}_n\text{)}_3\text{SnH}
\]

\(\text{Rf} = \text{C}_4\text{F}_9, \text{C}_6\text{F}_{13}, \text{C}_{10}\text{F}_{21}, n = 2,3\) (10)

Enantioselective free-radical chemistry has benefited through the development of chiral, non-racemic stannanes. Despite having been prepared on a limited number of occasions prior to 1996, the use of chiral stannanes in enantioselective free-radical chemistry was only reported on one occasion\(^{31}\). The field effectively lay dormant until Nanni and Curran reported the preparation and uses of (S)-4,5-dihydro-4-methyl-3H-dinaphtho[2,1-c:1′,2′-e]stannepin (11) prepared from (S)-2,2′-bis(bromomethyl)-1,1′-binaphthyl (equation 11)\(^{32}\) and a few years later Curran and Gualtieri reported the preparation of C\(_2\)-symmetric
Synthetic uses of $R_3MH$ (M = Ge, Sn, Pb)

In the meantime, Vitale and Podestá reported the preparation of mixed alkyldimethyltin hydrides (15)\(^{35}\) from the known bromide (16) (Scheme 2)\(^{36}\), as well as trimehtyltin hydride (17) for structural and ionic-reduction purposes\(^{35,37}\); this work followed on

---

\(12\)

\(13\)

\(14\)

**SCHEME 1**

In the meantime, Vitale and Podestá reported the preparation of mixed alkyldimethyltin hydrides (15)\(^{35}\) from the known bromide (16) (Scheme 2)\(^{36}\), as well as trimehtyltin hydride (17) for structural and ionic-reduction purposes\(^{35,37}\); this work followed on
from an earlier paper detailing the analogous dialkylmenthyltin hydrides\textsuperscript{38}. These preparations often lead to epimerization at C1 in the menthyl substituent, presumably due to electron-transfer processes\textsuperscript{39}. Dakternieks, Schiesser and coworkers were able to control this epimerization process during the preparation of menthylidiphenyltin hydride (18) and related compounds through the incorporation of a Lewis base during the Grignard chemistry (equation 12)\textsuperscript{39}. These same authors also report the preparation of menthyl-substituted stannanes (19–22) containing intramolecular coordinating substituents (Scheme 3)\textsuperscript{40}, as well as the preparation of some unstable oxazoline-substituted systems (23) (equation 13)\textsuperscript{41}. 
19. Synthetic uses of $R_3M$ ($M = Ge, Sn, Pb$)

\[ \text{MgCl} \xrightarrow{\text{Ph₃SnCl}} \xrightarrow{I_2 \text{ or } Ph_3P} \text{SnPh}_3 \xrightarrow{} \text{Sn(H)Ph}_2 \]

\[ \text{Sn(H)(men)Ph} \]

\[ \text{Li} \xrightarrow{\text{LiAlH}_4} \]

\[ \text{Sn(Br)(men)Ph} \]

\[ \text{men}_2\text{SnBr} \xrightarrow{} \]

\[ \text{Sn(Br)men}_2 \]

\[ \text{men} = \text{Menthol} \]

\[ \text{Sn(H)men}_2 \]

\[ \text{(19)} \]

\[ \text{(18)} \]

\[ \text{(20)} \]

SCHEME 3
\[ \text{LiAlH}_4 \rightarrow \text{Sn(\text{Br})(men)R}^3 \]

\[ \text{Sn(H)(men)R}^3 \]

\[ R^1 = \text{H, Me}; R^2 = \text{Me, i-Pr}; R^3 = \text{men, Ph} \]
The Schiesser group also recently described the preparation of some stannanes (24–27) derived from cholestanol (Scheme 4), cholic acid (Scheme 5) and lithocholic acid (equation 14), and their application to enantioselective radical chemistry.42,43

Tomas and his colleagues employed Diels–Alder methodology to prepare a series of racemic 3-substituted bicyclo[2.2.1]heptan-2-ylstannanes and related compounds (28–31) (Scheme 6).44 The use of optically-pure (R)-4,4-dimethyl-2-oxotetrahydrofuran-3-yl (E)-3-triphenylstannylprop-2-enoate afforded the optically-pure adduct (32) after separation
which was subsequently converted into stannane (28) with 94% enantiomeric excess. Further manipulation gave the chiral, non-racemic tin hydride (29)\(^{45}\). Standard lithiation chemistry has been employed in the preparation the alkyl-substituted systems (33–36)\(^{46}\).
19. Synthetic uses of $R_3MH$ ($M = \text{Ge}, \text{Sn}, \text{Pb}$)

\[
\begin{align*}
\text{CO}_2\text{Me} & \quad \text{Ph}_3\text{Sn} \\
\text{SnPh}_2\text{Cl} & \quad \text{CO}_2\text{Me} \\
\text{SnPh}_2\text{Cl} & \quad \text{CO}_2\text{Me} \\
\end{align*}
\]

\[
\begin{align*}
(29) & \quad \text{OR} \\
(28) & \quad \text{OR} \\
\text{Sn(H)Ph}_2 & \quad \text{CO}_2\text{Me} \\
\text{Sn(H)Ph}_2 & \quad \text{CO}_2\text{Me} \\
\end{align*}
\]

\[
\begin{align*}
\text{NaBH}_4 & \\
\text{NaBH}_4 & \\
\end{align*}
\]

\[
\begin{align*}
(31) & \quad \text{Sn(H)Ph}_2 \\
(30) & \quad \text{Sn(H)Ph}_2 \\
\end{align*}
\]

\[
\begin{align*}
(32) & \quad (33) \\
(34) & \quad \text{R} = \text{H, Me} \\
\end{align*}
\]

SCHEME 6
Dumartin and associates described the preparation of \textit{in situ} polymer-supported organotin hydrides for use as ‘clean’ reducing agents (equation 15)\textsuperscript{47}, while Deleuze and coworkers reported the preparation of a novel, macroporous polymer-supported organotin hydride (37), for use in catalytic free-radical reductions (equation 16)\textsuperscript{48,49}.

\begin{align}
\text{(15)}
\end{align}

\begin{align}
\text{(16)}
\end{align}

In order to facilitate solid-phase Stille coupling chemistry, Nicolaou and coworkers prepared polystyrene-di-butyltin hydride\textsuperscript{50}. While this polymer has been reported previously\textsuperscript{51}, the preparation on a 2\% cross-linked resin represents a novel extension.
III. TRIALKYL Tin HYDRIDES AS REAGENTS IN RADICAL CHAIN REACTIONS

A. General Aspects

The synthetic application of free-radical reactions has increased dramatically over the past twenty years. Nowadays, radical reactions can often be found driving the key steps of multistep chemical syntheses oriented towards the construction of complex natural products or other synthetic targets. The majority of radical reactions of interest to synthetic chemists are chain processes. Tributyltin hydride is by far the most commonly used reagent for the reduction of functional groups and formation of C−C bonds either inter- or intramolecularly (cyclization), although, as already alluded to, there are several problems associated with organotin compounds. The main drawback consists of the incomplete removal of allegedly toxic tin by-products from the final material.

The transformation of 6-bromo-1-hexene (38) into methylcyclopentane by the action of tributyltin hydride (Scheme 7) typifies the richness of the C−C bond forming chemistry in question. A knowledge of the critical rate constants (\(k_c\), \(k_H\) and \(k_{Br}\) in Scheme 7) allow, through control of substrate concentration, necessary selectivity criteria to be met. Specifically the 5-hexenyl radical (39) must undergo intramolecular addition to form the cyclopentylmethyl radical (40), 40 must abstract a hydrogen atom from tributyltin hydride and the tributylstannyl radical must abstract the halogen in 38 to form 39. These processes must proceed faster than any competing side reaction.

\[
\text{Scheme 7}
\]
B. Tributyltin, Trimethyltin and Triphenyltin Hydride (Bu₃SnH, Me₃SnH, Ph₃SnH)

The number of publications in the period of coverage of this chapter detailing the use of Bu₃SnH, Me₃SnH or Ph₃SnH in synthesis, either in direct reduction chemistry, or in multi-step transformations, is truly remarkable. Indeed, it is not practical for all examples to be included in this account. It is our intention, therefore, to present a comprehensive description of the diversity of the chemistry in question through the use of numerous selected examples, while the entire list of references is included for completeness.

1. Free-radical reduction chemistry

During the period 1996–2000 the use of Bu₃SnH, Ph₃SnH or Me₃SnH in simple free-radical reduction chemistry of halides was reported on numerous occasions. The versatility of these stannane reagents lies in their ability to reduce a variety of other common functional groups that act as radical precursors. These include sulphides, selenides, tellurides, thiono- and dithiocarbonates, selenoesters, nitro compounds, sulphoxide, sulphate and sulphonyl moieties, as well as other functionalities.

Examples of halide reduction chemistry include the Bu₃SnH-mediated reduction of iodide (41) en route to clavepictine A and B reported by Momose and coworkers (equation 17) as well as the reduction of iodide (42) during Danishefsky’s work towards the synthesis of epothilone A (equation 18). Herzog and Roewer demonstrated that trimethyltin hydride can be used to effect the reduction of haloallogilanes to the corresponding silane in the presence of a Lewis base such as triphenylphosphine (equation 19), while Crich and Mo reported the beneficial effect of catalytic benzeneselenol during the Bu₃SnH-mediated reduction and fragmentation of bromo-β-lactones (43) (equation 20).

\[ \text{Bu}_3\text{SnH} + \text{AIBN} \rightarrow \text{MOMO} \]

(41)

\[ \text{H} \]

\[ \text{MOMO} \]

\[ \text{SO}_2\text{Ph} \]

(41)

\[ \text{H} \]

\[ \text{MOMO} \]

\[ \text{Me} \]

\[ \text{SO}_2\text{Ph} \]

(17)
19. Synthetic uses of $R_3MH$ ($M = \text{Ge, Sn, Pb}$)

Hoshino and coworkers describe the synthesis of (S)-(+)-α-methoxymethylhydrocoumarin through the Bu$_3$SnH-mediated enantioselective reduction of iodide (44) in the presence of a chiral Lewis acid (equation 21)$^{100}$. On a similar theme, Guindon and Rancourt reported chelation-controlled diastereoselective radical reductions utilising Bu$_3$SnH in the presence of magnesium salts, an example of which is given in equation 22$^{109}$. It is interesting to note that while the syn product dominates in the presence of MgI$_2$, it is the anti product which is preferred in the absence of Lewis acid.
Lange and his associates reported the reductive ring expansion of the tricyclic iodide (45) during the synthesis of some terpene natural products (equation 23)\textsuperscript{125}. It is interesting to note that the stannane reacts exclusively with the iodide moiety in this transformation, with the xanthate functionality providing the final $\beta$-scission that completes the radical chain process. Banwell and coworkers described the Bu$_3$SnH-mediated removal of a bridgehead bromide in their synthesis of a highly-functionalised steroidal nucleus (equation 24)\textsuperscript{127}.

Roush and Bennett reported the consecutive removal of seven iodine atoms during their synthesis of the landomycin A hexasaccharide unit (46) (equation (25))\textsuperscript{151}. 

\[
\text{Bu}_3\text{SnH} / \text{Et}_3\text{B} \quad \text{MgI}_2 \text{ or no additive} \quad \text{Bu}_3\text{SnH} / \text{Et}_3\text{B}
\]

\[
\text{syn:anti} = 84:1 \quad R^1 = \text{Ph}, \quad R^2 = \text{i-Pr (MgI}_2) \quad 1:13 \quad \text{(no additive)}
\]
Sulphides can often be problematic as free-radical precursors mainly because of their reduced rate of reactivity towards tributyltin radicals when compared to bromides, iodides or selenides. However, several examples exist in which sulphides have effectively been reduced using tin hydrides. For example, Quiclet–Sire and coworkers reported the removal of the thiopyridyl moiety from the product of a Barton ester reaction using Bu$_3$SnH (equation 26). Beckwith and Duggan investigated the quasi-homo-anomeric interaction in some substituted tetrahydropyranyl radicals by careful analysis of the products of Bu$_3$SnD reduction of selected $p$-tolylthio precursors. Hoppe and coworkers described the removal of the thiophenyl moiety in substrate (47) (equation 27). Rigby and Laurent reported the selective reduction of one of the sulphide groups in several geminal sulphides (e.g. 48) during their synthetic studies (equation 28). Presumably, this transformation is the result of the activation of the sulphide undergoing reduction by the other sulphur on the same carbon.
Selenides are more effectively removed by the action of trialkylstannanes. For example, Jung and Xu reported the Bu₃SnH reduction of phenylselenide (49) during their preparation of L-2-deoxyribose from D-ribose (equation 29)¹⁸². This reaction proceeds with apparent benzoyl group migration and has been reported previously by Giese and coworkers³²⁰. Stojanovic and Renaud showed that tosylated N,Se-acetals (50) often undergo β-scission during reaction with Bu₃SnH under standard reaction conditions (equation 30)¹⁸⁶, while Pearson and Stevens utilised Bu₃SnH-mediated reduction of phenylselenide (51) in their preparation of tropane alkaloid analogues (equation 31)¹⁸⁹.

Danishefsky and coworkers showed that selenide (52) undergoes reduction upon treatment with Bu₃SnH in the presence of allyltributyltin, rather than allylation, as expected (equation 32)¹⁹⁷. In this last example, Uriel and Santoyo-González utilised Bu₃SnH reduction of a glycosidic phenyl selenide (53) in their synthesis of 2-deoxyglycopyranoyl thioureas (Scheme 8)¹⁵⁹. This example typifies the synthetic utility of phenyl selenides,
which are incorporated readily using standard chemistry that also often incorporates other functional groups.

\[
\begin{align*}
\text{SePh} & \quad \text{Bu}_3\text{SnH} / \text{AIBN} \\
\text{N} & \quad \quad \quad \text{SnBu}_3 \\
\text{H} & \quad \text{CBz} \\
\text{N} & \quad \quad \quad \text{CBz}
\end{align*}
\]

(52)

\[
\begin{align*}
\text{OAc} & \quad \text{R}^2 \\
\text{OAc} & \quad \text{R}^1 \\
\text{AcO} & \quad \text{SePh} \\
\text{O} & \quad \text{NCS}
\end{align*}
\]

(32)

During the period covered by this chapter, there appears to have been only one report of the reduction of a telluride; Ferraz, Sano and Scalfo described the routine reduction of a phenyltelluride using \text{Bu}_3\text{SnH}\text{.}^{201}

Thiono-, dithiocarbonates (xanthates) and related compounds often provide effective routes for the removal of unwanted oxygenation, especially secondary alcohols, through the Barton–McCombie reaction\textsuperscript{202}. For example, Font and his associates utilised this chemistry en route to grandisol in which the fluorophenylthionocarbonate (54) was reduced using tributyltin hydride under standard radical conditions (equation 33)\textsuperscript{210}. In this example the by-product (55) is also formed, presumably a result of the release of strain associated with the four-membered ring. White and Jeffrey described the \text{Bu}_3\text{SnH}-mediated reduction of xanthate (56) during their synthesis of the tricarbonyl subunit of rapamycin (equation 34)\textsuperscript{212}, while Schintzer and Ringe utilize a similar strategy in their syntheses of \(\beta\)-pinguisene (57) and \(\beta\)-pinguisenol (equation 35)\textsuperscript{214}. 

\[
\begin{align*}
\text{OAc} & \quad \text{R}^2 \\
\text{OAc} & \quad \text{R}^1 \\
\text{AcO} & \quad \text{SePh} \\
\text{O} & \quad \text{NCS}
\end{align*}
\]

(53)
19. Synthetic uses of $R_3MH$ ($M = \text{Ge, Sn, Pb}$)

(54) $\xrightarrow{\text{Bu}_3\text{SnH} / \text{AIBN}}$ (55) + (33)

(33) $\xrightarrow{\text{Bu}_3\text{SnH} / \text{AIBN}}$ (34)

(34) $\xrightarrow{\text{Bu}_3\text{SnH} / \text{AIBN}}$ (35)

(35) $\xrightarrow{\text{Bu}_3\text{SnH} / \text{AIBN}}$ (57)
Gössinger and coworkers reported the Bu$_3$SnH-mediated reduction of xanthate (58) in their work towards the synthesis of nodusmicin (equation 36)\textsuperscript{220}. Cornforth, Hanson and their associates investigated the unusual generation of methoxy groups during the reduction of xanthates (59) derived from lanosterol (equation 37) and proposed a mechanism to account for this observation\textsuperscript{222}. It should be noted that this transformation afforded primarily the expected deoxygenated product, with the methyl ether representing only 14% of the reaction mixture.
Zoretic and coworkers described the stannane-mediated deoxygenation of 60 as part of their synthesis of \( d,l \)-norlabdane oxide (61) and related odorants (equation 38)\(^{232}\). Martin and coworkers employed stannane-mediated deoxygenation of substrate (62) as part of their strategy for the synthesis of a segment of herbimycin A (equation 39)\(^{252}\). Camps and his associates reported the \( \text{Bu}_3\text{SnH} \)-mediated deoxygenation of the thiocarbonyl imidazolide (63) during their synthesis of analogues (e.g., 64) of huperon A (equation 40)\(^{258}\). Tachibana and coworkers described a convergent synthesis of a decacyclic ciguatoxin model in which a key step involved the removal of the thionocarbonate moiety in 65 by the application of \( \text{Bu}_3\text{SnH} \) (equation 41)\(^{262}\).

\[
\begin{align*}
\text{Bu}_3\text{SnH} &\quad \text{Pd-C} \\
\text{H}_2 &\quad \text{AIBN}
\end{align*}
\]
Hu, Sun and Scott described recently an efficient synthesis of some taxadiene derivatives\(^{266}\). In their approach, alcohol (66) is treated with carbon disulphide followed by methyl iodide under standard conditions for the formation of xanthates, to afford the dithiocarbonate (67) in a process that presumably involved a Claisen rearrangement (Scheme 9). Interestingly, 67 undergoes smooth reaction with Bu\(_3\)SnH to provide the required products (68, 69)\(^{266}\).
Kibayashi and coworkers described the stannane-mediated reduction of xanthate (70) in their work towards the preparation the marine alkaloid (−)-lepadin B (equation 42), while Danishefsky and his associates provide an elegant, fully synthetic route to the neurotrophic tricycloilliconone (71) involving the reduction of xanthate (72) (equation 43).

Selenoesters are effective radical precursors which can afford aldehydes by direct reduction with reagents such as Bu₃SnH, or decarbonylated (nor-aldehyde) products. For example, Stojanovic and Renaud described the decarbonylative reduction of phenylselenoester (73) during their synthetic investigations (equation 44). Similarly, Alcaide and his associates utilised decarbonylative reduction of a phenylselenoester during their
preparation of novel C4-unsubstituted $\beta$-lactams (equation 45)$^{281}$, while Keck and Grier described non-decarbonylative reduction chemistry for $N$-acyl(phenylseleno)oxazolidinones (equation 46)$^{132}$.

Nitro compounds are also able to be reduced by stannanes under free-radical conditions. For example, Kitayama described the reduction of the nitro moiety in 74 by the action of Bu$_3$SnH during his preparation of pheromones for *Bactrocera Nigrotibialis*, *Andrena Wilkella* and *Andrena Haemorrhhoa* (equation 47)$^{282}$. Petrini and coworkers reported the selective reduction of the nitro group in a series of $\omega$, $\omega$-dichloro-$\omega$-alkanoates (75); it is interesting to note that the chlorine atoms remain intact during the reaction with Bu$_3$SnH (equation 48)$^{283}$. Witczak and coworkers described the reduction of substrate (76)
with Bu$_3$SnH en route to $\beta$-(1,4)-3-deoxy-C-disaccharides derived from levoglucosenone (equation 49)$^{285}$. 

Crossley and his associates described new synthetic routes to $\alpha$-amino acids and $\gamma$-oxygenated $\alpha$-amino acids through Bu$_3$SnH-mediated denitration chemistry (equation 50)$^{287}$. Ikeda and his associates reported the stannane-mediated removal
of the nitro functionality in furan (77) in their studies towards the preparation of octahydrobenzo[b]furans (equation 51)\textsuperscript{284}; note the concomitant deconjugation of the double bond in the major product, presumably driven by radical stabilization factors. Uno, Kasahara and Ono denitrated 78 en route to novel α-branched serine derivatives (equation 52)\textsuperscript{289}.

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{CO}_2\text{Me} \\
& \quad \text{NHCBz} \\
\text{Bu}_3\text{SnH} & \quad \text{AIBN} \\
\downarrow & \\
\text{O}_2\text{N} & \quad \text{CO}_2\text{Me} \\
& \quad \text{NHCBz} \\
\text{Bu}_3\text{SnH} & \quad \text{AIBN} \\
\end{align*}
\]

(50)

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{CO}_2\text{Me} \\
& \quad \text{H} \\
\text{Bu}_3\text{SnH} & \quad \text{AIBN} \\
\end{align*}
\]

(major product)

(77)

Sulphoxides, sulphates and sulphonyl compounds have also been used as substrates in stannane-mediated reductions. Gethin and Simpkins reported the \text{Bu}_3\text{SnH}-mediated removal of the tosyl group in substrate (79) in their preparation of protected thymine polyoxin C (equation 53)\textsuperscript{293}. Similarly, Xu and Lu described the removal of the tosyl group in 80 under similar conditions during their synthesis of pentabromopseudilin (equation 54)\textsuperscript{294}. Padwa and his associates utilised \text{Bu}_3\text{SnH} to remove the sulphone moiety in cyclopentenone (81) (equation 55)\textsuperscript{295}, while Wnuk and coworkers discuss
the stannyl radical mediated cleavage of π-deficient heterocyclic sulphones during the synthesis of α-fluoro esters (equation 56)\textsuperscript{197}. 

\[ \text{AIBN} \xrightarrow{Bu_3SnH} \text{Bu}_3\text{SnH} \]

(53)

(79)

(54)

(80)

(55)

(81)
During the time frame covered by this chapter, stannanes have been reported to have been involved in radical chemistry not involving the more traditional functionalities. For example, Marzi and coworkers reported that the reduction of cyclic thionocarbonates (e.g. 82) with Bu₃SnH under standard radical conditions affords cyclic acetals that can then be further transformed into 1,2-diols (equation 57)²¹⁹. This transformation represents a new approach to the protection of these diols. Zehl and Cech described the use of Bu₃SnH in the reduction of azide (83) to the corresponding amine (equation 58)³⁰⁵, while Hanessian and his associates reported the Ph₃SnH-mediated free-radical reduction of the tertiary oxalate (84) (equation 59)³⁰⁹. This transformation represents a departure from the more typical reduction of a pyridinethioneoxycarbonyl (PTOC) oxalate ester³²¹.
Shimizu and coworkers reported the use of Bu$_3$SnH for the removal of unwanted dithi-anyl groups in substituted 1,4-disilacyclohexanes (85) during their general preparation of disilacyclohexanes (equation 60)$^{311}$. Similarly, Kiyooka and his associates described the stannane-mediated removal of the thioacetal moiety in 86 during their enantioselective synthesis of a key intermediate towards the preparation of polyene macrolide filipoin III (equation 61)$^{316}$. Hiemstra and coworkers utilised Bu$_3$SnH to demercurate a key intermediate (87) during their preparation of (+)-gelsedine (equation 62)$^{315}$. In this last example, Young and coworkers describe the Ph$_3$SnH-mediated reduction of the doubly-conjugated double bond in $\beta$-ionone (88) during their preparation of theaspirane and theaspirone (equation 63)$^{319}$. This transformation had previously been reported by Wolf and Zink$^{322}$. 

![Diagram](image-url)
19. Synthetic uses of $R_3MH$ ($M = \text{Ge, Sn, Pb}$)
2. Intermolecular addition chemistry

One of the major applications of trialkyltin hydrides in synthesis has been in the formation of C–C and other bonds through the use of free-radical addition chemistry\textsuperscript{132,289,323–370}. For example, Motherwell and his associates used this free-radical methodology for the preparation of novel difluoromethylene-linked serine-\textit{O}-glycopeptide analogues (89), an example of which is depicted in equation 64\textsuperscript{338}. Junker and Fessner described the stereoselective synthesis of C-glycosylphosphonates (90) involving free-radical addition chemistry (equation 65)\textsuperscript{346}. Khan and Prabhudas reported a simple Bu\textsubscript{3}SnH-mediated preparation of bridgehead functionalised norbornene derivatives (equation 66)\textsuperscript{368}, while Naito and coworkers described a novel solid-phase synthesis use of Bu\textsubscript{3}SnH-mediated free-radical addition chemistry in the preparation of some \textit{\alpha}-amino acid derivatives (91) (equation 67)\textsuperscript{364}. Sibi, Ji and coworkers reported significant enantioselectivity during chiral Lewis acid catalysed conjugate radical addition reactions, an example of which is illustrated in equation 68\textsuperscript{331}. Indeed, other workers have also benefited through the stereochemical control provided by Lewis acids\textsuperscript{371}. For example, Tadano and his associates reported very high stereoselectivities in Lewis acid mediated conjugate radical additions in their preparation of glucopyranoside derivatives (equation 69)\textsuperscript{369}. It is interesting to note that in this example, the origin of the stereocontrol rests with the substrates, while in the former example the chiral Lewis acid played the controlling role in the chemistry.
19. Synthetic uses of R₃MH (M = Ge, Sn, Pb)

\[
\begin{align*}
&\text{AcO} & & \text{OAc} \\
&\text{AcO} & & \text{O} \\
&\text{AcO} & & \text{Br} \\
\end{align*}
\]

\[+\]

\[
\begin{align*}
&\text{OR} \\
&\text{OR} \\
&\text{OAc} \\
&\text{AcO} \\
&\text{AcO} \\
&\text{AcO} \\
&\text{P} \\
&\text{OR} \\
&\text{OR}
\end{align*}
\]

\[\xrightarrow{\text{AIBN Bu₃SnH}}\]

(65)

\[
\begin{align*}
&\text{AcO} & & \text{OAc} \\
&\text{AcO} & & \text{O} \\
&\text{AcO} & & \text{Br} \\
\end{align*}
\]

\[\xrightarrow{\alpha : \beta > 91:9}\]

(90)

\[
\begin{align*}
&\text{MeO} & & \text{OMe} \\
&\text{Br} & & \text{Br} \\
&\text{Br} & & \text{Br} \\
&\text{CO₂Me} & & \text{CO₂Me} \\
\end{align*}
\]

\[+\]

\[
\begin{align*}
&\text{R} \\
\end{align*}
\]

\[\xrightarrow{\text{AIBN Bu₃SnH}}\]

(66)

\[
\begin{align*}
&\text{MeO} & & \text{OMe} \\
&\text{Br} & & \text{Br} \\
&\text{Br} & & \text{Br} \\
&\text{CO₂Me} & & \text{CO₂Me} \\
\end{align*}
\]

\[+\]

\[
\begin{align*}
&\text{MeO} & & \text{OMe} \\
&\text{Br} & & \text{Br} \\
&\text{Br} & & \text{Br} \\
&\text{CO₂Me} & & \text{CO₂Me} \\
\end{align*}
\]

R = CN, CO₂Me, CH₂OH
\[
\begin{align*}
\text{P} & \text{O} \quad \text{O} \quad \text{N=O} \quad \text{Bn} \\
& \quad \text{Bu}_3\text{SnH} / \text{RI} \\
\rightarrow & \quad \text{P} & \text{O} \quad \text{O} \quad \text{NH} \quad \text{Bn} \\
& \quad \text{R} \\
\end{align*}
\]

\[\text{(67)}\]

\[
\text{HO}_2\text{C} \quad \text{NH} \quad \text{Bn} \\
\quad \text{R} \\
\]

\[\text{(91)}\]

\[\text{R} = \text{Et}, \text{i-Pr}, \text{t-Bu}, \text{s-Bu}, \text{i-Bu}, 1-\text{Ad}, \text{c-Hex}\]

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{N} & \quad \text{C} \quad \text{Me} \\
\end{align*}
\]

\[\text{(68)}\]

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{N} & \quad \text{C} \quad \text{Me} \\
\end{align*}
\]

\[\text{(69)}\]
Free-radical cyclization chemistry is now an integral part of the chemical armory available to the synthetic chemist. Indeed, during the period covered by this chapter, stannane-mediated cyclizations form by far the largest subset of chemical reactions. Mostly, this chemistry has been employed to form C–C bonds through the use of intramolecular homolytic addition methodology, although some examples involving the formation of bonds to heteroatoms via homolytic substitution chemistry are also provided. As was the case with other applications of stannanes, this section will focus on some selected examples of the chemistry in question in order to highlight the diversity available to the synthesis practitioner.

The most utilised reactions in this class involve the ‘classical’ 5- and 6-exo-trig cyclization and is typified by conversion of selenide (92) into the skeleton (93) of Garsubellin A as reported by Nicolaou and coworkers (equation 70). The radical required during the cyclization protocol can be generated in a tandem sequence as demonstrated by Marco-Contelles and Rodríguez, who reported the preparation of polyfunctionalised cyclopentanes (94) through the use of Bu$_3$SnH-mediated ring closure (equation 71). In this example, intermolecular addition of the tributylstannyl radical to the alkyne moiety in 95 is followed by rapid 5-exo intramolecular attack at the hydrazone functionality to afford the desired compound.
SCHEME 10
Bose and colleagues described the construction of tetracyclic isoquinolines and quinazolines via aryl radical cyclization (equation 72)\textsuperscript{510}. Sometimes, the radical formed as a result of 5-\textit{exo} cyclization can undergo further rearrangement as was discovered by Engman and coworkers, who report the preparation of antioxidant 2,3-dihydrobenzothiophenes (96, 97) by radical ring closure (Scheme 10)\textsuperscript{516}.

Alonso and his colleagues employed 5-\textit{exo} cyclization as part of their strategy for the synthesis of intermediates en route to (−)-tetrodotoxin\textsuperscript{660}. In this example, the radical generated after reaction of the precursor (98) with \textit{in situ} generated Bu\textsubscript{3}SnH undergoes 5-\textit{exo} ring closure onto the oxime functionality to afford the tricyclic adduct (99) (equation 73). Sometimes, intramolecular hydrogen transfer prior to cyclization can form an integral part of the overall synthetic strategy, as reported recently by Jones and coworkers during their preparation of spirooxindoles (100) (Scheme 11)\textsuperscript{663}. Malacria and coworkers employed cyclization followed by 1,4-hydrogen transfer and intermolecular addition in their recent strategy for the preparation of optically pure 1,2,3-triols (equation 74)\textsuperscript{370}. Crich and his associates investigated hydrogen transfer/cyclization methodology in their cyclization of conformationally constrained 1,3-dioxolanyl radicals (equation 75)\textsuperscript{543}.
SCHEME 11
Cyclizations onto triple bonds have also been employed commonly in the constructions of cyclic organic molecules. For example, Rainier and Kennedy utilised a tandem Bu$_3$SnH addition/cyclization strategy in their construction of some substituted indoles (101), an example of which is depicted in equation 76$^{659}$. 
Under appropriate circumstances, free-radical methods can also be used to prepare macrocyclic systems. For example, Maillard and coworkers prepared the 12-membered macrocyclic ether (102) by Bu$_3$SnH-mediated intramolecular homolytic addition to a remote, but activated ($\alpha$, $\beta$ unsaturated) olefin as depicted in equation 77$^{460}$. Tozer and coworkers employed 7-, 8- and 9-endo cyclization in their preparations of conformationally constrained amino acids (103), an example of which is provided in equation 78$^{448}$. 
Marco-Contelles and de Opazo utilised 8-endo-trig and 7-exo-dig cyclizations, mediated by Bu₃SnH, in their construction of chiral, polyfunctionalised medium-sized carbocycles. For example, treatment of iodide (104) with Bu₃SnH under standard radical conditions afforded 7-membered carbocycles (105) in moderate yield (equation 79). Prado and coworkers reported the synthesis of benzolactams by 11-endo aryl radical cyclization, an example of which is highlighted in equation 80.

While intramolecular addition chemistry has provided numerous opportunities for the preparation of bonds to carbon, there are significantly fewer examples of radical reactions that form bonds to heteroatoms. Homolytic substitution chemistry is an efficient and effective method for the formation of bonds to higher heteroatoms. Often, this chemistry is performed without the requirement for chain carriers such as Bu₃SnH. However, there are numerous examples of stannane-mediated homolytic substitution chemistry. For example, Crich and Yao use Bu₃SnH-mediated intramolecular homolytic substitution chemistry to generate acyl radicals and in doing so produce dihydrobenzothiophene as a by-product (equation 81), while work in our laboratories has demonstrated that selenocephalosporin analogues (e.g. 106) are readily available through the application of this chemistry (equation 82).
SCHEME 12

Bu$_3$SnH
AIBN
4. Tandem/cascade cyclization sequences

One of the most significant advantages of free-radical cyclization chemistry is its ability to be included in tandem or cascade sequences in which the adduct radical of a cyclization step becomes involved in subsequent cyclization chemistry. Under the right conditions, the cascade will propagate until no further intramolecular addition is possible, at which time hydrogen abstraction from a chain carrying species such as Bu₃SnH affords the final product. There are many practitioners of this art. For example, Malacria and his associates investigated the total synthesis of epi-illudol (107) via a Bu₃SnH-mediated transannular tandem sequence as depicted in Scheme 12. Lee and coworkers described a 5-exo, 7-endo sequence for the construction of the Guaianolide skeleton (108) (equation 83), while Double and Pattenden reported a series of radical cascades involving enamide bonds that lead to azasteroids (e.g. 109) (equation 84). This work follows on from earlier studies in which the same group described the preparation of steroidal structures (e.g. 110) through the use of a Bu₃SnH-mediated cascade (equation 85).
Takasu and coworkers reported the construction of the dodecahydrophenanthrene system (111) through the use of a Bu$_3$SnH-mediated 6-endo, 6-endo, 6-exo cascade process (equation 86)$^{707}$, while Sha and coworkers described the total synthesis of (+)-paniculatine (112) by a tandem sequence involving $\alpha$-carbonyl radicals (equation 87)$^{710}$. 

\[
\text{Bu}_3\text{SnH} \quad \text{AIBN} \quad \text{Bu}_3\text{SnH} \\
\text{PhSe} \quad \text{O} \\
\text{H} \quad \text{H} \\
\text{O} \quad \text{H} \\
(110) \\
(111)
\]
5. Free-radical hydrostannylation reactions

Intermolecular free-radical additions of stannyl radicals to multiple bonds have emerged as important methods for the preparation of tetraorganostannanes which can be reacted further to afford new C–C bonds through transition metal mediated coupling processes (e.g. Stille coupling). There are numerous examples of this chemistry \(^{715–737}\), and this treatise will focus on a few selected examples.

Lhermitte and Carboni reported the hydrostannylation of alkynylboranes as an efficient process for the preparation of alkenyl diamino- and dialkoxyboranes (equation 88)\(^ {715}\). Regitz and his associates described the free-radical hydrostannylation of Becker-type phosphaalkenes (113) (equation 89)\(^ {719}\). The regiochemical control available during this transformation is noteworthy. Mouriño and coworkers reported the hydrostannylation of terminal acetylene (114) as part of their strategy for the synthesis of 1α,25-dihydroxyvitamin D\(_2\) (equation 90)\(^ {720}\), while Ahmed and Forsyth utilised free-radical hydrostannylation during their preparation of the C31–C46 domain of the phorboxazole natural products (equation 91)\(^ {723}\). Pearson and Lovering described the use of hydrostannylation followed by Stille coupling protocol in their preparation of key
intermediate (115) during work towards the total synthesis of (±)-crinine, (±)-6-epicrinine, (−)-amabiline and (−)-augustamine (equation 92)\(^{27}\).

\[
\begin{align*}
R^1 \quad \equiv \quad BR^2_2 & \quad \xrightarrow{\text{Bu}_3\text{SnH}} \quad \text{Bu}_3\text{Sn} \quad \equiv \quad BR^2_2 \\
& \quad + \\
\quad R^1 \quad \equiv \quad \text{Bu}, \text{CO}_2\text{CH}_2\text{Ph}, \\
R^2 & \equiv \quad \text{i}-\text{Pr}_2\text{N}, \text{c-Hex}_2\text{N}, \text{BuO}
\end{align*}
\]

\[(88)\]

\[
\begin{align*}
\text{TMS} \quad \equiv \quad \text{OTMs} & \quad \xrightarrow{\text{Bu}_3\text{SnH or Ph}_3\text{SnH}} \quad \text{TMS} \quad \equiv \quad \text{OTMs} \\
P \quad \equiv \quad \text{C} \quad \equiv \quad \text{H} & \quad \xrightarrow{\text{AIBN}} \quad \text{R}_3\text{Sn} \quad \equiv \quad \text{R}^1 \\
R^1 & \equiv \quad \text{t-Bu, t-C}_5\text{H}_11, \text{c-Hex, 1-Me-c-Hex, 1-Ad}; \\
R^2 & \equiv \quad \text{Bu, Ph}
\end{align*}
\]

\[(89)\]

\[
\begin{align*}
\equiv \quad \text{OMOM} & \quad \xrightarrow{\text{Bu}_3\text{SnH}} \quad \text{Bu}_3\text{Sn} \quad \equiv \quad \text{OMOM} \\
\quad \equiv \quad \text{OMOM} & \quad \xrightarrow{\text{Bu}_3\text{SnH}} \quad \text{OMe} \quad \equiv \quad \text{OMe} \quad \equiv \quad \text{OMe} \\
\quad \equiv \quad \text{OMe} & \quad \xrightarrow{\text{Bu}_3\text{SnH}} \quad \text{OMe} \quad \equiv \quad \text{OMe} \quad \equiv \quad \text{OMe}
\end{align*}
\]

\[(90)\]

\[(91)\]
Dussault and coworkers described the preparation of allylstannanes (116, 117) as part of their synthetic studies (equation 93). It is interesting to note the preferred geometries of the products which appear to be dependent on the nature of the stannane employed. In this last example, Yu and Oberdorfer reported the use of free-radical hydrostannylation in their preparation of (tributylstannyl)vinyl-substituted 2-deoxyuridine derivatives (e.g. 118) for use in halogenation and radiohalogenation reactions (equation 94).
6. Miscellaneous radical reactions

There are numerous reports of stannane-mediated free-radical chemistry that does not fit neatly into the categories discussed above. Some of these publications describe unusual outcomes and chemistry that is specific to a small subset of substrates, while others report radical rearrangements and fragmentations that take place after the initial, tin-mediated, radical-forming event. We have chosen a small set of examples that illustrate these concepts.

Banwell and Cameron utilised a Bu₃SnH-mediated ring-expansion process as part of their preparation of the carbon skeleton associated with manicol (equation 95). Kim and coworkers investigated 1,6-stannylation translocations between enoxy oxygen and alkoxy oxygen as part of their mechanistic investigations surrounding homolytic substitution processes (equation 96). This transformation involves addition of the stannyl radical to the double bond in 119, followed by 1,6-homolytic translocation and subsequent destannylation. Crimmins and his associates described the stannane-mediated rearrangement of cyclobutylcarbonyl radicals generated during their total synthesis of (±)-lubiminol (equation 97). Renaud and coworkers described the preparation...
of ortho-arylbenzaldehyde derivatives (121) by stannane-mediated free-radical ipso-substitution chemistry (equation 98).

\[ \text{Bu}_3\text{SnH} \quad \text{AIBN} \]

\[ \text{CO}_2\text{Et} \quad \text{H} \quad \text{H} \]

\[ \text{CO}_2\text{Et} \quad \text{H} \quad \text{H} \]

(119)

\[ \text{OH} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{OH} \]

(120)
Chmielewski and colleagues reported a $\text{Bu}_3\text{SnH}$-mediated radical-induced isoxazolinedine–isoxazolidin-5-one transformation (equation 99)\textsuperscript{778}, while Sulsky and coworkers described conformational switching in the synthesis of a spiro[2H-indol]-3(1H)-ones (e.g. 122) by radical cyclization, an example of which is depicted in equation 100\textsuperscript{787}. In this final example, Takekawa and Shishido described the selective cleavage of substituted cyclopropanes via stannane-induced radical fragmentation, an example of which is illustrated in equation 101\textsuperscript{791}. \[ \text{equation 98} \]

\[ \text{equation 101} \]

$X = \text{H, CN, CF}_3, \text{OMe}$
C. Other Tin Hydrides

While the large bulk of free-radical chemistry has been carried out using reagents such as tributyl, trimethyl and triphenyltin hydride, there are several examples of the use of designer stannanes that satisfy desired niche criteria\(^\text{26–30,32–35,39–43,47–50,802–807}\). Their syntheses are described above. Some stannanes have been modified to improve their physical (solubility/separation/reactivity) properties\(^\text{27–30,47–50,804}\), while others have been tailor-made to aid in chirality transfer and to effect enantioselective outcomes during free-radical chemistry\(^\text{26,32–35,39–43}\).

For example, the fluorous stannanes (10) reported by Curran and coworkers (equation 10) are effective substitutes for Bu\(_3\)SnH in a wide cross-section of free-radical transformations\(^\text{27–30}\), as are the polymer-bound systems (37) described by Deleuze\(^\text{48,49}\).
Yoshida and coworkers described the control of free-radical reactivity during reduction by dynamic coordination; pyridylethyl-substituted tin hydrides (123, 124) appear to selectively reduce alkyl iodides and bromides in preference to chlorides, as illustrated in equations 102 and 103. Dumartin and his associates reported the immobilization of substrates required for the synthesis of 17α-(iodovinyl)estradiol through hydrostannylation with a polymer-supported tin hydride (equation 104). Baba and coworkers described the use of Bu₂SnIH in the synthesis of nitrogen heterocycles (e.g. 125) (equation 105).
Podestá and coworkers investigated 1,2-stereoinduction in the asymmetric hydrostannylation of substituted ethylenes with (−)-menthyldimethyltin hydride (equation 106)\(^802\). It is interesting to note that for the transformations investigated, high diastereoselectivity was observed. Nanni and Curran described the enantioselective reduction of bromide (126) with (S)-4,5-dihydro-4-methyl-3H-dinaphtho[2,1-c:1′,2′-e]stannepin (11) and reported enantioselectivities of up to 41% (equation 107)\(^32\). Metzger and colleagues demonstrated that the related stannane (13) provided enantioselectivities of up to 52% during the reduction of bromoester (127) (equation 108)\(^33\). In addition, the asymmetric tin hydrides (14) were demonstrated to provide enantioselectivities of up to approximately 25% at \(-30^\circ\text{C}\) in their reduction of analogous substrates (128) (equation 109)\(^806\).

Finally, Dakternieks, Schiesser and coworkers reported the highest enantioselectivity for a free-radical reduction reaction (96% ee) by combining the controlling effects of both chiral, non-racemic stannane (15, 17, 18–22, 27) and sterically demanding Lewis acid\(^807\). In the example provided in equation 110, the authors demonstrate that the chirality of the Lewis acid was largely irrelevant because both enantiomeric forms of Jacobsen’s catalyst provide essentially the same outcome. Several other examples are provided\(^807\).
(126) Et₃B / −78 °C

(127) Et₃B / −78 °C

(128) Et₃B / −30 °C

\( R^1 = n\text{-Bu, Ph}; R^2 = \text{Me, Et, } i\text{-Pr, } t\text{-Bu} \)

(109) Ph

(110) (S,S)-Jacobsen’s catalyst

(111) 9-BBN

96% ee
IV. TRIALKYLTIN HYDRIDES IN NON-RADICAL CHEMISTRY

As already demonstrated, stannane chemistry often involves the intermediacy of free radicals. There are some notable examples, however, of non-radical transformations involving trialkyltin hydrides. This (much smaller) subset of reactions is dominated by transition metal catalysed hydrostannylation chemistry, chemistry that rivals the free-radical examples provided above. In addition, there are a few examples of ionic reduction chemistry involving these reagents.

Ferri and Alami investigated the use of palladium-mediated hydrostannylation of dienynes (e.g. 129) in their preparation of precursors related to the neocarzinostatin chromophore (equation 111). While most transformations proceeded with little regioselectivity, some examples, most notably with TMS substitution, provided good selectivity. Xiang, Mahadevan and Fuchs reported the stereo- and regioselective syntheses of α- and β-vinyl and dienyl triflones via Stille coupling; hydrostannylation provided the Stille precursors (e.g. 130) (equation 112). Crisp and Gebauer investigated the hydrostannylation of propargylglycine derivatives facilitated by a number of transition metal catalysts (equation 113), while Lautens and coworkers described the regioselective hydrostannylation of allenes catalysed by Pd(OH)₂/C (equation 114).

\[
\begin{align*}
\text{TMS} & \quad \text{Bu₃SnH} & \quad \text{Bu₃SnH or Ph₃SnH} \\
\text{R} & \quad \text{Bu₃SnH or Ph₃SnH} & \quad \text{Bu₃SnH or Ph₃SnH} \\
\text{R} & \quad \text{Bu₃SnH or Ph₃SnH} & \quad \text{Bu₃SnH or Ph₃SnH} \\
\end{align*}
\]

\[
\begin{align*}
\text{TMS} & \quad \text{Bu₃SnH} & \quad \text{Bu₃SnH} \\
\text{SnBu₃} & \quad \text{Bu₃SnH} & \quad \text{Bu₃SnH} \\
\text{SnBu₃} & \quad \text{Bu₃SnH} & \quad \text{Bu₃SnH} \\
\end{align*}
\]
Uenishi and coworkers utilised palladium-catalysed hydrostannylation of dibromoalkenes (e.g. 131) as a method for the preparation of precursors en route to (Z)-alkenyl bromides (equation 115)\(^{831}\). These transformations effectively amount to hydrogenolysis and are believed to proceed by the mechanism depicted in Scheme 13\(^{831}\).

Kazmaier and his associates introduced Mo(CO)\(_3\)(CNBu-\(t\))\(_3\)(MoB\(_3\)I\(_3\)) as a new and efficient catalyst for regioselective hydrostannylation chemistry (equation 116)\(^{844}\), while Smith and Lodise described the assembly of a subtarget of 13-deoxytedanolide using hydrostannylation as an important step (equation 117)\(^{845}\). Rizzacasa and his colleagues utilised palladium-catalysed hydrostannylation in the preparation of an important synthon.
Bertrand and his associates reported the hydrostannylation of phosphorus vinyl ylides (133) by the action of tributyltin hydride in the absence of either a catalyst or free-radical initiator (equation 119). Yamamoto and coworkers described the Lewis acid catalysed hydrostannylation of C—C multiple bonds by Bu₃SnH produced in situ by the reaction...
of Bu₃SnCl with Et₃SiH (equation 120).\(^{862}\)

\[
\begin{align*}
R_2P &= C \equiv P(H)R_2 \quad \text{Bu₃SnH} \\
\text{Bu₃SnH} &\quad \text{Bu₃SnCl} + \text{Et₃SiH} \\
\end{align*}
\]

\(R = i-\text{Pr}_2\text{N}\)

\[
R^1 \quad \equiv \quad R^2 \\
\text{SnBu₃} + \text{Bu₃SnCl} + \text{Et₃SiH} \\
\]

\(\text{Lewis acid}\)

\[
R^1 = R^2 = n-C_6H_{13}, \text{Ph}; \quad R^1 = c-\text{Hex}, \text{PhCH}_2, \quad p-\text{XC}_6H_4 (X = H, \text{Me}, \text{MeO}), \quad R^2 = H
\]

### V. TRIALKYLGERMANIUM AND LEAD HYDRIDES IN SYNTHESIS

As discussed earlier in this chapter, trialkylgermanium hydrides are sometimes used in place of the more favoured tin counterparts, especially in radical chemistry when the rate constant for the primary bond-forming process lies outside the range acceptable for stannane chemistry. The reader will recognize without too much difficulty the scarcity of reports utilising germanium reagents when compared to those employing the analogous tin reagents. This is largely due to the relative expense of germanium compared to tin, but the lack of user-friendly NMR techniques for germanium compounds is also a contributing factor. Nevertheless, in the period covered by this review there have been some notable uses of germanes in preparative chemistry.\(^{26,309,413,863–865}\) To the best of our knowledge, there have been no applications of lead hydrides in synthesis during the same period.

The preparations of novel germanium hydrides have been discussed above. In some of these papers, the synthetic utility of these new reagents is also explored. For example, Oshima and coworkers described the use of tri-2-furanylgermanium hydride (2) as an alternative reagent for the generation of alkyl radicals from the corresponding halide and demonstrated standard reduction and cyclization protocols.\(^{19,863}\) While Mochida and coworkers examined the reactivity of novel polymer-supported germanes as free-radical reducing agents.\(^{25}\)

In other reports, Kim and coworkers reported the 1,5-translocation of the triphenylgermyl group between enoxy and alkoxy oxygen, an example of which is illustrated in equation 121.\(^{749}\) In addition to the stannane-based rearrangements described above (equation 96), Ryu and his associates demonstrated the difference between the products obtained in Bu₃GeH-mediated carbonylation/cyclization chemistry over the more traditional tin reagent (equation 122) and attribute the outcome to the poorer hydrogen-donating ability of the germane.\(^{413}\) Nishiyama and colleagues described the Et₃GeD-mediated selective deoxygenation and deuteriation of proline derivatives (equation 123).\(^{307}\)
19. Synthetic uses of $R_3MH$ ($M = Ge, Sn, Pb$)

In these final examples, Otero and coworkers described the reaction of a niobocene hydride (134) with triphenylgermanium hydride to afford niobocene germyl complexes (135) (equation 124)\(^864\), Spino and Barriault reported the radical cyclization of polyenes (136) mediated either by trialkyltin or trialkylgermanium hydride, an example of which is depicted in equation 125\(^705\), while Wittman and coworkers used Bu$_3$GeH during their construction of 7-deoxy-6-hydroxypaclitaxel (equation 126)\(^865\); the use of Bu$_3$SnH was not successful in this case as the stannane appeared to also remove the 10-acetate in the precursor (137).
Lastly, Gualtieri reported the use of binaphthyl-substituted germanes (8, 9) in enantioselective radical chemistry\(^\text{26}\). For example, an enantioselectivity of 59\% was reported for the reaction of 126 with 8 at \(-60^\circ\) (equation 127). To the best of our knowledge, this represents the first account of the use of a chiral germanium hydride in free-radical reduction chemistry.

VI. ACKNOWLEDGEMENT

We gratefully acknowledge the assistance of Miss Olympia Stamkos in the final stage checking of the references to this chapter.
19. Synthetic uses of $R_3MH$ ($M = \text{Ge, Sn, Pb}$)

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19. Synthetic uses of R₃MH (M = Ge, Sn, Pb) 

19. Synthetic uses of $R_3MH$ (M = Ge, Sn, Pb)

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19. Synthetic uses of R$_3$MH (M = Ge, Sn, Pb)

CHAPTER 20

Trichlorogermane, a new superacid in organic chemistry

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I. INTRODUCTION

Advances in the chemistry of haloforms and its analogue HMHal₃ (M = C, Si, Sn) served the development of organic and organometallic chemistry in just degree. Thus, preparative carbene chemistry started from the chemistry of dichlorocarbenes¹ and investigation of base hydrolysis of chloroform led not only to simple and effective methods of dichlorocyclopropane synthesis², but also to the beginning of a new discipline—phase transfer catalysis³. The study of thermolysis of haloforms led to the creation of the original and highly effective method of synthesis of halodiaromatic compounds and, especially, of deficient fluoroaromatics⁴.

Silicachloroform HSiCl₃, germanachloroform HGeCl₃ and the acidic form of stannachloroform H⁺SnCl₃⁻ were and remain basic reagents of group 14 for hydrometallation of unsaturated compounds. The lead analog of chloroform is unknown; the calculated value of its exothermic decomposition: HPbCl₃ → PbCl₂ + HCl is 29 kcal mol⁻¹⁵.

Trichlorogermane is a demarcative compound in this series because it exists in both covalent (HGeCl₃) and ionic acidic (H⁺GeCl₃⁻) forms⁶. The easy accessibility and high reactivity of HGeCl₃ together with a great variety of its chemical properties determine its special place among the key starting materials for the synthesis of organogermanium compounds up to the present day. Compounds of potential pharmacological activity, such as germatranes and germasesquioxides⁷,⁸, germanium containing nucleosides⁹, antibiotics and steroids¹⁰ can be easily obtained via reactions of trichlorogermane.

The great diversity of the chemical properties of trichlorogermane is especially astonishing and even discouraging. Thus, hydrogermylation reactions of various multiple bonds by trichlorogermane, which can proceed via either ionic or radical mechanisms, are widely known. Likewise, hydrogermylation of cyclopropane and aromatic compounds are also known. In the latter case, the superacidic properties of trichlorogermane develop most spectacularly.

Numerous reactions of trichlorogermane with organic halides, resulting in compounds of general formula RGeCl₃, are of preparative importance. Here again, two basic mechanisms are possible: nucleophilic Cl⁻ substitution by the GeCl₃⁻ and insertion of dichlorogermylene, previously generated from trichlorogermane, in C–Hal bonds.

Trichlorogermane, and especially its etherates, behave as a source of dichlorogermylene in many reactions. Investigations in this direction and, primarily, synthesis and studies of molecular complexes of GeCl₂ with n-donor ligands largely determined the development of the chemistry of germelenes and other carbenoids of the group 14 elements.

Trichlorogermane reactions involving participation of dichlorogermylene are not oxidation–reduction reactions in the usual sense of this term, though they are described by Ge²⁺/Ge⁴⁺ transfers. At the same time, the reductive properties of trichlorogermane can be illustrated by the reduction of nitrobenzenes to anilines.

Finally, the reaction of double germylation, such as formation of Cl₃GeCH₂CH₂GeCl₃ from ethylene and the etherate of trichlorogermane, is of great importance.
Experimental data of reactions of trichlorogermane are reviewed elsewhere. The main aim of this chapter is to gather investigations of the mechanistic aspects of reactions of trichlorogermane and to apply these data for providing a rational explanation of the experimental facts.

II. SYNTHESIS, STRUCTURE AND PHYSICAL PROPERTIES OF TRICHLOROGERMANE

Germanium is disposed in the center of group 14 of the periodic table of the elements. Increased stability of divalent species, which is more pronounced for tin and lead, begins from this element. The main characteristics of these atoms, such as atomic radius, energy of ionization, electron affinity, electronegativity and other features, are presented in parallel in a review.

Formally, HGeCl₃ belongs to inorganic chemistry and should be named trichlorogermandium hydride. We will follow the organic chemistry nomenclature and use the name trichlorogermane.

The simple ‘elementary synthesis’ of trichlorogermane from metallic Ge involves passing of dry HCl gas over Ge powder in a quartz tube at an elevated temperature in the presence of Cu powder. Consequently GeCl₄ is present in crude trichlorogermane obtained by such ‘elementary synthesis’ up to 20–40%. Pure trichlorogermane can be obtained in 40% yield by interaction of dry GeS and HCl followed by distillation. Extrusion of highly pure trichlorogermane by AlCl₃ from its etherates, which in turn can be obtained in an appropriate quality from trichlorogermane formed by the ‘elementary synthesis’, is probably the most convenient method.

Precautions are necessary when operating with trichlorogermane which is dry and free of GeCl₄, since impurities are formed as a result of any oxidative contact with air according to \( \text{HGeCl}_3 + \text{O}_2 \rightarrow \text{GeCl}_2 + \text{GeCl}_4 + \text{H}_2\text{O} \). Moreover, trichlorogermane can partially lose HCl even at \(-30\,^\circ\text{C}\) and therefore can be enriched by GeCl₂ and Ge subchlorides. That is the reason why experimental measurements of the physical properties of purified trichlorogermane are only few. There are no data on X-ray, electron diffraction spectroscopy in the vapor phase, mass-spectrometry and dipole moment determinations.

Trichlorogermane is colorless, mobile and a volatile liquid, \( d_0 = 1.93\,\text{g cm}^{-3} \), \( \text{mp} = -71\,\text{^\circ C} \), \( \text{bp} = 75.2\,\text{^\circ C} \). AM1 calculations give rise to the following geometric parameters of HGeCl₃ of \( C_{3v} \) symmetry: bond lengths of Ge–H = 1.559 Å, Ge–Cl = 2.131 Å, and bond angle of ClGeH = 111.6°. As follows from Raman spectroscopy data, dry trichlorogermane has a tetrahedral structure with calculated bond lengths of Ge–H = 1.55 Å, Ge–Cl = 2.11 Å, and Cl–Ge–Cl angle = 108.17°. The values of the valent and deformation frequencies of Ge–H are 699 and 2159 cm⁻¹ and the force constant is 2.7 × 10⁵ dyn cm⁻¹. In contrast, the spectrum of trichlorogermane in hydrochloric acid solution is completely different from the tetrahedral spectrum and belongs to the trigonal-pyramidal ion GeCl₃⁻. Bond lengths of Ge–Cl are 2.29–2.30 Å and Cl–Ge–Cl angles 93.4–98.3° were obtained for this trigonal-pyramidal species by X-ray analysis of [BnEt₃N]⁺GeCl₃⁻.

The extraordinarily big shift of the nuclear quadrupole resonance frequency in the etherate of trichlorogermane in comparison with trichlorogermane itself (9 MHz; from 23 to 14 MHz) can also be explained by a change in the coordination of the central atom to the trigonal-pyramidal form.

The principal thermodynamic functions calculated from the spectral data are collected elsewhere. The Ge–H chemical shift in the \(^1\text{H} \text{NMR} \) spectrum is at 7.6 ppm and has a half-width of \( ca. \) 7.2 Hz. This can be taken as evidence for exchange in the presence
of protic impurities. Attempts to obtain a $^{73}\text{Ge}$ NMR spectrum of HGeCl$_3$ and find out Ge–H satellites by using natural isotopic abundance of Ge had failed.$^{22}$

Among the different salts of the type MGeCl$_3$, the Rb and Cs salts, but not the Li and Na salts, are stable and well studied. This is accounted for in terms of ‘sharp’ and ‘soft’ acids and bases. In contrast to the small and ‘sharp’ Li$^+$ and Na$^+$ ions, the big and ‘soft’ Rb$^+$ and Cs$^+$ ions fit well the bulky and soft GeCl$_3^-$ anion.

### III. ACIDIC AND SUPERACIDIC PROPERTIES OF TRICHLOROGERMANE

#### A. Chemical Examples and Determinations

The acidic properties of covalent trichlorogermane cannot be characterized by the extent of dissociation. Unlike the etherate (Et$_2$O)$_2$HGeCl$_3$, free HGeCl$_3$ does not react with magnesium with the evolution of hydrogen. This simple observation attests to the fact that trichlorogermane behaves as an acid being ionized in basic solution, for instance, in ether (equation 1).

$$\text{HGe}^{+}\text{Cl}_3 \rightleftharpoons \text{H}^+\text{Ge}^{2+}\text{Cl}_3^- \rightleftharpoons \text{HCl} + \text{Ge}^{2+}\text{Cl}_2$$

If H$^+\text{GeCl}_3^-$ is considered as the conjugate Brønsted–Lewis acid of HCl and GeCl$_2$, it follows that the dichloride GeCl$_2$ must be characterized as a Lewis acid. According to the electron deficiency criterion, the GeCl$_2$ molecule, which possesses a vacant p-orbital, is, like AlCl$_3$, BF$_3$, ZnCl$_2$ etc., a Lewis acid and forms complexes of the type B•GeCl$_2$ with Lewis bases. The complexes of this type were already prepared in 1966. Among these molecular complexes, C$_4$H$_8$O$_2$•GeCl$_2^{23,24}$, Ph$_3$P•GeCl$_2^{25}$ and C$_5$H$_5$N•GeCl$_2^{26}$ have been studied in detail. As a Lewis acid, GeCl$_2$ may exhibit catalytic activity in Friedel–Crafts reactions. Although this activity has not been particularly studied, we should note the ability of polymeric germanium dichloride (GeCl$_2$)$_x$ to catalyze self-alkylation (condensation) reactions of benzyl chloride.$^{27}$ Hence, the acid H$^+\text{GeCl}_3^-$ fits into the series of superacids H$^+\text{AlCl}_4^-$, H$^+\text{BF}_4^-$ etc. which are also referred to as Friedel–Crafts acids.$^{28}$

The exact determination of the acidic properties of trichlorogermane is experimentally difficult. First, it should be remembered that solvate-free trichlorogermane is a covalent compound. Only the presence of species such as an ether, amine or phosphine change the nature of trichlorogermane so that it easily ionizes. Hence, the acidic properties of H$^+\text{[GeIICl}_3]$ in the solvated form can only be estimated indirectly.

Compounds which have absolute values of the Hammett acidity function ($H_o$) greater than that of 100% H$_2$SO$_4$ ($H_o = -11.9$) are classified as superacids.$^{29}$ It has been found that, like other superacids, trichlorogermane bleaches colored nitroaniline indicators, including 2,4,6-trinitroaniline, which are used for the determination of the Hammett acidity function $H_o$. However, the quantitative determination of $H_o$ by means of these reagents is not possible since trichlorogermane, being a strong reducing agent, is capable of reducing the NO$_2$ groups in the aromatic nitro-substituted indicators to amino groups.$^{30}$

Due to this difficulty, trichlorogermane has been classified as a superacid by means of the IR-spectroscopic method used for estimating the proton donating capabilities of acids.$^{31}$ This method is based on the fact that, when acids AH and a base B interact strongly, the protonated form BH$^+$ is considered as an acid which forms a hydrogen bond in the ion pairs BH$^+$•••A$^-$. When this occurs, the shift in the B–H vibrational frequencies (more correctly, the gravity centers of the continuous absorption) is used for the comparative estimation of the strength of bases A$^-$, i.e. for the estimation of the effective p$K_a$ values of the corresponding acids AH. By using this method, it was shown that the acidity of HGeCl$_3$ is close to the acidity of HClO$_4$, having a $H_o$ value of \(ca \ -13.0^{28}\).
The superacidic properties of trichlorogermane are clearly manifested in the properties of its etherates (vide infra) and the ability of DGeCl₃ to participate in a deuterium–hydrogen exchange reaction with methylbenzenes³² (Section VIII.E).

The surprising reactivity of trichlorogermane, which is greater than the reactivity of the other hydrides of group IV.B elements, becomes comprehensible when viewed from the point of view of its superacidity. Several reactions of trichlorogermane, which take place at room temperature or on moderate heating in the absence of any catalyst, are shown in Figure 1. In parallel, other reactions, such as aldol condensation of carbonyl compounds or cleavage of ether C—O bonds, take place due to the acidic properties of trichlorogermane. The formation of the products can be explained by the formation and participation of intermediate carbocations, arenium ions, acyl cations and oxonium ions.

It is impossible not to note the remarkable similarity between Figure 1 and the scheme for the formation of stable carbocations presented in Olah’s ‘superacids’ review²⁸. It is only for the activation of the C—H bond in hydrocarbons that trichlorogermane turns out to be an insufficiently strong acid.

The basic difference between HGeCl₃ and other superacids lies in the properties of the GeCl₃⁻ counterion. It is known that the counterions of classical superacids are characterized by an exceptionally low nucleophilicity which is widely used for the preparation and study of stable carbocations. On the other hand, HGeCl₃ is an example of a superacid whose counterion GeCl₃⁻ tends to undergo a rapid combination with many organic cations to form stable covalent compounds having a strong enough Ge—C bond (bond energy of
57–59 kcal mol$^{-1}$). However, as will be discussed below, the GeCl$_3^-$ anion does not recombine with all cations. The existence of a stable iminium salt, a cyclohexenyl cation and a σ-complex with a GeCl$_3^-$ counterion provides a convincing example for this. Hence, trichlorogermapne is an unusual example of an acid with an anion having an intermediate nucleophilicity with accompanying protonating ability corresponding to those of superacids.

B. Etherates of Trichlorogermapne

Investigations of the etherates of trichlorogermapne also confirm that H$^+$GeCl$_3^-$ is to be classified as a Friedel–Crafts superacid. The exothermic reaction of diethyl ether with trichlorogermapne leads to the etherate (Et$_2$O)$_2$•HGeCl$_3$, which is an oily liquid of salt-like structure that does not mix with an excess of ether. Other simple ethers also form similar etherates with HGeCl$_3$. In the majority of cases these species act as sources of GeCl$_2$. The structure of the etherate [Et$_2$O → H ← OEt$_2$]$^+$GeCl$_3^-$ was first proposed on the basis of the IR and NMR spectra.

More recently, it was shown that the etherates of Friedel–Crafts superacids, including the etherate of trichlorogermapne, are systems with a short (strong) hydrogen bond which manifests itself in a characteristic manner in $^1$H and $^{13}$C NMR spectra and as a continuous absorption (continuum) in the 1000–3000 cm$^{-1}$ region in the IR spectra. A complete X-ray structural investigation has been carried out for etherate (Et$_2$O)$_2$•HZnCl$_3$ and its deuterio analogue (Et$_2$O)$_2$•DZnCl$_3$. It was shown that (Et$_2$O)$_2$•H(D)ZnCl$_3$ crystals consist of the centrosymmetric dianions Zn$_2$Cl$_6^{2-}$ and [Et$_2$O•••H(D)•••OEt$_2$]$^+$ cations. The O•••H•••O bond length of 2.39 Å has one of the shortest distances for hydrogen bonds involving oxygen atoms.

No doubt, the ether moiety of the etherate of trichlorogermapne has the same structure as a [Et$_2$O•••H•••OEt$_2$]$^+$ cation. The principal difference between Zn and Ge etherates is only in the structure of the GeCl$_3^-$ anion, which is monomeric. According to estimates, the lengths and ionicities of the bonds in the GeCl$_3^-$ anion must be close to those for the [BnEt$_3$N]$^+$GeCl$_3^-$ salt and for the C$_4$H$_8$O$_2$•GeCl$_2$ complex, since the $^{35}$Cl NQR frequencies for these two compounds are in the same frequency region of 13.4–14.4 MHz.

C. Stable Organic Salts with a GeCl$_3^-$ Anion

The ability of trichlorogermapne as an acid to form stable organic salts having the GeCl$_3^-$ anion was first observed in the study of the reaction of HGeCl$_3$ with triphenylamine. It was found that at room temperature their interaction lead to the formation of an unusual iminium salt, i.e. trichlorogermapnate 3,5-bis(trichlorogermyl)cyclohexylidendiphenyliminium in 92% yield (equation 2).
A detailed follow-up of the reaction by $^{13}$C NMR spectroscopy has shown that the initially formed species is an isomer of 1 with a *trans*-configuration of the germyl groups with respect to the plane of the cyclohexane ring which exists in the twist-conformation. Over a period of two hours at 25°C, 85% of the *trans*-isomer 1 isomerizes into the *cis*-isomer of 1 and there is no further change in the ratio of the isomers. The crystalline *cis*-isomer of 1 has been isolated in a pure form and fully characterized.

A principal result was obtained in the study of HGeCl$_3$ reaction with 1,3-diethoxybenzene. In this reaction at $-50^\circ$C in CD$_2$Cl$_2$ the 1,3-diethoxy-5-trichlorogermylcyclohexenyl cation 2, stable under these conditions during many hours, was formed (equation 3)$^{37}$.

\begin{equation}
\text{EtO} \quad + \quad \text{HGeCl}_3 \quad \xrightarrow{50^\circ \text{C}} \quad \begin{array}{c}
\text{EtO} \\
\text{Cl}_3\text{Ge} \\
\text{OEt}
\end{array} \quad \text{GeCl}_3^- \\
(2)
\end{equation}

This first carbocation of the allyl type stabilized by a GeCl$_3^-$ anion is being formed in a yield close to quantitative and it was easily characterized at $-50^\circ$C by IR, UV, $^1$H and $^{13}$C NMR spectra.

Finally, in the case of the reaction of HGeCl$_3$ with 1,3,5-trimethoxybenzene the authors hoped to detect experimentally the $\sigma$-complex. Actually, as shown in equation 4, in the course of this reaction in a CD$_2$Cl$_2$ solution a quantitative formation of the arenium ion 3 was observed$^{38}$.

\begin{equation}
\text{MeO} \quad + \quad \text{HGeCl}_3 \quad \xrightarrow{20^\circ \text{C}} \quad \begin{array}{c}
\text{MeO} \\
\text{MeO} \\
\text{OMe}
\end{array} \quad \text{GeCl}_3^- \\
(3)
\end{equation}

This ion was stable for an hour even at room temperature. It was characterized by IR, UV, $^1$H and $^{13}$C NMR spectra. It can be assumed that the GeCl$_3^-$ anion has a quite low nucleophilicity in these salts, similarly to the anions of classic superacids.

At the end of this section one point should be especially emphasized: the superacidic properties of ionic H$^+$GeCl$_3^-$ are not astonishing, but rather the existence of HGeCl$_3$ itself in a covalent form. Quantum chemical calculations show that the affinity of GeCl$_3^-$ to the proton is only slightly different from the ionization potential of the hydrogen atom$^{39}$. In other words, the ‘sharp’ proton H$^+$ and the ‘soft’ anion GeCl$_3^-$ should separate if the electrostatic interaction is compensated by the energy of solvation.
Besides, the extents of dissociation of water-free superacids are insignificant, since the acids themselves are poor solvative media. They are less basic than water and poorly solvate protons. On the other hand, the solvation by superacids of the negatively charged anions is higher than in water solution. This is why the strength of acids is manifested by their protonation ability, rather than by the extent of dissociation\(^\text{40}\). This accounts for the high protonating ability of superacids, and trichlorogermane in particular, in the absence of ionizing solvents.

**IV. ELECTROCHEMICAL INVESTIGATION OF HGeCl\(_3\) AND GeCl\(_4\)**

Electrochemistry of organogermanium compounds is still insufficiently studied. However, a systematic electrochemical study of basic germanium chlorides HGeCl\(_3\) and GeCl\(_4\) was carried out\(^\text{41,42}\). The main principles of the electrode processes and the nature of the intermediates formed were determined.

**A. Oxidation**

The polarization curves of CsGeCl\(_3\), PyHGeCl\(_3\) and HGeCl\(_3\)•2Et\(_2\)O oxidation (0.1 N Et\(_4\)NClO\(_4\) in absolute CH\(_3\)CN, Pt rotating disk electrode) gave one anodic wave \((E_{1/2} = 0.5 \text{ V})\), corresponding to anion GeCl\(_3^-\) oxidation. In the course of the experiment the height of this wave decreases and another wave \((E_{1/2} = 0.9 \text{ V})\), corresponding to Cl\(^-\) oxidation, appears. This was explained by GeCl\(_3^-\) dissociation to GeCl\(_2\) and Cl\(^-\) under favorable conditions.

Trichlorogermane itself is ionized in CH\(_3\)CN solution. Therefore, as in the above mentioned cases, the anion GeCl\(_3^-\) undergoes oxidation. The polarization curve of trichlorogermane oxidation under the same conditions gave an anodic one-electron wave with \(E_{1/2} = 0.48 \text{ V}\).

In general, the trichlorogermane oxidation is described by equation 5.

\[
\begin{align*}
\text{HGeCl}_3 & \rightleftharpoons \text{H}^+ + \text{GeCl}_3^- \rightleftharpoons \text{GeCl}_3^* \xrightarrow{\text{dimerization}} \text{Ge}_2\text{Cl}_6 \\
\text{(GeCl)}_x & \leftrightarrow \text{GeCl}_2 + \text{GeCl}_4
\end{align*}
\]

Preparative electrolysis of HGeCl\(_3\)•2Et\(_2\)O leads, as expected, to the formation of GeCl\(_4\) and Ge-subchlorides.

**B. Reduction**

The reduction of GeCl\(_4\) also proceeds easily. The polarizing curve for the reduction of GeCl\(_4\) (0.1 N Bu\(_4\)NClO\(_4\) in absolute CH\(_3\)CN, Pt rotating disk electrode) has a single two-electron cathodic wave with \(E_{1/2} = -0.35 \text{ V}\). The electron number was determined coulometrically. At the controlled potential electrolysis \(E = -0.4 - 0.5 \text{ V}\) the height of the cathodic wave decreased and, at the same time, two anodic waves with \(E_{1/2} = 0.5 \text{ V}\) and \(E_{1/2} = 0.9 \text{ V}\) appeared. Judging from the \(E_{1/2}\) value, these waves could correspond to GeCl\(_3^-\) and Cl\(^-\) oxidation. According to the Pt rotating ring-disk electrode experiment, the GeCl\(_3^-\) anion is relatively stable and exists for a while in solution before its dissociation into GeCl\(_2\) and Cl\(^-\).
In general, the GeCl$_4$ reduction is reflected by equation 6.

\[
\text{GeCl}_4 + 2e^- \rightarrow \text{Cl}^- + \text{GeCl}_3^- \rightarrow \text{Cl}^- + \text{GeCl}_2 \rightarrow (\text{GeCl})_x
\] (6)

Some organogeranium compounds were first synthesized by interaction of different RHal species and electrochemically generated anion GeCl$_3^-$ (equation 7).

\[
\text{GeCl}_3^- + \text{RHal} \rightarrow \text{RGeCl}_3 + \text{Hal}^-
\] (7)

\[
\text{R} = \text{Me, Ph, Bn, AlI, Ac}
\]

\[
\text{Hal} = \text{Cl, Br, I}
\]

The counterion of the electrochemically generated GeCl$_3^-$ is the cation of the supporting electrolyte. By changing the electrolyte, it is possible to vary the GeCl$_3^-$ lifetime and to change the route of the electrochemical processes.

Thus, the results of the electrochemical study confirm the ready Ge$^{II} - \text{Ge}^{IV}$ transformation in chemical reactions. The easy oxidation of GeCl$_3^-$ to the GeCl$_3^+$ radical should be especially noted since it explains the appearance of GeCl$_3^+$ radicals in chemical reactions free of radical initiators.

**V. REACTIONS OF TRICHLOROGERMANE WITH ORGANIC HALIDES**

Interaction of trichlorogermane, and especially its etherates and aminates, with reactive organic halides results in nucleophilic substitution on organic halides by the trichlorogermyl group (equation 8)\textsuperscript{43,44}.

\[
\text{HGeCl}_3 + \text{R} - \text{Cl} \rightarrow \text{RGeCl}_3 + \text{HCl}
\] (8)

\[
\text{R} = \text{AlI, Bn, MeOCH}_2, \text{Me}_3\text{C, Ph}_3\text{C, 1-Ad etc.}
\]

Halohydrocarbons with labile bromine atom react even more easily. On the other hand, organic halides with less labile halogen atoms require more drastic reaction conditions, and sometimes even the application of pressure. In its entirety the reaction is a useful method for synthesis of organotrichlorogermanes. There are no analogous reactions in the chemistry of chloroform and trichlorosilane and the logical explanation of the phenomena can be found in the concept of HGeCl$_3$ superacidity.

This reaction, inaptly named condensation reaction\textsuperscript{43}, proceeds either by a nucleophilic substitution mechanism or by insertion of dichlorogermylene into the C–Cl bond. The nucleophilic substitution mechanism is doubtful. In accordance with quantum-chemical calculations, the negative charge in the anion GeCl$_3^-$ is distributed on chlorine atoms and a movement of anion to the cation from the ‘rear’ results in Cl$^-$ loss and GeCl$_2$ formation\textsuperscript{39}.

As shown by calculations, the carbenoid mechanism of dichlorogermylene insertion in ordinary C–Cl bond begins by electrophilic attack of the vacant p-orbital of the Ge atom on the electrons of the bond\textsuperscript{45,46}. The vacant p-orbital does not interact with the unpaired electrons of the chlorine atoms. When the distance between the reactants decreases and becomes close to the value of the C–Cl bond length, inactivated transfer of Cl to the germylene center occurs with formation of a radical pair, followed by its recombination. The closer the components of the radical pair, the smaller the probability of radicals movement away from one another. The theoretical interest concerning the details of the germylene insertion mechanism is continuing. Thus, a quantum-chemical examination of
the hypothetical insertion reaction of GeCl₂ into the C–H bond of methane was carried out recently⁴⁷,⁴⁸.

The insertion reaction can be easily modeled by using the dioxane complex of dichlorogermylene²⁴,⁴⁹. Kinetic investigation of the reaction with benzyl chloride was carried out⁵⁰. The experimental data were in line with kinetic equation 9, which involves participation of a free dichlorogermylene in the insertion step (in dioxane solution, where the equilibrium is shifted to the left, the insertion reaction does not occur).

$$ \text{C}_4\text{H}_8\text{O}_2 \cdot \text{GeCl}_2 \xrightleftharpoons[k_1]{k_{-1}} \text{GeCl}_2 + \text{C}_4\text{H}_8\text{O}_2 $$

$$ \text{BnCl} + \text{GeCl}_2 \xrightarrow{k_2} \text{BnGeCl}_3 \tag{9} $$

The experimental value of the energy of activation for the GeCl₂ insertion into the C–Cl bond was first found to be $E_a = 14.1$ kcal mol⁻¹. This value is substantially higher than the energy of activation for carbene insertion into ordinary bonds, estimated to be 5–7 kcal mol⁻¹⁵¹. This fact demonstrates the difference in reactivity and selectivity of the divalent species. A large and negative value of the entropy of activation ($\Delta S^\# = -35.9 \pm 4.4 \text{ eu}$) shows that the transition state of the dichlorogermylene insertion step is highly ordered.

Some other attempts to distinguish the two above mentioned mechanisms meet difficulties resulting from halogen lability. Thus, using in the reaction the optically active isomer of PhCH(Me)Cl led to complete racemization in both the starting material and the products²². Radiochemical investigation of the reaction with Bn³⁶Cl failed because full halogen exchange between the precursors took place²⁷.

A concerted insertion mechanism with highly ordered transition state, close to three-centered, was corroborated by examination of the kinetic isotope effect, which was measured by competitive GeCl₂ insertion reactions into the C–Cl bonds of labeled ¹⁴CCl₄ and ¹²CCl₄. The value obtained, $k_{14}/k_{12} = 1.01 \pm 0.01$, is very close to that calculated from the stretching frequencies and the ratio of the masses and moments of inertia of the isotopic molecules for a synchronous reaction (0.993) and differs significantly from the calculated value for a dissociative mechanism (0.900)⁵².

Finally, radiochemical investigation of the interaction of HGeCl₃ and C³⁶Cl₄ excluded an ionic mechanism for Cl₃CGeCl₃ formation in the reaction shown in equation 10.

$$ \text{CCl}_4 + \text{HGeCl}_3 \xrightarrow{k} \text{HCCl}_3 + \text{GeCl}_4 (83\%) $$

$$ \text{Cl}_3\text{CGeCl}_3 + \text{HCl (17\%)} $$

The value for the relative radioactivity of chlorine in the Cl₃CGeCl₃ attests to a carbene-like mechanism in its formation with a probability of 99%⁵³.

### VI. REACTIONS OF TRICHLOROGERMANE WITH UNSATURATED COMPOUNDS

**A. Ionic and Radical Mechanisms in Reactions of Hydrogermylation**

Trichlorogermane reactions with olefins and acetylenes, including functionally substituted compounds, are one of the basic methods of obtaining organogermanium derivatives. Trichlorogermane adds easily in the absence of any catalyst to olefinic and acetylenic
bonds, even unactivated ones. Numerous examples of such reactions are collected, for example, in a monograph\(^7\) and a review\(^11\). Having in mind the acidic properties of trichlorogermane, one can assume that hydrogermylation reactions will proceed by an ionic mechanism with formation of products according to ‘Markovnikov’ regioselectivity. However, numerous literature data testify to an opposite tendency. With very rare exceptions, addition to olefins and acetylenes proceeds against ‘Markovnikov’ orientation. Moreover, the original papers and reviews assert the formation of only ‘anti-Markovnikov’ adducts. Such a type of addition was called the ‘Farmer rule’\(^54\). In spite of the presence of a large amount of experimental data, the mechanism of the reaction was practically unstudied. Thus, addition of trichlorogermane to the allyl but not the vinyl group in dimethylallylvinyilsilane was logically ascribed to an ionic mechanism\(^55\). A study of the regioselectivity of the hydrogermylation of isopropenylacetylene shows that the olefinic bond is more active than the acetylenic bond\(^56\). The authors prefer a radical mechanism for the reaction, but they did not study it.

A detailed study of the reactions of trichlorogermane with unsaturated compounds was performed\(^57\text{–}59\). It became clear that among selected olefins only 1-heptene forms the anti-Markovnikov adduct in the reaction with trichlorogermane. In contrast to the generally accepted opinion, in the reactions with 1-methylcyclohexene (equation 11), styrene (equation 12), 2,3-dimethyl-1-butene (equation 13) and isobutene (equation 14) both regioisomers 4 and 5, 6 and 7, 8 and 9, and 10 and 11 appear in commensurable amounts (together with oligomeric products; see later, equation 16).

\[
\begin{array}{cccc}
\text{PhCH} &=& \text{CH}_2 + \text{HGeCl}_3 & \xrightarrow{-5^\circ\text{C}} & \text{PhCH}_2\text{CH}_2\text{GeCl}_3 + \text{PhCH}(\text{GeCl}_3)\text{Me} \\
& (6) & 28.5\% & (7) & 12.5\% \\
\text{Me}_2\text{CHC(Me)} &=& \text{CH}_2 + \text{HGeCl}_3 & \xrightarrow{-5^\circ\text{C}} & \text{Me}_2\text{CHCH(Me)CH}_2\text{GeCl}_3 \\
& (8) & 49\% & + & \text{Me}_2\text{CHC(GeCl}_3\text{)Me}_2 \\
& (9) & 10\% \\
\text{Me}_2\text{C} &=& \text{CH}_2 + \text{HGeCl}_3 & \xrightarrow{-10^\circ\text{C}} & \text{Me}_2\text{CHCH}_2\text{GeCl}_3 + \text{Me}_3\text{CGeCl}_3 \\
& (10) & 50\% & (11) & 8\%
\end{array}
\]

Reaction of trichlorogermane with excess of styrene at \(-5^\circ\text{C}\) leads to the formation of both isomers with a 2.3 : 1 predominance of the ‘anti-Markovnikov’ product. This ratio can be modified by varying the reaction conditions. Thus, if the reaction is carried out in concentrated HCl, the yield of 7 rises up to give an opposite regiochemistry with a ratio 6 : 7 = 1 : 9. The role of concentrated HCl consists in the ionization of trichlorogermane and shift of equilibrium \(\text{GeCl}_3^- \rightleftharpoons \text{GeCl}_2 + \text{Cl}^-\) to the left in the presence of excess of chloride anion.
The results obtained\textsuperscript{57} were explained by competition of ionic and radical mechanisms, which lead to ‘Markovnikov’ and ‘anti-Markovnikov’ adducts, respectively. At this competition the nature of the unsaturated compound play an important role in determining the preferred mechanism. Thus, the major formation of ‘Markovnikov’ adducts and therefore the preference of the ionic mechanism in the series of olefins styrene $> 1$-methylcyclohexene $> 2,3$-dimethyl-1-butene $> 1$-heptene correlates with the ability of substituents to stabilize the intermediate carbenium ion.

Formation of the ‘anti-Markovnikov’ adduct points to the intermediacy of $\text{GeCl}_3$ radicals. Formation of the radicals is explained by one electron transfer in different ionic pairs and separation of the formed radical pairs without recombination. This one-electron transfer at the stage of trichlorogermane ionization is expected because of the low potential of $\text{GeCl}_3^-$ oxidation ($E_{1/2} = 0.48$ V) and was confirmed by examination of CIDNP in the reactions (see equation 19 below).

Reaction of trichlorogermane with 1-heptene (equation 15) to form 12 was studied most carefully\textsuperscript{57}. The authors believe that 1-heptene serves as an effective mediator in electron transfers and thus assists in the radical mechanism.

$$\text{Me(CH}_2)_4\text{CH}=\text{CH}_2 + \text{HGeCl}_3 \xrightarrow{-5{\degree}\text{C}} \text{Me(CH}_2)_4\text{CH}_2\text{CH}_2\text{GeCl}_3$$

Numbers attempts to obtain the ‘Markovnikov’ adduct by varying the reaction conditions, including its realization in concentrated HCl, had failed. Moreover, in a competitive reaction of a mixture of 1-heptene and styrene only the anti-Markovnikov adducts were formed for both olefins and, surprisingly, 1-heptene was found to be more reactive than styrene. This is also in agreement with the concept of two mechanisms. Here, 1-heptene assists in the formation of $\text{GeCl}_3$ radicals and styrene acts as a radical trap, forming selectively only the anti-Markovnikov adduct.

The radical pathway in the hydrogermylation of isobutene is confirmed by formation of the oligomer 13, whose structure also testifies to a dichlorogermylene participation (equation 16)\textsuperscript{57}.

Formation of oligomers with alternate olefin-$\text{GeCl}_2$ links is especially characteristic for etherates of trichlorogermane. Gradual addition of trichlorogermane to ether solution of an olefin or 1,3-diene at low temperature ($-20-70$ °C) is optimal for oligomer formation and in this case the yield of the oligomers is close to 100%. The molecular mass of the oligomers is not high, being 2000–6000\textsuperscript{60}.
B. Stereochemistry of the Hydrogermylation

The stereochemistry of the radical addition was studied in the reaction of trichloroger-
mane with 1-methylcyclohexene, which gives both 14 and 15 (equation 17).

\[
\begin{align*}
\text{Me} & \\
\text{1. } & \text{HGeCl}_3 \\
\text{2. MeMgBr} & \\
\text{(14)} & + \text{(15)}
\end{align*}
\]

\(\text{Me}^+\) NMR spectroscopy and a double resonance technique were applied for solving the stereochemical problem\(^5^7\). It was necessary to decide if the stereoisomer 14a or 14b is the product (Figure 2).

The spin–spin coupling constants of \(J(H^2H_e) = 3.8\text{ Hz}\) and \(J(H^2H_a) = 10.3\text{ Hz}\) strongly testify in favor of an axial position of \(H^2\). Having in mind the above mentioned constants, the third coupling constant \(J(H^1H^2) = 3.8\text{ Hz}\) was obtained from the ordinary NMR spectrum. This value serves as evidence for the equatorial position of \(H^1\), i.e. the structure corresponds to stereoisomer 14a. Thus, the radical addition of trichlorogermaine to 1-methylcyclohexene proceeds solely as an anti-addition with a diequatorial disposition of the entering groups.

The stereochemistry of the ionic addition was investigated in the reaction shown in equation 18\(^5^8\).

\[
\begin{align*}
\text{Me} & \\
\text{H}_a & \\
\text{H}_e & \\
\text{H}^1 & \text{GeMe}_3 \\
\text{H}^2 & \\
\text{Me} & \\
\text{H}^1 & \text{H}^2 & \text{COOMe} \\
\text{H}^1 & \text{GeCl}_3 & \text{D} & \text{COOMe} \\
\end{align*}
\]

A vicinal spin–spin coupling constant \(J(H^1H^2) = 2.4\text{ Hz}\) was obtained from the \(^1\text{H}\) NMR spectrum. This value indicates a threo-configuration of 16 that, in turn, supports a
stereospecific cis-addition of DGeCl₃ to the C=C bond of the ester. Such stereoselectivity is explained by a mechanism involving 'ion pairs'.

C. Chemically Induced Dynamic Nuclear Polarization in Reactions of Hydrogermylation

CIDNP effects were found in the reactions of trichlorogerme with styrene, 2-methyl-2-butene and 2,3-dimethyl-2-butene. Analysis of the CIDNP effects was carried out by the Kaptein rules⁶¹ and testifies for the radical participation in these reactions⁵⁹.

The integral character of the CIDNP effects show a considerable difference in the g-values of the radical pair partners. One of these partners is a germanium-centered radical and the other is a hydrocarbon radical.

\[
\begin{align*}
RR^1C\equiv CHR^2 + HGeCl_3 &\rightarrow RR^1C^+\underset{T}{\text{CH}_2R^2}\text{GeCl}_3^- \\
RR^1C^*\longrightarrow CH_2R^2\text{GeCl}_3^- &\rightleftharpoons RR^1C^*\longrightarrow CH_2R^2\text{GeCl}_3^+ \\
\text{diffusion in volume} &\rightarrow RR^1C^*\longrightarrow CH_2R^2, \text{GeCl}_3^* \\
HGeCl_3; RR^1C\equiv CHR^2 &\rightarrow RR^1C^*\longrightarrow CHR^2\text{GeCl}_3 \\
&\rightarrow RR^1CHCH_2R^2\text{GeCl}_3 + \text{GeCl}_3^* \\
\end{align*}
\]

It was assumed that protonation of the precursor olefin by trichlorogerme occurs in the first step with formation of ionic pair RR¹C⁺/CH₂R²/GeCl₃⁻ (equation 19, polarized molecules are doubly underlined). The following step is a single electron transfer with formation of a singlet radical pair. CIDNP effects appear as a result of singlet–triplet conversion in this pair. Since in the singlet pair metathesis occurs with formation of polarized precursor olefins and trichlorogerme, the CIDNP effects are observed in both the precursors and the final products.

Formation of polarized 'anti-Markovnikov' adducts here results from GeCl₃⁺ attack on the polarized olefin.

D. Reactions with Conjugated Dienes

Reaction of trichlorogerme with butadiene (equation 20) and isoprene leads to formation of cyclic and oligomeric compounds, together with the usual products of
hydrogermylation\[62\]. Formation of germacyclopentene \(18\) becomes predominant when the etherate of trichlorogermane is used whereas the yield of butenyltrichlorogermane \(17\) does not exceed 1–2\%\[27\]. The reaction seems to proceed by the GeCl\(_2\) participation mechanism, which was confirmed by model reactions of GeCl\(_2\)-dioxane\[63\]. The cyclic product \(18\) was found to form predominantly at higher temperatures, whereas the oligomeric product \(19\) is preferred at lower temperatures.

\[
\begin{align*}
\text{CH}_2\equiv\text{CHCH} &= \text{CH}_2 \quad \xrightarrow{\text{HGeCl}_3} \quad \text{CH}_3\text{CH} &= \text{CHCH}_2\text{GeCl}_3
\end{align*}
\]

(17) \hspace{1.5cm} (18) \hspace{1.5cm} (20)

Two possible mechanisms were taken into consideration: a concerted 1,4-cycloaddition and a 1,2-cycloaddition involving the intermediate formation of vinylgermacyclopropanes. In accordance with Woodward–Hoffmann conservation of orbital symmetry restrictions on the concerted mechanism, a 1,4-cycloaddition to give \(20\) and \(21\) proceeds in the case of 1,2-dimethylenecycloalkanes (equations 21 and 22), but not in cases of 1,3-cyclohexadiene and 1,3-cyclooctadiene.

\[
\begin{align*}
\text{GeCl}_2 \quad \text{dioxane} &\quad \xrightarrow{} \quad \text{GeCl}_2 \quad \text{dioxane} \\
\text{Cl} &\quad \text{Cl} \\
\text{Cl} &\quad \text{Cl}
\end{align*}
\]

(21) \hspace{1.5cm} (22)

The experimentally obtained value of the secondary kinetic isotope effect served as a strong argument in favor of a concerted mechanism involving conrotation or disrotation of terminal CH\(_2\) and CHD groups in 1,3-butadiene and 1,4-dideuterio-1,3-butadiene (equation 23)\[64\].

\[
\begin{align*}
\left[ \begin{array}{c}
\text{Ge} \\
\text{Cl} \\
\text{Cl}
\end{array} \right] \\
\text{or} \\
\left[ \begin{array}{c}
\text{Ge} \\
\text{Cl} \\
\text{Cl}
\end{array} \right]
\end{align*}
\]

(23)

The preference for a concerted 1,4-cycloaddition was also confirmed by theoretical calculations\[65,66\].
A concerted 1,6-cycloaddition of dichlorogermylene to cis-hexatriene resulting in 1,1-dichloro-1-germacyclohepta-3,5-diene (22) was found for the first time (equation 24)\textsuperscript{63,67}.

\[
\begin{align*}
\text{GeCl}_2 \text{ dioxane} & \quad \text{GeCl}_2 \text{ dioxane} \\
\text{GeCl}_2 & \text{GeCl}_2 \\
\end{align*}
\]

(22)

It is noteworthy that the product of a possible 1,4-cycloaddition of dichlorogermylene to hexatriene, i.e. 1,1-dichloro-2-vinyl-1-germacyclo-3-pentene, was not observed at all in the reaction mixture.

E. Reactions with \(\alpha,\beta\)-Unsaturated Carbonyl Compounds

Reactions of trichlorogermane with \(\alpha,\beta\)-unsaturated carbonyl compounds are widely used for synthesis of biologically active germanium sesquioxides\textsuperscript{8,68,69}, for example, for the synthesis of carboxyethylgermanium sesquioxide 24 via the adduct 23 (equation 25).

\[
\begin{align*}
\text{CH}_2=\text{CH}_2\text{COOH} + \text{HGeCl}_3 & \rightarrow \text{Cl}_3\text{GeCH}_2\text{CH}_2\text{COOH} \xrightarrow{\text{H}_2\text{O}} (\text{O}_{1.5}\text{GeCH}_2\text{CH}_2\text{COOH}_2) \\
\end{align*}
\]

(23) (24) (25)

The reaction seems to proceed by an ionic mechanism\textsuperscript{58}. An initial 1,4-addition can be proposed by analogy with the reaction of H\(^+\)SnCl\(_3\)\textsuperscript{\text{--}}, and this is followed by rearrangement to the product of formal 1,2-addition\textsuperscript{70}.

A new type of trichlorogermyl group/hydrogen replacement was found in the reaction of trichlorogermane with \(\beta\)-thienylacrylic acid (equation 26).

\[
\begin{align*}
\text{S} & \text{CH} \equiv \text{CHCOOH} \\
\text{HGeCl}_3 & \quad \Delta \\
\text{S} & \text{CHCH}_2\text{COOH} \quad \text{Cl}_3\text{Ge} \\
\text{Cl}_3\text{Ge} & \text{Cl}_3\text{Ge} \\
\text{S} & \text{CHCH}_2\text{COOH} \\
\text{HGeCl}_3 & \quad \text{excess} \\
\text{Cl}_3\text{Ge} & \text{Cl}_3\text{Ge} \\
\text{S} & \text{CHCH}_2\text{COOH} \\
\end{align*}
\]

(25) (26) (27)
20. Trichlorogermane, a new superacid in organic chemistry

The protodegermylation of adduct 25 to form 26 occurs under thermolysis. In the case of 27, hydrogermylation of the thiophene double bonds by action of excess of trichlorogermane occurs. The hydrogenative function of trichlorogermane was also marked in the reaction of alkoxybenzenes as shown below in Section VIII.

F. Reactions with Cyclopropane Derivatives

Cyclopropanes can be regarded as unsaturated compounds, but their ability to react with opening of the ring is limited to additions of halogens, acids and mercury oxide salts\(^7\) and to participation in the reaction of metathesis\(^7\). The reactions of cyclopropane derivatives with HGeCl\(_3\) confirm the superacidic character of the latter. Trichlorogermane adds easily to alkyl- and arylcyclopropanes to give linear products with high yield. As shown in equation 27 for the case of phenylcyclopropane, the exclusive formation of the \(\alpha\)-isomer can be explained by the strong stabilization inferred by the phenyl group on the intermediate carbocation.

\[
\begin{align*}
\text{Ph} & \quad + \quad \text{HGeCl}_3 & \quad \rightarrow & \quad \text{PhCHCH}_2\text{CH}_3 \\
& & \quad \text{GeCl}_3 & \quad (85\%) \\
\end{align*}
\]

In other cases such selectivity is absent. Two isomeric octyltrichlorogermanes are obtained in reaction of trichlorogermane with \(n\)-amylcyclopropane and 1-methyl-2-butylcyclopropane and three isomeric methyltrichlorogermylecyclohexanes are obtained in the reaction with norcarane\(^7\).

It is known that ketones, which are capable of aldol condensation, react with trichlorogermane in a particular way. First, an aldol condensation occurs and then trichlorogermane adds to the \(\text{C} = \text{C}\) double bond of the product of condensation\(^7\). However, in the case of methyl cyclopropyl ketone, the condensation does not occur and a single isomer derived from the ring opening reaction is formed with 65\% yield (equation 28)\(^7\).

\[
\begin{align*}
\text{C} & \quad \text{Me} & \quad + & \quad \text{HGeCl}_3 & \quad \rightarrow & \quad \text{Cl}_3\text{GeCH}_2\text{CH}_2\text{CH}_2 & \quad \text{C} & \quad \text{Me} \\
\text{O} & & & & & \text{O} & \quad (65\%) \\
\end{align*}
\]

The terminal position of the trichlorogermyle group is explained by a steric factor and an additional O \(\rightarrow\) Ge coordination.

In the reaction with spiroheptadiene, the unexpected compound 28 was isolated (equation 29)\(^7\). Its formation was a result of an anionotropic allylic rearrangement.

\[
\begin{align*}
\text{Et} & \quad \text{GeCl}_3 & \quad \rightarrow & \quad \text{Cl}_3\text{Ge} & \quad \text{Et} \\
\text{Cl}_3\text{Ge} & \quad \text{Et} & \quad \text{Cl}_3\text{Ge} & \quad \text{Et} \quad \text{(28)} \\
\end{align*}
\]

Migration of GeCl\(_3\) groups under the acidic action of trichlorogermane is a quite common phenomenon\(^\text{10}\).
VII. DOUBLE GERMYLATION

A. Discovery and Reactions

An example of double germylation was first discovered in the reaction of trichlorogermane etherate with allyl chloride, as shown in equation 30\(^7\). Product 29 with two GeCl\(_3\) groups was obtained together with the product of condensation.

\[
\begin{align*}
\text{CH}_2=\text{CHCH}_2\text{Cl} + \text{HGeCl}_3 & \rightarrow \text{CH}_2=\text{CHCH}_2\text{GeCl}_3 + \text{Cl}_2\text{GeCH}_2\text{CH(GeCl}_3\text{)}\text{CH}_2\text{Cl} \\
& (16\%) \quad (29) \quad (30) 
\end{align*}
\]

Propylene, 1-butene and cyclohexene can also lead to reactions of double germylation\(^7\). Later, unusual products of double germylation were obtained as the only monomeric products in reactions with ethylene and acetylene\(^8\). Thus, if trichlorogermane itself reacts with ethylene and acetylene by a simple hydrogermylation route, then bubbling of the gases through trichlorogermane etherate leads to formation of double germylation products 30 and 31 (equation 31)\(^8\).

\[
\begin{align*}
2\text{R}_2\text{O} \cdot \text{HGeCl}_3 & \rightarrow \text{Cl}_3\text{GeCH}_2\text{CH}_2\text{GeCl}_3 + (\text{Cl}_2\text{GeCH}_2\text{CH}_2 \cdots)_n \\
& (30) \quad (31)
\end{align*}
\]

Participation of dichlorogermylene was assumed to play the key role in these reactions, as shown in equation 32. Theoretical examination of the GeCl\(_2\) interaction with ethylene showed that formation of a three-membered cycle with a Ge-atom is energetically not profitable, and therefore asymmetric \(\pi\)-complex 32 could be the intermediate instead of germacyclopropane 33\(^6\). Recent computations (DFT, Gaussian 94) confirmed the formation and calculated the geometry of such a complex in detail\(^6\). The primary formation of 34 and 30 in commensurable amounts was confirmed by observing the Ge–H bond in the IR and NMR spectra of the reaction mixture after distillation and by the easy transformation of 34 to 30 under the reaction conditions\(^2,7,9\).

\[
\begin{align*}
\text{CH}_2=\text{CH}_2 + \text{GeCl}_2 & \rightarrow \begin{bmatrix}
\text{CH}_2 \cdots \text{CH}_2 \\
\text{Cl}_2\text{Ge}
\end{bmatrix} \quad \text{or} \quad \begin{bmatrix}
\text{CH}_2 \cdots \text{CH}_2 \\
\text{Ge} \\
\text{Cl} \\
\text{Cl}
\end{bmatrix} \\
& (32) \quad (33) 
\end{align*}
\]

\[
\begin{align*}
\text{Cl}_3\text{GeCH}_2\text{CH}_2\text{GeCl}_3 + \text{Cl}_2\text{HGeCH}_2\text{CH}_2\text{GeCl}_3 & \rightarrow \text{Cl}_3\text{GeCH}_2\text{CH}_2\text{GeCl}_3 \quad \text{Cl}_2\text{HGeCH}_2\text{CH}_2\text{GeCl}_3 \\
& (30) \quad (34)
\end{align*}
\]

It should be noted that tribromogermylane forms the product of double germylation Br\(_3\)GeCH\(_2\)CH\(_2\)GeBr\(_3\) in its reaction with ethylene even in the absence of ether\(^8\).
B. Double Germylation of 9-Me-Anthracene

A surprising example of a double germylation reaction was first found in the aromatic series. Addition of two GeCl₃ groups into 9,10-positions of anthracene and 9-methylantracene (MA) proceeds in the absence of ether, but require bubbling of air through the reaction mixture simultaneously with addition of trichlorogermane. It should be noted that addition of trichlorogermane to MA in inert atmosphere leads to high yield of 9-trichlorogermyl-9-methyl-9,10-dihydroanthracene. Moreover, hidden radical steps of the reaction were revealed by studying CIDNP effects (see Section VIII.F).

In the presence of air at 5 °C, reaction of HGeCl₃ with MA occurs in a different manner to give quantitatively the double germylation product trans-9,10-bis(trichlorogermyl)-9-methyl-9,10-dihydroanthracene (equation 33). A trans-configuration for this product was suggested on the basis of comparison with an authentic sample of the cis-isomer obtained alternatively. This configuration is not sterically hindered and its formation can be ascribed to any mechanism.

![Diagram of the reaction](image)

The hidden radical steps mentioned above in an inert atmosphere may indicate a radical mechanism of the reaction in the presence of air. It was assumed that the cation-radical [MA]⁺⁺ (formed by a direct oxidation of MA or by a secondary conversion of the σ-complex [MAH]⁺ and detected by UV-spectroscopy) can participate in the reaction. Regarding the detailed mechanism, numerous routes of the cation-radical [MA]⁺⁺ with two anions GeCl₃⁻ in the presence of air can give the double germylation product 35. Alternative mechanisms for the direct oxidation which form GeCl₃⁺ radicals of trichlorogermane must also be considered. Furthermore, the radicals can add to MA in the 9 and 10 positions one after another or via a preliminary formation of Ge₂Cl₆. Whereas this mechanism is attractive due to its simplicity, extensive data on hydrogermylation reactions of numerous unsaturated compounds (at conditions not excluding the presence of oxygen) are
The nature of the unsaturated compounds dictate the reaction pathway to a great extent, but it still remains unclear why a radical mechanism predominates in some cases and why a radical hydrogermylation may lead to a radical double germylation.

On raising the temperature from 5 to 80°C, the reaction in the presence of air does not stop with the formation of 35. Quantitative hydrolysis of the latter by water formed in reaction gives rise to the polycyclic compound 37 (equation 34).

\[
\begin{align*}
\text{MeGeCl}_3 + \text{GeCl}_3\text{H} & \xrightarrow{+ \text{H}_2\text{O}, 80^\circ\text{C}} \text{MeGeCl}_3\text{GeCl}_2\text{O} \\
& \downarrow \text{(34)}
\end{align*}
\]

Methylation of 37 by excess of MeMgBr and further work-up of the reaction mixture by dilute HCl lead to the monochloride 38. Repeated methylation of 38 results in the cis-isomer 39 of 36 (equation 35).

\[
\begin{align*}
\text{MeGeCl}_3\text{GeCl}_2\text{O} & \xrightarrow{1. \text{MeMgBr}, 2. \text{dilute HCl}} \text{MeGeMe}_3\text{GeMe}_2\text{Cl} \\
& \downarrow \text{(38)}
\end{align*}
\]

\[
\begin{align*}
\text{MeGeMe}_3\text{GeMe}_2\text{Cl} & \xrightarrow{\text{MeMgBr}} \text{MeGeMe}_3\text{GeMe}_3 \\
& \downarrow \text{(39)}
\end{align*}
\]
The crystal structures of 35–39 were characterized. Compound 38 is a single isomer according to the $^1$H NMR spectrum. This means that only one Ge–O bond in 37 was broken during methylation. Positions 9 and 10 for the Me and GeMe$_2$Cl groups in compound 38, respectively, were determined on the base of the molecular ion fragmentation pathway in the mass spectrum, in particular, the presence of an intensive $[\text{M–Me}_3\text{GeCl}]^+$ ion with $m/z = 307$. Such fragmentation is energetically feasible if both groups in positions 9 and 10 are cleaved synchronously, thus resulting in aromatization of the middle ring.

The methylated isomers 36 and 39 have different melting points and $^1$H NMR spectra. Since compound 39 was obtained from 37, which has a cis-configuration of the two germyl groups about the central cyclohexane ring, the structure of 39 was assumed to be that of a cis-isomer. Consequently, the trans-structure was assigned for compounds 35 and 36.

Antracene reacts with trichlorogermane at 5°C in the presence of air similarly to MA, giving 9,10-bis(trichlorogermyl)-9,10-dihydroanthracene 40 with yield close to 100% (equation 36).

\[
\begin{align*}
\text{Antracene} + 2\text{HGeCl}_3 + \text{O}_2 &\rightarrow 9,10\text{-bis(trichlorogermyl)-9,10-dihydroanthracene} \\
&\quad(40)
\end{align*}
\]

An additional aim of this section is to draw attention to the worthwhile reexamination of many reactions of trichlorogermane at conditions where small amounts of oxygen were added carefully to the reaction mixture. Another interesting point is to reexamine the classical superacid reactions under similar conditions.

Relevant examples are the different actions of the CF$_3$SO$_3$H superacid on dodecamethylruthenocene in inert atmosphere and in the presence of air\(^8\). Another example is the oxidation of methane with oxygen in concentrated sulfuric acid in the presence of Pt catalysts to form methanol derivatives\(^8\).

**VIII. REACTIONS OF HGeCl$_3$ WITH AROMATIC COMPOUNDS**

The uncatalyzed hydrogermylation reaction of aromatic multiple bonds by trichlorogermane was discovered in 1965 by two of the authors of the present review. The reactions between anisole, naphthalene and thiophene and HGeCl$_3$ were investigated in their works\(^32,8\).

The proposed mechanism of the reaction, shown in equation 37, involves the initial formation of $\pi$-complexes and subsequent protonation of the aromatic ring with the formation of $\sigma$-complexes.
The formation of π-complexes has been confirmed by a study of the NMR spectra of HGeCl₃ solutions in aromatic substrates. Upon such complex formation, the germyl hydrogen signal is observed to shift to higher fields, from 7.6 to ca 6.0 ppm, as a consequence of the effect of the magnetic anisotropy of the aromatic nucleus. Attempts to observe directly the intermediate σ-complexes in the reactions turned out to be unsuccessful owing to the low concentrations of these complexes and their short lifetimes. Indirect data on the formation of σ-complexes were obtained from experiments on deuterium exchange between DGeCl₃ and methylbenzenes. Deuterium exchange is the simplest electrophilic substitution reaction and its presence implies the formation of the corresponding σ-complexes (equation 38).

While deuterium exchange between DGeCl₃ and benzene and toluene does not occur at room temperature, trichlorogermane behaves as a strong acid with the more basic methylbenzenes, i.e., m-xylene, mesitylene and isodurene, by promoting rapid deuterium exchange. With mesitylene, for example, the equilibrium is established at 20 °C after 60 minutes.
Successful observation of the stable $\sigma$-complex in the case of trimethoxybenzene (see Section III.C) is another indirect confirmation of the reaction pathway.

Trichlorogermane does not react with phenyl halides and naphthyl halides. This is again indicative of the electrophilic nature of the interaction between trichlorogermane and the aromatic compounds.

The reactions of trichlorogermane with phenoxy- and alkoxybenzenes, methylbenzenes and condensed aromatics\textsuperscript{86,87} have been studied under different conditions and additional data concerning their mechanisms have been obtained.

A. Reaction with Anisole

A detailed study of the reaction between HGeCl$_3$ and anisole has revealed a strong dependence of the nature and ratio of the formed products on the conditions under which the reaction is carried out\textsuperscript{88}. The reaction between an excess of HGeCl$_3$ and anisole (a molar ratio of 3 : 1) at room temperature takes place most selectively (equation 39) and, over a period of 72 hours, leads to 1-methoxy-$\sigma$-1,3-$\tau$-1,3-trans-tris(trichlorogermyl)cyclohexane (42-$\tau$-cis,trans) in a yield of 82%. It has been established by using $^1$H NMR spectra that an intermediate compound is formed during the course of this reaction, and that its concentration attains a maximum value of 22% after 12 to 16 hours and subsequently decreases. This product, which is the double hydrogermylation product of anisole, 3-methoxy-3,5-bis(trichlorogermyl)cyclohexene 41, was isolated and identified in the form of the methylated derivative 43. Similarly, compound 42-$\tau$-cis,trans was converted to methylated derivative 44-$\tau$-cis,trans.

\[
\begin{align*}
\text{MeO} & \quad \text{MeO} & \quad \text{MeO} \\
\text{HGeCl}_3 & \quad \text{HGeCl}_3 & \quad \text{HGeCl}_3 \\
20^\circ \text{C} & \quad 20^\circ \text{C} & \\
\text{MeO GeCl}_3 & \quad \text{MeO GeCl}_3 & \\
(41) & \quad (42-$\tau$-cis,trans) & \\
\text{MeMgBr} & \quad \text{MeMgBr} & \\
\text{MeO GeMe}_3 & \quad \text{MeO GeMe}_3 & \\
(43) & \quad (44-$\tau$-cis,trans) & \\
\end{align*}
\]

This reaction takes place less selectively (equation 40) when anisole and HGeCl$_3$ are boiled together at 110 $^\circ$C. In this case, a cis,cis-isomer of the product of the exhaustive hydrogermylation of anisole is predominantly formed and isolated in the form of...
the methylated derivative 1-methoxy-r,1,3-cis,5-cis-tris(trimethylgermyl)cyclohexane, 45-cis,cis (23% yield). The (45-cis, cis) : (45-cis, trans) ratio in the mixture was 3 : 1.

\[
\text{MeO} \quad \text{MeO} \\
1. \text{HGeCl}_3; 110 ^\circ C \quad 2. \text{MeMgBr}
\]

\[
\begin{align*}
\text{MeO} & \quad \text{MeO} \\
\text{GeMe}_3 & \quad \text{GeMe}_3 \\
\text{MeGe} & \quad \text{MeGe} \\
\text{GeMe}_3 & \quad \text{GeMe}_3 \\
\end{align*}
\]

(40)

1-Methoxy-3,5-bis(trimethylgermyl)cyclohexane 46 (15% yield), 1-(4-methoxyphenyl)-r,1,3-cis-5-cis-5-tris(trimethylgermyl)cyclohexane 47 (20% yield) and also 3,5-bis(trimethylgermyl)cyclohexanone 48 (15% yield, ratio of cis- and trans-isomers 3 : 1) were isolated from the reaction mixture together with 45.

The formation of the hydrogenolysis and alkylation products together with the hydrogermylation products are common in the reaction of HGeCl₃ with aromatic compounds. We will encounter later such pathways of reaction in the reaction with diphenyl ether (see Section VIII. C).

A similar acid catalyzed reaction (equation 41), called hydrodimerization, was found for benzene and alkylbenzenes, which are converted over polyfunctional zeolite catalysts to phenylcyclohexane derivatives \(^{89}\).

\[
\text{H}_2, \text{zeolite catalysis} \quad \text{H}_2 \quad \text{zeolite catalysis}
\]

(41)
B. Reaction with 1,4-Dimethoxybenzene

As would be expected, the presence of a second electron-donating group in 1,4-dimethoxybenzene appreciably increases its rate of reaction with HGeCl₃ in comparison with anisole. With a threefold molar excess of HGeCl₃, the reaction at room temperature is complete after a period of 4 to 5 hours and leads to the formation of 1,4-dimethoxy-1,2,4-tris(trichlorogermyl)cyclohexane 49 in 85% yield (equation 42)²⁸.

\[
\text{MeO} \;
\begin{array}{c}
\text{MeO} \\
\end{array} 
\xrightarrow{\text{HGeCl₃; 20 °C}} 
\begin{array}{c}
\text{MeO} \\
\text{GeCl₃} \\
\text{MeO} \\
\text{GeCl₃} \\
\text{MeO} \\
\text{GeCl₃} \\
\text{MeO}
\end{array}
\]

(42)

The occurrence in 49 of bulky trichlorogermyl groups in a vicinal position and at geminal centers is the reason for its facile hydrogenolysis (protodegermylation) under the action of an excess of trichlorogermane at 80 °C (equation 43). The yield of 50 attained a value of 43%. 50 is converted with MeMgBr to 51.

\[
\text{MeO} \;
\begin{array}{c}
\text{GeCl₃} \\
\text{MeO} \\
\text{GeCl₃} \\
\text{MeO} \\
\text{GeCl₃} \\
\text{MeO}
\end{array} 
\xrightarrow{\text{HGeCl₃; 80 °C}} 
\begin{array}{c}
\text{MeO} \\
\text{GeMe₃} \\
\text{MeO} \\
\text{GeMe₃} \\
\text{MeO} \\
\text{GeMe₃} \\
\text{MeO}
\end{array}
\]

(43)

The treatment of 49 with an excess of MeMgBr in ether and subsequent hydrolysis of the product did not lead to the corresponding tris(trimethylgermyl) derivative but yielded a mixture of 4-methoxy-4-trimethylgermylcyclohexanone 52 (35%), 4-methoxy-1,4-bis(trimethylgermyl)cyclohexene 53 (17%) and 1,4-dimethoxybenzene (21%) (equation 44).

\[
\begin{array}{c}
\text{MeO} \\
\text{GeMe₃}
\end{array} 
\xrightarrow{\text{1. MeMgBr}} 
\begin{array}{c}
\text{MeO} \\
\text{GeMe₃} \\
\text{MeO} \\
\text{GeMe₃} \\
\text{MeO} \\
\text{GeMe₃} \\
\text{MeO}
\end{array} 
\xrightarrow{\text{2. H₂O}} 
\begin{array}{c}
\text{MeO} \\
\text{GeMe₃} \\
\text{MeO} \\
\text{GeMe₃} \\
\text{MeO}
\end{array}
\]

(44)
C. Reaction with Diphenyl Ether

When HGeCl$_3$ is reacted with an excess of diphenyl ether 54 at 100–150 °C, the hydrogermylation of the aromatic multiple bonds is accompanied by another example of unusual alkylation reaction, which is shown in equation 45.\(^{90}\)

\[
\begin{align*}
\text{HGeCl}_3 \quad &\text{Cl}_3\text{Ge} \\
\text{O} \quad &\text{GeCl}_3 \\
\text{O} \quad &\text{GeCl}_3 \\
\text{Me}_3\text{Ge} \\
\text{MeMgBr} \\
\end{align*}
\]

\[
\begin{align*}
\text{1,3,5-tris(trichlorogermyl)-1-(p-phenoxyphe} \\
\text{nyl)cyclohexane 55 was characterized in} \\
\text{the form of its methylated derivative 56 by, among other methods, its X-ray structural} \\
\text{analysis. The structure of 56 indicates that the reaction between HGeCl}_3 \text{ and diphenyl} \\
\text{ether must include three steps in which one of the benzene nuclei of the ether is exhaus-} \\
\text{tively germylated, the ether C—O bond is broken and the excess diphenyl ether is alkylated} \\
\text{in the \textit{para}-position by the carbenium ion formed upon the rupture of the C—O bond.} \\
\text{The first stage of this reaction was confirmed by us by isolating the product of} \\
\text{hydrogermylation 57 when the reaction was carried out under milder conditions at 20 °C} \\
\text{(equation 46).}
\end{align*}
\]
Fission of the C—O ether linkage in 57 with the formation of the ion pair 58 is then possible (equation 47). It is to be noted that the ability of HGeCl₃ to cleave the C—O bond in light ethers is well known.¹⁵

Finally, the carbenium ion moiety of the ion pair 58 alkylates the excess diphenyl ether in the *para*-position with respect to the phenoxy group, giving the final product 55. Hence, the catalytic alkylating function of HGeCl₃ in the Friedel–Craft reactions was established for the first time.

Such examples are rare because GeCl₃⁻ counterion, unlike the counterions of classical superacids, usually recombines with the carbenium ions with the formation of Ge—C bonds. In the present case, the ion pair 58 does not yield a stable recombination product and instead it participates in an intermolecular reaction. This is probably due to the fact that, for steric reasons, the recombination product with two geminal GeCl₃ groups is unstable at an elevated temperature.

Another mechanistic possibility involves a single electron transfer within the ion pair 58 with the formation of the corresponding radical pair 59 (equation 48), since the GeCl₃ substituent in 58 must *a priori* destabilize the carbenium center due to the negative I-effect.

---

¹⁵ The superscript number refers to the page number in the original text where this information is located.
In this case, the final alkylation step will naturally proceed by a radical substitution mechanism. One’s attention is drawn to the high overall yield (>70%) of 56, which implies that the selectivity of each step is not <90%.

The cyclohexane ring in 56 has a chair conformation with the three trimethylgermyl substituents in equatorial positions.

**D. Reaction with Triphenylamine**

The majority of aromatic amines (tribenzylamine, diphenylamine, \(N,N\)-diethylaniline) do not undergo hydrogermylation but form aminates with \(\text{HGeCl}_3\) which are inert to the action of an excess of \(\text{HGeCl}_3\). An exception is triphenylamine which, at room temperature, with \(\text{HGeCl}_3\) forms the unusual iminium salt, 3,5-bis(trichlorogermyl)cyclohexylidenediphenyliminium trichlorogermanate 1 (Section III.C).

A change in the conditions under which the reaction between triphenylamine and \(\text{HGeCl}_3\) is carried out leads to the formation of other products. For instance, when the temperature of the reaction is increased from 20 to 80 °C and there is a 4 to 5-fold molar excess of \(\text{HGeCl}_3\), the \(\text{cis-1}\), which is initially formed, is converted into the formal hydrogenation product 1-diphenylamino-3,5-bis(trichlorogermyl)cyclohexane 60, which is isolated with a yield of 53% in the form of the methylated derivative 61 (equation 49).

\[
\text{Ph}_2\text{N} \quad \text{cis-1} \quad \text{HGeCl}_3 \quad 80 ^\circ \text{C} \quad \text{Ph}_2\text{N} \\
\text{Cl}_3\text{Ge} \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \ Quad
E. Reactions with Benzene and Methylbenzenes

It was pointed out earlier that benzene and methylbenzenes do not add to $\text{HGeCl}_3$ under normal conditions although some of them do participate in deuterium exchange with $\text{DGeCl}_3$. The general hydrogermylation equation (equation 50) vividly reflects a sequence of heterolytic stages of exhaustive addition to the aromatic double bonds.

The stages controlling the reaction course are undoubtedly represented here by stages of $\sigma$-complex and cyclohexadiene derivative formation. We suggested that the protonating ability of $\text{HGeCl}_3$ could be increased by the addition of strong Lewis acids, thus making it sufficiently reactive with those aromatic compounds to which it is usually inert.

This operation is quite usual when modified sulfuric or hydrofluoric acids increase its $H_0$ value by the addition of such Lewis acids as $\text{SO}_3$, $\text{BF}_3$ or $\text{SbF}_5$. Indeed, it was found that in the presence of small amounts of $\text{AlCl}_3$ in a sealed glass tube at 70°C, benzene and toluene react during 3–5 days with $\text{HGeCl}_3$ according to the hydrogermylation scheme. The hydrogermylation is followed by alkylation, giving a complex mixture of isomeric products (equation 51).

\[
\begin{align*}
\text{Cl}_3\text{Ge} & \rightarrow \text{Cl}_3\text{Ge} \quad \text{GeCl}_3 \\
\text{Cl}_3\text{Ge} & \rightarrow \text{Cl}_3\text{Ge} \quad \text{GeCl}_3
\end{align*}
\]

(50)
However, not only the protonating ability of HGeCl₃ or systems derived from it determine the addition to aromatic carbon–carbon bonds, in contrast to the behavior of other HX acids. The specific features of HGeCl₃ are probably manifested at the step of the cyclohexadiene derivative formation. Energy is obviously lost during the conversion from σ-complex to cyclohexadiene. The formation of the cyclohexadiene–GeCl₂ molecular complex (the GeCl₂ present in the reaction mixture is a result of a well-known reaction, cf. Section III) is likely to be responsible for the equilibrium shift in the direction of the cyclohexadiene. It is likely that application of some other compounds which provide such shift by complexation with cyclohexadiene will enhance the addition of other HX acids to aromatic double bonds.

Finally, the application of pressure may speed up some steps and be advantageous. Indeed, it has been found that, under a pressure of 5 to 14 kbar, benzene and methylbenzenes react with HGeCl₃ quite readily\(^\text{92}\).

Mesitylene undergoes hydrogermylation the most readily and selectively. At a HGeCl₃ : mesitylene molar ratio of 2 : 1, the conversion of both compounds after 2 hours at 80°C and a pressure of 10 kbar is close to 100%. The corresponding cyclohexene \(\text{(62)}\) (equation 52) is the main product (yield 93%) of the double hydrogermylation. No products involving the addition of three molecules of HGeCl₃ were formed, even at significant excess of the latter.

![Diagram](attachment:diagram.png)

The two compounds \(\text{62}\) and \(\text{63}\) were isolated and characterized. As in the previously described examples, methylation of the chlorides by MeMgBr proceeded smoothly without any side reactions in which germyl groups are split off.

In the reaction between toluene or \(m\)-xylene and HGeCl₃ at 80°C and 5–10 kbar, depending on their molar ratio, isomeric cyclohexenes were also the main products of the double hydrogermylation (equation 53). These were isolated in the form of their methyl
derivatives 64 (overall yield 50%). Here, products 65 of the exhaustive hydrogermylation are also formed in small amounts (1–6%).

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{R} & \quad \text{R} \\
\end{align*}
\]

1. HGeCl₃, 5–10 kbar
2. MeMgBr

\[
\begin{align*}
\text{Me} & \quad \text{GeMe₃} \\
\text{R} & \quad \text{GeMe₃} \\
\text{Me} & \quad \text{GeMe₃} \\
\text{R} & \quad \text{GeMe₃} \\
\end{align*}
\]

(64) up to 50%

(65) 1–6%

The reaction with benzene proceeds under the most drastic conditions. At a molar ratio HGeCl₃ : benzene = 2.5 : 1, a temperature of 140 °C and a pressure of 14 kbar, the degree of conversion of benzene did not exceed 70% after 6 hours. A complex mixture of products is formed among which, after treatment of the reaction mixture with an excess of MeMgBr in ether, the products 66, 67 and 68 of the double and complete hydrogermylation which are formed in very small yields were identified by using gas chromatography–mass spectrometry combination (equation 54).

\[
\begin{align*}
\text{Cl} & \quad \text{GeMe₃} \\
\text{GeMe₃} & \quad \text{GeMe₃} \\
\end{align*}
\]

(66) (67) (68)

A molecular mechanism is most likely for the addition of HGeCl₃ to methylbenzenes under a high pressure.
F. Reactions with Condensed Aromatics

Hydrogermylation of naphthalene\textsuperscript{79}, phenanthrene\textsuperscript{79}, anthracene and 9-Me-anthracene\textsuperscript{82} to form \textbf{69–71} proceed in the usual way, in accordance with equations \textbf{55–57}. Reactions with anthracene and 9-methylanthracene (MA) in benzene solution at inert atmosphere\textsuperscript{82} lead to a single isomer of 9-trichlorogermyl-9-methyl-9,10-dihydroanthracene \textbf{71} (R = Me) in close to quantitative yield. The structure of \textbf{71} shows that protonation takes place in the 10 position of MA in accordance with the orientation effect of the Me group, as happens in the reactions of MA with classical superacids which give a stable $\sigma$-complex\textsuperscript{93}.

\begin{equation}
\begin{array}{c}
R \\
\end{array} \quad \frac{HGeCl_3}{\text{HGeCl}_3} \quad \begin{array}{c}
R \\
\end{array}
\text{(69) 70–75\%}
\end{equation}

\begin{equation}
\begin{array}{c}
\end{array} \quad \frac{HGeCl_3}{\text{HGeCl}_3} \quad \begin{array}{c}
\end{array}
\text{(70) 90\%}
\end{equation}

\begin{equation}
\begin{array}{c}
\end{array} \quad \frac{HGeCl_3}{\text{HGeCl}_3} \quad \begin{array}{c}
\end{array}
\text{(71) ca 100\%}
\end{equation}

Some evidence of the reaction mechanism was obtained from the UV spectra. Dissolving MA in dry trichlorogermane at low temperature leads to an intensively blue $[\text{MA}]^{+}\cdot$ cation-radical. Generation of the intensively colored cation-radical MA$^{+}\cdot$ was ascribed to a secondary reaction of the weakly colored $\sigma$-complex $[\text{MAH}]^{+}$ with $[\text{MA}]^{94,95}$ (equations \textbf{58} and \textbf{59}).

\begin{equation}
\text{MA} + \text{HGeCl}_3 \leftrightarrow [\text{MAH}]^{+}\text{GeCl}_3^{-}
\end{equation}

\begin{equation}
[\text{MAH}]^{+} + \text{MA} \leftrightarrow [\text{MA}]^{+\cdot} + [\text{MAH}]^{+}\cdot
\end{equation}

The absorption maximum at 640 nm in the UV spectrum of the dark-blue solution of MA in trichlorogermane at $-70$ to $-90^\circ\text{C}$ belongs to the cation-radical $[\text{MA}]^{+\cdot}$ and disappears on raising the temperature when the reaction is over.
A surprising color effect has been observed due to a decrease in the mixture temperature when 1 ml of trichlorogermane reacts with a small yellow crystal of 9-Me-anthracene. When one such sample was allowed to freeze in liquid nitrogen without stirring, another sample was stirred energetically by a glass stick when freezing. The first sample remained colorless in solution after freezing, whereas the second one became black-blue because deeply-colored cation-radicals of 9-Me-anthracene were torn off the crystal.

The well-known literature ESR spectrum of the cation-radical$^9$ was not observed for the blue solutions of MA in trichlorogermane, probably due to the existence of [MA]$^{++}$ and [MAH]$^{++}$ in the poor electrolyte HGeCl$_3$ as a singlet pair. Attempts to observe absorption bands of the CH$_2$ group of the σ-complex by means of a diffused light version of IR spectroscopy had failed$^{22}$. Nevertheless, a CIDNP effect was observed in the reaction of MA with trichlorogermane when it was carried out in a resonance cell of an NMR spectrometer. The intensive positive integral CIDNP effect of the aromatic protons surely testifies in favor of hidden radical stages, some of which were observed experimentally$^9$.

It should be noted that when compound 71 (R = H) is treated with AlCl$_3$+ gaseous HCl, it loses HGeCl$_3$ and forms the arenium σ-complex 72 (equation 60)$^{22}$.

\[
\begin{align*}
\text{H} & \quad \text{GeCl}_3 & \quad \text{AlCl}_3 + \text{HCl} & \quad \text{CH}_2\text{Cl}_2 \\
\text{H} & \quad \text{H} \\
(71), \text{R} = \text{H} & \quad (72)
\end{align*}
\]

IX. CONCLUSIONS

Trichlorogermane, which is a well-known compound in organometallic chemistry, has been characterized as a new superacid in organic chemistry. This reagent has great potential, including its use as a new tool in investigating various aspects of carbenium ions.

The unusual superacidic properties of trichlorogermane are clearly manifested in its reactions with aromatic compounds. Here, the hydrogermylation of the aromatic nucleus is the basic pathway of the reaction between trichlorogermane and aromatic compounds. In many cases the reaction is accompanied by processes of protodegermylation, alkylation, trans–cis isomerization of the trichlorogermyl derivatives of cyclohexane and formation of some organic salts with GeCl$_3$– counterion.

The hydrogermylation of unsaturated compounds by trichlorogermane is an efficient new method for the synthesis of organogermainian derivatives of different classes. Replacement of germyl groups in these compounds with other functional groups is still a challenging task, which may be regarded as potentially important in fine organic synthesis.

Finally, the unusual behavior of trichlorogermane is a reason to seek analogy between classical superacids.

X. REFERENCES

20. Trichlorogermane, a new superacid in organic chemistry

1519


I. INTRODUCTION

When compared to the photochemistry of organosilicon compounds, the photochemistry of the organometallic compounds of the heavier elements is less well developed. However, the importance of studying the photochemistry of these systems stems from significant differences between their photochemical behaviour and that of their more common silicon analogues. For instance, studies on mixed metal systems have demonstrated a considerable difference between the thermal stability of germylene versus silylene intermediates, which can have a dramatic effect on the final product distribution of photochemical reactions. Furthermore, the need to develop new processes for the generation of high-purity metal films of these elements highlights the need for a fuller understanding of their photochemical properties. Consequently, while the available literature on the photochemical
properties of Ge, Sn and Pb compounds is relatively limited, it still represents an important resource worthy of periodic review.

We have organized this review of the photochemistry of organometallic compounds of the heavier group 14 elements by compound class, with the exception of photoinduced electron transfer processes which we treat under a separate heading. This review describes the recent literature which has appeared since the publication in 1995 of an earlier review of this topic.

II. SATURATED OLIGOMERIC SYSTEMS

A. Homometallic Systems

The direct photolysis, by low-pressure Hg arc output, of permethylated linear polygermanes Me(Me₂Ge)ₙMe (n = 3 to 6) has been investigated in cyclohexane solution. The photoproducts were analysed by GC-MS techniques and their mechanisms of formation probed by use of trapping agents such as CCl₄ or dienes. Studies conducted in the presence of CCl₄ produced polygermyl chlorides in high yield, confirming that homolytic cleavage of the germanium–germanium bond is an important photochemical event. Photolyses in the presence of 2,3-dimethyl-1,3-butadiene (DMBD) produced only low yields of the expected germylene trapping product, 1,1,3,4-tetramethyl-1-germacyclopenta-3-ene, indicating that while germylene species are produced, it is only with low efficiency. The ultimate products of the photochemistry are lower-order polygermanes as outlined in Table 1, while Table 2 contains the products and yields obtained in the trapping experiments. These results are consistent with a mechanism involving both homolytic cleavage of the Ge–Ge bond and germylene formation (Scheme 1).

\[
\text{Me(Me₂Ge)}ₙ\text{Me} \xrightarrow{hν} [\text{Me(Me₂Ge)}ₙ\text{Me}]^* \rightarrow (n-3)\text{Me₂Ge}^+ + \text{Me(Me₂Ge)}₃\text{Me} \\
\text{Me(Me₂Ge)}ₙ^* + \text{Me(Me₂Ge)}ₙ₋ₘ \rightarrow \text{polygermanes} \\
\text{Me(Me₂Ge)}ₙ \text{Me (n = 3 to 6; m < n)}
\]

SCHEME 1

B. Heterometallic Systems

The investigation of mixed metal catenates represents an interesting challenge, particularly in view of difficulties with their syntheses. However, the photochemistry of

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
<th>Conversion (%)</th>
<th>Yield (%)</th>
<th>Yield (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Me(Me₂Ge)₃Me</td>
<td>Me(Me₂Ge)⁴Me</td>
<td>Me(Me₂Ge)⁵Me</td>
</tr>
<tr>
<td>Me(Me₂Ge)₃Me</td>
<td>217.5</td>
<td>2.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Me(Me₂Ge)⁴Me</td>
<td>232.5</td>
<td>39.7</td>
<td>66.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Me(Me₂Ge)⁵Me</td>
<td>245.5</td>
<td>75.4</td>
<td>4.0</td>
<td>41.9</td>
<td></td>
</tr>
<tr>
<td>Me(Me₂Ge)⁶Me</td>
<td>222.0</td>
<td>92.3</td>
<td>8.2</td>
<td>10.9</td>
<td>25.3</td>
</tr>
</tbody>
</table>
TABLE 2. Photoproducts and yields (based on starting polygermanes) obtained from the photolysis of permethylated polygermanes \((n = 4\) or \(5\)) in the presence of trapping agents

<table>
<thead>
<tr>
<th>Compound</th>
<th>Trapping agent</th>
<th>(\text{Me(Me}_2\text{Ge)}_3\text{Me})</th>
<th>(\text{Me(Me}_2\text{Ge)}_4\text{Me})</th>
<th>(\text{Me}_2\text{GeCl}_2)</th>
<th>(\text{Me}_5\text{Ge}_2\text{Cl})</th>
<th>(\text{Me}_7\text{Ge}_3\text{Cl})</th>
<th>(\text{Me}_9\text{Ge}_4\text{Cl})</th>
<th>GCP&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Me(Me}_2\text{Ge)}_4\text{Me})</td>
<td>DMBD&lt;sup&gt;b&lt;/sup&gt;</td>
<td>70.0</td>
<td></td>
<td>29.4</td>
<td>37.3</td>
<td>38.7</td>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>(\text{CCl}_4)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>42.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Me(Me}_2\text{Ge)}_5\text{Me})</td>
<td>DMBD&lt;sup&gt;b&lt;/sup&gt;</td>
<td>8.1</td>
<td></td>
<td>26.0</td>
<td></td>
<td></td>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>(\text{CCl}_4)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>3.8</td>
<td></td>
<td>15.0</td>
<td>25.0</td>
<td>54.5</td>
<td>56.8</td>
<td>6.1</td>
</tr>
</tbody>
</table>

<sup>a</sup>1,1,3,4-Tetramethyl-1-germacyclopent-3-ene.

<sup>b</sup>Room-temperature photolysis for 5 hours.

<sup>c</sup>Room-temperature photolysis for 1 hour.
Me$_3$CSiMe$_2$GeMe$_2$SnMe$_3$ was reported$^3$, and can be understood in terms of the three reaction types in Scheme 2. These involve photoelimination of either dimethylgermylene or dimethyl stannylene or cleavage of the Ge–Sn bond to form radicals. All of these products were detected by GC-MS techniques. Interestingly, experiments on this compound, which were conducted in the presence of trapping agents for either stannylene or germylene (Ph$_3$GeH, Et$_3$SiH, Me$_3$GeH, n-Bu$_3$SnH, DMBD or dimethyl disulphide), did not produce the expected trapping products. Furthermore, the product distribution obtained did not vary significantly from that observed in the absence of trapping agents, apart from the apparent quenching of the radical pathway. It would appear that radical generation may interfere with the ability of the trapping agents to react with the germylene and stannylene species. Similar observations have been reported for other R$_2$Ge$^••$ species, which suggests that such intermediates are capable of electron transfer processes producing ion-based chemistry$^4$.

\[
\begin{align*}
\text{Me}_3\text{CSiMe}_2\text{GeMe}_2\text{SnMe}_3 & \xrightarrow{\text{hv}} \text{Me}_3\text{CSiMe}_2\text{SnMe}_3 + \text{Me}_2\text{Ge}^• \\
& \quad \text{Me}_3\text{CSiMe}_2\text{GeMe}_3 + \text{Me}_2\text{Sn}^• \\
& \quad [\text{Me}_3\text{CSiMe}_2\text{GeMe}_2]^• + [\text{Me}_3\text{Sn}]^• \\
& \quad \text{Me}_3\text{CSiMe}_2\text{GeMe}_2\text{H} + (\text{Me}_3\text{Sn})_2
\end{align*}
\]

**SCHEME 2**

**III. ALKYL COMPOUNDS**

Metalloalkyl compounds of the heavier group 14 elements are used as precursor sources in the deposition of thin metallic films for use in the electronics industries$^5,6$. Photoinduced dealkylation is potentially a very useful technique in the deposition of metals from the gas phase, although in general such films contain high concentrations of carbonatious components. Photodealkylation of alkylgermanium compounds using UV photons can be problematic because of the opaque nature of the germanium films produced. This inhibits further film growth. One possible solution to this problem is to use infrared photons with suitable sensitzers, to effect the dealkylation reaction. The germanium film, being transparent in the infrared region, would not act as a self-filter for further film growth. Mixtures of tetramethylgermane and sulphur hexafluoride (as sensitizer) were irradiated with the output of a CO$_2$ laser, the nature of the gaseous products being determined by mass spectrometry$^7$. The principal gaseous products formed were ethane, ethene and ethyne. A gray solid deposit was assumed to be germanium.

Deposition of germanium films from the liquid phase has also been achieved$^8$. In this work a series of organogermanes compounds were used including those containing methyl, vinyl, ethyl, propenyl, allyl and phenyl substituents. Dodecane was used as the solvent. Backscattering analysis of the deposited germanium film following ArF excimer irradiation confirmed that it consisted exclusively of germanium with no evidence of organic contaminants.

**IV. ARYL COMPOUNDS**

Aryldisilanes have been the subject of numerous photochemical investigations over many years$^9$. In general, photolysis of this class of compound produced three distinct
intermediate types, cyclic or acyclic silenes or silyl radicals (Scheme 3). The formation of the silene species is thought to derive from a singlet excited state, while a triplet state has been implicated in the formation of the free radicals. UV-monitored flash photolysis has been used to probe the chemistry of a range of reactive intermediates produced from these precursors. The photochemistry of 1,1,1-trimethyl-2,2,2-triphenyldisilane has proved particularly useful in identifying the cyclic silene, 1-silahexatriene species (1), as an important intermediate species, by permitting the isolation of its ketone adducts.

**Scheme 3**

This study has been extended to include the mixed silane-germane and the digermane systems Ph$_3$SiGeMe$_3$, Ph$_3$GeSiMe$_3$ and Ph$_3$GeGeMe$_3$. Photolysis of these materials produced transient absorptions in the 330–335 nm range and also an absorption centred at approximately 490 nm. The former absorption was assigned to the silyl or germyl radical species on the basis of band positions and the fact that they are quenched by chloroform with a rate constant ($1.7 \times 10^8$ M$^{-1}$ s$^{-1}$) which agrees with published values for the reaction of these radicals with CHCl$_3$. The latter absorption, which previously was assigned to Ph$_2$Ge, is now thought to correspond to the substituted (1-germa)hexatriene (2).

**V. CONJUGATED CATENATES**

Systems which contain $\sigma$(E-E)-$\pi$ conjugated systems (E = Si or Ge) have been the subject of many photochemical investigations. For the most part investigations have focussed on silicon systems, that first identified carbon–silicon double-bonded species as photoproducts. Later studies also indicated that arylsilanes undergo 1,3-sigmatropic shift reactions as well as extrusion processes yielding silylenes. ESR studies have
identified silyl radicals following photolysis of Si—Si bonded species, and the range of photoproducts formed was rationalized in terms of a radical pair mechanism\textsuperscript{21}. Furthermore, the results of flash photolysis experiments also suggest a radical pair mechanism in the photochemistry of arylgermanes\textsuperscript{22}.

The photochemistry of furylated catenates of the group 14 elements has been reported\textsuperscript{23}. Irradiation of 2-(pentamethyldisilanyl)furan and 2-(pentamethyldigermanyl)furan in alkane solution under a variety of conditions yielded the products as outlined in Table 3, which were identified by GC and NMR spectroscopy. These data indicate differences in the behaviour of the germanium system when compared to the silicon. For instance, photolysis of 2-(C\textsubscript{4}H\textsubscript{3}O)Si\textsubscript{2}Me\textsubscript{5} in the presence of \textit{t}-BuOH produced significant quantities of the \textit{t}-butoxide product, while similar photolysis of the analogous germanium compound did not. Also, the yield of chloro-compounds was significantly lower for the germanium system than for the silicon. Failure to observe butoxide products in the photolysis of the germanium compounds has been explained by proposing that the germyl radicals, unlike the silyl analogues, do not undergo the expected disproportionation reaction (Scheme 4)\textsuperscript{24}. However, the presence of 2-(C\textsubscript{4}H\textsubscript{3}O)EMe\textsubscript{3} (E = Si or Ge) in the photosylate does imply the generation of dimethylsilylene and dimethylgermylene in these systems. While photolysis of 2-(C\textsubscript{4}H\textsubscript{3}O)Si\textsubscript{2}Me\textsubscript{5} in the presence of triethylsilane, a known trapping agent for silenes, generates triethylsilyldimethylsilane, photolyses in the presence of trapping agents for germenes (2-methyl-1,3-butadiene or 2,3-dimethyl-1,2-butadiene) failed to yield the expected germacyclopentadiene products (Table 3).

\begin{equation}
\text{SCHEME 4}
\end{equation}

Time-resolved measurements, using 266 nm radiation and monitoring in the 300–700 nm region, revealed two well-resolved features at 310 nm and 370 nm,
### TABLE 3. Photoproducts and yield from the photolysis of the furylated group 14 catenates in cyclohexane$^a$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Trapping agent$^b$</th>
<th>Photolysis conditions</th>
<th>Conversion (%)</th>
<th>Photoproducts (yields %)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-(Pentamethyldisilanylfuran)</td>
<td>None$^d$</td>
<td>189 nm, 2 min</td>
<td>58–85</td>
<td>Me$_3$SiH (22–38)</td>
</tr>
<tr>
<td>CCL$_4$</td>
<td>189 nm, 2 min</td>
<td>41–44</td>
<td></td>
<td>Me$_3$SiH (2–17), Me$_3$SiCl (3)</td>
</tr>
<tr>
<td>t-BuOH</td>
<td>189 nm, 2 min</td>
<td>54</td>
<td></td>
<td>Me$_3$SiH (19), 2-(C$_4$H$_3$O)SiMe$_2$(O'Bu-t) (43)</td>
</tr>
<tr>
<td>EtOH</td>
<td>189 nm, 2 min</td>
<td>53</td>
<td></td>
<td>Me$_3$SiH (23), (Me$_3$Si)$_2$O (5), 2-(C$_4$H$_3$O)SiMe$_3$ (5), 2-(C$_4$H$_3$O)SiMe$_2$(OEt) (37)</td>
</tr>
<tr>
<td>Et$_3$SiH</td>
<td>189 nm, 2 min</td>
<td>56</td>
<td></td>
<td>Me$_3$SiH (35), Et$_3$SiMe$_2$SiH (2), 2-(C$_4$H$_3$O)SiMe$_3$ (1)</td>
</tr>
<tr>
<td>2-(Pentamethyldigermanyl)furan</td>
<td>None</td>
<td>254 nm, 3–5 h</td>
<td>46</td>
<td>Me$_3$GeH (3-5), 2-(C$_4$H$_3$O)GeMe$_3$ (11–20)</td>
</tr>
<tr>
<td>CCL$_4$</td>
<td>254 nm, 40 min</td>
<td>52</td>
<td></td>
<td>Me$_3$GeCl$^f$, ClMe$_2$GeGeMe$_3$ (17)</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>254 nm, 60 min</td>
<td>61</td>
<td></td>
<td>Me$_3$GeCl (14), ClMe$_2$GeGeMe$_3$ (10)</td>
</tr>
<tr>
<td>t-BuOH</td>
<td>254 nm, 3 h</td>
<td>57</td>
<td></td>
<td>Me$_3$GeH (3), 2-(C$_4$H$_3$O)GeMe$_3$ (8)</td>
</tr>
<tr>
<td>MBD</td>
<td>254 nm, 9 h</td>
<td>42</td>
<td></td>
<td>Me$_3$GeH (3–10), 2-(C$_4$H$_3$O)GeMe$_3$ (8–18)</td>
</tr>
<tr>
<td>DMBD</td>
<td>254 nm, 9 h</td>
<td>51</td>
<td></td>
<td>Me$_3$GeH (9), 2-(C$_4$H$_3$O)GeMe$_3$ (11)</td>
</tr>
</tbody>
</table>

$^a$Concentration of 2-(C$_4$H$_3$O)Si$_2$Me$_5$ = 0.03 M and 2-(C$_4$H$_3$O)Ge$_2$Me$_5$ = 0.05 M.

$^b$1 : 20 ratio of compound:trapping agent.

$^c$Yield based on consumption of starting material.

$^d$Solvent = pentadecane.

$^e$Solvent = tridecane.

$^f$Yields were not estimated because of poor resolution in GCL separations.

MBD = 2-methyl-1,3-butadiene, DMBD = 2,3-dimethyl-1,3-butadiene.
TABLE 4. Disappearance ($k_d$) and quenching ($k_q$) rate constants for the silyl and germyl radicals generated upon irradiation of 2-(C$_4$H$_3$O)E$_2$Me$_5$ (E = Si or Ge)

<table>
<thead>
<tr>
<th>Radical</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$k_d \times 10^6$ s$^{-1}$</th>
<th>$k_q \times 10^6$ M$^{-1}$ s$^{-1}$ O$_2$</th>
<th>$k_q \times 10^6$ M$^{-1}$ s$^{-1}$ CCl$_4$</th>
<th>$k_q \times 10^6$ M$^{-1}$ s$^{-1}$ Et$_3$SiH</th>
<th>$k_q \times 10^6$ M$^{-1}$ s$^{-1}$ EtOH</th>
<th>$k_q \times 10^6$ M$^{-1}$ s$^{-1}$ DMBD</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-(C$_4$H$_3$O)SiMe$_2^*$</td>
<td>320</td>
<td>0.44</td>
<td>$3.1 \times 10^3$</td>
<td>$1.6 \times 10^2$</td>
<td>$2.2 \times 10$</td>
<td>$a$</td>
<td>$b$</td>
</tr>
<tr>
<td></td>
<td>370</td>
<td>0.63</td>
<td>$2.5 \times 10^3$</td>
<td>$a$</td>
<td>$1.7 \times 10$</td>
<td>$a$</td>
<td></td>
</tr>
<tr>
<td>2-(C$_4$H$_3$O)GeMe$_2^*$</td>
<td>310</td>
<td>0.36</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>380</td>
<td>1–1.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Not quenched.

$^b$Signal too weak for reliable kinetic analysis.
following photolysis of both 2-(C₄H₃O)Si₂Me₅ and 2-(C₄H₃O)Ge₂Me₅. The 310 nm feature consisted of two components one with a half-life of 2–3 µs, and a second with a half-life of approximately 40 µs. The shorter-lived species were assigned to the furyl-substituted silyl and germyl radicals, based on their spectral characteristics and reactivity towards added quenching agents (see Table 4), which are consistent with rate constants measured for related systems²². These decayed following first-order kinetics, suggesting that the radical species were reacting either with the solvent or alternatively with the parent compound. The nature of the longer-lived species remains somewhat uncertain but is likely to be associated with the long-lived component of the absorption between 370–380 nm. This absorption also has two time-resolved components with half-lives of 1.6 µs for the silicon system and 0.8 µs for the germanium. The long-lived component has a half-life similar to that of the long-lived species absorbing at shorter wavelengths. Interestingly, and as outlined in Table 4, the short-lived species generated from the silicon system was not quenched by either CCl₄ or EtOH. However, the equivalent species obtained from the germanium precursor was quenched by both CCl₄ and DMBD, although the signals were too weak to provide reliable kinetic parameters.

It is clear from these experiments that the primary photochemical process for these group 14 catenates is homolytic cleavage of the E/NUL E bond (Scheme 4). In chlorinated solvents the radicals formed abstract a chlorine atom, yielding the corresponding chlorides. However, the observation of relatively large yields of hydrosilanes was in direct contrast to the absence of hydrogermanes, which points to a significant difference in the reaction mechanisms for the two systems. In particular, the disproportionation reaction to produce silenes and hydrosilanes was favoured while this reaction was not significant for the germanium system. In contrast, the germyl radical pair either abstracts a hydrogen atom from the solvent or couples at the ipso-position, producing the diradical as an important reaction path.

VI. METAL OXANES

A series of trapping experiments coupled with flash photolysis techniques has been used to study the photochemistry of digermoxanes²⁶. In general, the photochemistry of these systems is characterized by the homolytic cleavage of the germanium–oxygen bond producing germyl and germoxyl radicals. The photochemistry of a range of aryl-substituted digermoxanes and cyclic germoxanes has been reported. Photolysis of the digermane compounds in alkane solution using a low-pressure mercury lamp produced polymeric materials of moderately high weight averaged molecular mass (typically 1 x 10² to 9 x 10² a.m.u.). Elemental analysis of the polymers confirmed that they contained germanium atoms. Flash photolysis experiments using an excitation wavelength of 266 nm resulted in a transient species with absorptions in the region 300–400 nm. In the case of (Ph₂MeGe)₂O and (Ph₃Ge)₂O, two features were observed in this region, while (PhMe₂Ge)₂O yielded only one, although it appeared to consist of two unresolved components. For the diphenyl and triphenyl derivatives, the high-energy feature was assigned to the appropriate germyl radicals. They compare well with the germyl radical spectrum obtained by hydrogen abstraction from Ph₃Me₃–nGeH²⁷,²⁸, where the λ_max of the transient absorption spectrum for Ph₃Me₃–nGe was reported at 315, 330 and 332 nm respectively for n = 1, 2 or 3. These transient features decayed with second-order kinetics, which suggests that they were undergoing dimerisation presumably to form digermane species. They were also quenched by the addition of carbon tetrachloride, oxygen and dimethyl-1,3-butadiene as expected for germyl radicals (equation 1). These results are summarized in Table 5. Interestingly, the quenching of these absorptions resulted in a build-up of the longer-wavelength absorptions, indicating that the germyl radicals react...
TABLE 5. Spectroscopic properties and rate constants for the disappearance of transient absorptions following 266 nm photolysis of (Ph_nMe_{3-n}Ge)_2O in cyclohexane

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ_{max}</th>
<th>k/ε</th>
<th>k(M^{-1}s^{-1})_O_2</th>
<th>k(M^{-1}s^{-1})_CCl_4</th>
<th>k(M^{-1}s^{-1})_Diene</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PhMe_2Ge)_2O</td>
<td>320</td>
<td>9.1 × 10^5</td>
<td>2.0 × 10^9</td>
<td>1.1 × 10^8</td>
<td>NQ</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>6.5 × 10^5</td>
<td>2.3 × 10^9</td>
<td>NQ</td>
<td>2.0 × 10^9</td>
</tr>
<tr>
<td>(Ph_2MeGe)_2O</td>
<td>320</td>
<td>8.2 × 10^5</td>
<td>1.2 × 10^9</td>
<td>2.0 × 10^8</td>
<td>NQ</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>1.3 × 10^9</td>
<td>2.2 × 10^9</td>
<td>NQ</td>
<td>1.4 × 10^9</td>
</tr>
<tr>
<td>(Ph_3Ge)_2O</td>
<td>330</td>
<td>7.5 × 10^5</td>
<td>1.1 × 10^9</td>
<td>1.2 × 10^9</td>
<td>NQ</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>2.5 × 10^9</td>
<td>2.6 × 10^9</td>
<td>NQ</td>
<td>2.0 × 10^9</td>
</tr>
</tbody>
</table>

*ε = molar extinction coefficient.
NQ = not quenched.

with oxygen, yielding the species that absorb at longer wavelengths. Consequently, these long-wavelength absorptions can be assigned to germoxy radicals (equation 2), which decayed following second-order kinetics to give digermyl peroxides (equation 3).

\[
\begin{align*}
\text{Ph}_n\text{Me}_{3-n}\text{Ge}^* + \text{CCl}_4 & \rightarrow \text{Ph}_n\text{Me}_{3-n}\text{GeCl} + ^*\text{CCl}_3 \\
\text{Ph}_n\text{Me}_{3-n}\text{Ge}^* + \text{O}_2 & \rightarrow \text{Ph}_n\text{Me}_{3-n}\text{GeO}^* + \text{O}^* \\
2\text{Ph}_n\text{Me}_{3-n}\text{GeO}^* & \rightarrow \text{Ph}_n\text{Me}_{3-n}\text{GeOOGeMe}_{3-n}\text{Ph}_n
\end{align*}
\]

**VII. PHOTOINDUCED ELECTRON TRANSFER**

Compounds that contain heavier group 14 to group 14 or group 14 to carbon bonds can act as excellent electron donors. These bonds are subject to cleavage by various organic electrophiles, and because of their low ionization potentials they undergo efficient electron transfer reactions at rates limited only by the rate of electron transfer from the group 14 compound. Such reactions have received considerable attention for silicon–silicon systems, but those of the heavier elements such as germanium or tin have been less well studied. Photoinduced electron transfer reactions can also lead to interesting chemistry, including chlorinative cleavage of the metal–metal bonds in group 14 catenates. For instance, the germanium–germanium bond in a range of permethyloligogermanes can be oxidatively cleaved in the presence of only catalytic amounts of π-acceptors. The low ionization potentials (IPs) of permethyloligogermanes means that they are susceptible to donor–acceptor interactions, which can ultimately lead to electron transfer processes. Irradiation of octamethyltrigermane in CCl_4–MeCN mixtures (1:430 by volume) using the visible output of a high-pressure Hg arc lamp in the presence of a range of π-acceptor molecules produced Me_3GeCl, Me_5Ge_2Cl and Cl_3CCCl_3 in varying yields. These results are summarised in Table 6. The efficiency of conversion to products is directly proportional to the electron affinity of the acceptor species. Quenching experiments on the fluorescence of the acceptors confirmed that electron transfer was occurring, but at a rate below the diffusion-controlled limit (Table 7).

The proposed mechanism for the chlorinative cleavage involves the initial excitation of the acceptor to its lowest-energy singlet state. Electron transfer to the permethyloligogermane produces initially the radical anion of the acceptor and the radical cation of the...
germane. The oligogermane then undergoes spontaneous scission forming Me(Me₂Ge)₃⁺ and Me(Me₂Ge)ₙ₋ₚ⁺, which abstracts a chlorine atom from the CCl₄ solvent producing Me(Me₂Ge)ₙ₋ₚCl and CCl₃⁺, which ultimately dimerises yielding (CCl₃)₂. The cationic species is reduced by the acceptor radical anion yielding Me(Me₂Ge)ₙ⁺ and finally Me(Me₂Ge)ₙCl by abstraction of a further chlorine atom from the solvent. In contrast to studies on the silicon analogues, there appears to be little selectivity between the terminal and internal metal–metal bonds in the germane compounds, however.

Photoinduced electron transfer processes are also responsible for the carbon–carbon bond formation in fullerene systems. The use of photoexcited C₆₀ as an acceptor expands the range of functionalization chemistry for this material. The addition of silyl acetals to the triplet excited state of C₆₀ occurs efficiently, yielding the fullerene with ester functionality. The asymmetric allylic stannane Me₂CDCHCH₂SnBu₃ has also been shown to add to C₆₀ to yield exclusively C₆₀-1,2-CH₂CH-CDMe₂, in which the allylic group is introduced at the α-position, and no γ-adduct is formed. Such regioselective addition of Me₂CdCHCH₂SnBu₃ has also been reported for the photoreduction of the methylacridinium ion by photoinduced electron transfer from Me₂CDCHCH₂SnBu₃ to the singlet excited state of the methylacridinium ion. The γ-adduct is exclusively formed under thermal conditions, however. A possible explanation for this is that, in the electron transfer reaction, the Sn–C bond is significantly lengthened in the radical cation before the C–C bond formation. This leads to a more favourable α-addition because of the greater steric constraints of the two methyl groups on the γ-position.

The ability of Sn(IV) organometallic compounds to act as both electron donors or acceptors has resulted in their use in photochromic systems. Addition of 2-aminomethylpyridine to a solution of Sn(n-Bu)₄ₓₙX₄₋ₓ (X = CH₃COO, Cl or F) results in the formation of a deeply coloured solution, possibly the result of complex formation or, more likely, the formation of a charge-transfer complex. Irradiation of the solution efficiently bleaches the colour, which then recovers upon heating.
The addition of alkynes to disilenes and digermenes to yield disilacyclobutenes and digermacyclobutenes is thought to proceed by a stepwise mechanism involving either radical or zwitterionic intermediates. The photochemical generation of germasilenes from cyclo-SiGe$_2$Mes$_6$ (Mes = 2,4,6-trimethylphenyl) offers the opportunity to investigate the regioselectivity of this class of reaction$^{39}$. Initial photolysis of cyclo-SiGe$_2$Mes$_6$ results in the extrusion of Mes$_2$Ge••, which can be trapped by added HSiEt$_3$ (equation 4). The germasilene may then undergo cycloaddition with added alkynes. For example, photolysis of Si,Si-di-$t$-butyltetramesitylgermasilene in the presence of phenylacetylene produced a silagermacyclobutene compound and the 1,4-digermine as indicated in Scheme 6. The 1,4-digermine was formed by the reaction of the phenylacetylene with dimesitylgermylene, while reaction with the silagermene produced the silagermacyclobutene. Hydrolysis of the dimetallacyclobutene with aqueous base cleanly produced compound 3, confirming that the addition of phenylacetylene to germasilenes is regioselective and that the phenyl substituent is located $\alpha$ to the germanium atom.

\[
\text{Mes} \quad \begin{array}{c} \text{Mes} \\ \text{Ge} \\ \text{Si} \\ \text{Mes} \\ \text{Mes} \\ \text{Mes} \\ \end{array} \quad \xrightarrow{h\nu} \quad \begin{array}{c} \text{Mes} \\ \text{Si} \\ \text{Ge} \\ \text{Mes} \\ \text{Mes} \\ \text{Mes} \\ \end{array} + \text{Mes}_2\text{Ge} : \quad (4)
\]

\[
\text{t-Bu} \quad \begin{array}{c} \text{t-Bu} \\ \text{Si} \\ \text{Ge} \\ \text{Mes} \\ \text{Mes} \\ \text{Mes} \\ \end{array} \quad \xrightarrow{h\nu \text{PhC} \equiv \text{CH}} \quad \begin{array}{c} \text{t-Bu} \\ \text{Si} \\ \text{Ge} \\ \text{Mes} \\ \text{Mes} \\ \text{Mes} \\ \text{H} \\ \text{Ph} \\ \text{Ph} \\ \text{Ge} \\ \text{Mes} \\ \text{Mes} \\ \text{Mes} \\ \text{Mes} \\ \text{Mes} \\ \text{Mes} \\ \text{Mes} \\ \text{Mes} \\ \text{Mes} \\ \text{Mes} \\ \text{Mes} \\ \text{Mes} \\ \text{Mes} \\ \text{Mes} \\ \text{Mes} \\ \end{array} + \quad (4)
\]

VIII. METAL–METAL MULTIPLE-BONDED SYSTEMS
Addition of methyl-Grignard reagents across the double bond in germasilenes was also investigated\textsuperscript{40}. Unlike the thermal chemistry of these systems, their photochemistry is reasonably straightforward. Again cyclo-SiGe\textsubscript{2}Mes\textsubscript{6} is used as a source of the germasilene and (Me\textsubscript{3}Si)\textsubscript{3}SiH was used to trap Mes\textsubscript{2}Ge. Two products were identified as presented in equation 5, which demonstrates that the methyl group adds regioselectively to the silicon end of the germasilene. The source of the siloxy groups remains uncertain; however, oxidation of the HSi(SiMe\textsubscript{3})\textsubscript{3} is a likely possibility.

\[
\text{CH}_3\text{MgBr}/(\text{Me}_3\text{Si})_3\text{SiH} \xrightarrow{h\nu} \text{Mes} \quad \text{Si} \quad \text{Ge} \quad \text{Mes} \quad \text{Mes} \quad \text{Mes} \quad \text{Mes} \quad \text{H} \quad \text{CH}_3 \quad \text{H} \\
\text{Mes} \quad \text{SiMe}_3 \\
\text{Mes} \quad \text{Ge} \quad \text{Si} \quad \text{OSiMe}_3 \quad \text{H} \quad \text{OSiMe}_3 \\
\text{Mes} \quad \text{Ge} \quad \text{Si} \quad \text{OSiMe}_3 \quad \text{H} \quad \text{OSiMe}_3
\]

**IX. SYSTEMS INVOLVING TRANSITION METAL FRAGMENTS**

The photochemistry of oligosilyl derivatives of the (η\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5})Fe(CO)\textsubscript{2} (Fp) system has been extensively investigated\textsuperscript{41}. The primary photoprocess involves loss of CO, followed by α-elimination to form silyl(silylene) species, Fp(=SiR\textsubscript{2})(SiR\textsubscript{3}) (equation 6, E,E\textsuperscript{'} = group 6 element). Subsequent 1,3-alkyl, aryl and silyl migrations, isomerizations and silylene expulsions yield a complex range of products. The bimetallic disilyl complex FpSiMe\textsubscript{2}Me\textsubscript{2}SiFp when irradiated yielded all isomers of the silylene-bridged diiron complexes, Fp\textsubscript{2}(\mu-SiMe(SiMe\textsubscript{3})(\mu-CO), while prolonged photolysis produced the bis(silylene)-bridged species Fp\textsubscript{2}(\mu-SiMe\textsubscript{2})\textsubscript{2}\textsuperscript{42}. Again these reactions proceed following equilibration of silyl(silylene) intermediates.

\[
\text{hv}/-\text{CO} \xrightarrow{\text{CO}} \text{Fe} \quad \text{Me}_2 \quad \text{E} \quad \text{E}'\text{Me}_3 \\
\text{OC} \quad \text{Fe} \quad \text{Me}_2 \quad \text{E} \quad \text{E}'\text{Me}_3 \\
\text{OC} \quad \text{Fe} \quad \text{E}'\text{Me}_3 \\
\text{OC} \quad \text{Fe} \quad \text{E}'\text{Me}_3
\]
To investigate the effects of different group 14 elements on the stability of the coordinated silylenes, a range of systems was investigated including FpSiMe₂GeMe₂Fp, FpGeMe₂SnMe₃ and FpSnMe₂GeMe₃⁴³. Initial photolysis of FpSiMe₂GeMe₂Fp, with the output of a medium pressure mercury lamp filtered through Pyrex, was followed by both ¹H and ²⁹Si NMR spectroscopy. The three geometric isomers containing both bridging CO and germylene groups (Scheme 7) were observed as principle products with only trace amounts of the silylene–germylene bridged products. No evidence was obtained for the formation of the (µ-CO)(µ-SiMeGeMe₂) species. These results are consistent with those observed for the FpSiMe₂SiMe₂Fp system (see above); however, prolonged irradiation resulted in the quantitative formation of the silylene–germylene isomers. The observed products are explained in terms of the general mechanism outlined in Scheme 8. The exclusive formation of the germyleyne-bridged intermediate strongly suggests that the equilibrium between the germylene and silylene intermediates greatly favours the germylene species (Species A in Scheme 8). This conclusion is further supported by studies on tungsten germyl silyl systems⁴⁴.

Irradiation of FpGeMe₂SnMe₃ produced FpGeMe₃ and FpSnMe₃ formed in a 60 : 40 ratio (see Scheme 9), indicating that the stannylene intermediate is marginally favoured
SCHEME 9
21. The photochemistry of organometallic compounds of germanium, tin and lead over the germynene isomer. Perhaps of more interest was the observation of the isomerization product FpSnMe₂GeMe₃. However, photolysis of FpSnMe₂GeMe₃ failed to produce any FpGeMe₂SnMe₃. The possibility that the isomerization occurred by the insertion of SnMe₂ into FpGeMe₃ was ruled out by experiments conducted in the presence of stannylen traps. Consequently, it is proposed that the isomerization occurs subsequent to 1,3-methyl migration in the (stannyl)germylene iron intermediate (Scheme 9).

The photochemistry of oligosilyl systems containing the \((\eta^5-C_5H_5)Fe(CO)_3(Fp)\) moiety directly bonded to a silicon atom has been extensively investigated\(^{45}\). Following the photochemical expulsion of one CO ligand, the resulting intermediates undergo silyl-shift reactions producing silylene species, which in turn can eliminate silylene (Scheme 10). Silylgermyl or germysilyl analogues were also studied, but in these systems the germynene intermediate was formed preferentially and it was the subsequent chemistry of this intermediate that predominates (Scheme 11)\(^{46}\). The photochemistry of higher-order oligomeric systems has also been investigated. While the

![Scheme 10](image1)

![Scheme 11](image2)
SCHEME 12
tetrasilyliron complexes Fp(SiMe2)3SiMe2Ph undergo clean photochemical rearrangement to FpSi(SiMe3)2(SiMe2Ph), the photochemistry of the oligosilylgermyl systems is more complex. In these systems the photointermediates rearrange to yield products containing Fe–Ge bonds, reinforcing earlier observations that Fe–Ge bonds are more stable than their Fe–Si analogues, and are thus favoured when a dynamic equilibrium between them is possible. The two complexes FpSiMe2SiMe2GeMe2Ph and Fp*SiMe2SiMe2GeMe2Ph [Fp* = (η5-C5Me5)Fe(CO)3] rearranged cleanly to produce the single product FpGe(SiMe3)2(SiMe2Ph) or Fp*Ge(SiMe3)2(SiMe2Ph). The multi-step mechanism for this reaction is outlined in Scheme 12.

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CHAPTER 22

Organometallic polymers of germanium, tin and lead

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I. SCOPE AND LIMITATIONS

The development of new materials is closely associated with the civilization of mankind but only nowadays research focusing on all kinds of potentially new materials is called ‘materials science’. A new compound should be classified as a material when it is used in some sort of technical application or when at least it is potentially useful for a technical process. The number of organometallic polymers and supramolecular organometallic compounds which fulfill these requirements are still relatively rare, although there is a steadily increasing interest in so-called inorganic and organometallic polymers. Several review articles have been written to focus on several aspects of synthesis, structure and properties of inorganic and organometallic polymers. In the family of Group 14 element-containing polymers, silicon has received most attention and materials such as silicones have become important industrial products. The total quantity of silicones produced worldwide was estimated at approximately $1.3 \times 10^6$ tons in 1995. Organometallic polymers in which the heavier Group 14 elements germanium, tin and lead are incorporated in significant amounts have not entered the stage of industrial applications yet, but there is growing interest in such inorganic–organic polymers for which a modification of chemical and physical properties are to be expected and these compounds should give access to potential applications in diverse areas of industrial chemistry. For example, polystannanes might be used in photoresists for microlithography, polymer-supported organotin hydrides might be economically and ecologically useful reducing agents in organic synthesis and selected coordination polymers might be used as molecular sieves or solid catalysts.

The scope of this review includes three areas of germanium-, tin- and lead-containing polymers, namely polymetallanes, polymer-supported organoelement compounds and organometallic coordination polymers. The article is limited to those systems in which at least one Group 14 element–carbon bond is present. Thus, the large number of publications dealing with (i) inorganic germanium, tin and lead compounds embedded into an organic polymer matrix and, in addition, (ii) the use of inorganic and organometallic compounds as Lewis-acidic catalysts for the preparation of organic polymers are not the subject of this article. The literature mainly covers the years 1995 to the mid-2000, but selected work published earlier is included in order to give a comprehensive review.

The objectives of this article are (i) to give an overview on the compounds prepared mainly during the last five years, (ii) to compare synthetic routes, (iii) to discuss the structures and some structure–property relationships and (iv) to highlight important future directions for organometallic polymers containing germanium, tin and lead, respectively.
II. ORGANOMETALLIC POLYMERS CONTAINING TIN AND GERMANIUM IN THE BACKBONE

A. Polymetallanes

Currently, there is growing interest in polymers the frameworks of which are constructed from the Group 14 elements silicon, germanium and tin. Several reviews on polysilanes have appeared in the literature. In the first section of this article we focus on recent developments in the chemistry of polygermanes and polystannanes. The chemistry and structure–property relationship of oligostannanes and low molecular weight polystannanes was the subject of earlier reviews.

Formally, linear polymetallanes of the general formula \( R(MR_2)_nR \) \((R = \text{alkyl, aryl}; M = \text{Ge, Sn})\) can be viewed as structural analogues of polymeric hydrocarbons \( R(CR_2)_nR \). However, the electronic properties of polymetallanes do not resemble those of saturated hydrocarbon polymers, but show similarities to those of unsaturated conjugated polyenes. Theoretical and experimental studies have demonstrated that in oligo- and polymetallanes an intense low-energy absorption maximum occurs, which shifts to higher wavelengths with increasing chain length. This unique feature results from a so-called ‘\( \sigma \)-delocalization’ along the molecular backbone of the polymetallanes and has prompted Adams and Dräger to suggest the term ‘molecular metals’ for organopolystannanes with long chains. In Section II.A.1 below we describe the synthesis and characteristic physico-chemical features of polygermanes, and in Section II.A.2 the syntheses and properties of polystannanes are reported.

1. Polygermanes

a. Introduction. Syntheses, structures, properties and potential applications of polysilanes have been extensively studied, but their heavier analogues have received limited attention. The general characteristic properties of polysilanes and polygermanes are very similar, but the increased atomic size of germanium and the increased Ge–Ge bond length influence the \( \sigma \)-conjugation in the polymer backbone. Theoretical studies on the electronic properties of polygermanes were carried out. It was shown that the band gap \( E_g \) decreases in the order Si > Ge > Sn, which is the result of the lengthening of the corresponding element–element bonds. A synthetic drawback for the use of germanium-containing polymers is the lack of cheap commercial sources for germanium precursors. However, in 1985 Trefonas and West described the preparation of the first soluble high molecular weight germanium homopolymer and of some silicon–germanium copolymers starting from \( n\)-Bu\(_2\)GeCl\(_2\). In this section recent developments in the preparation of high molecular weight polygermanes are reported and the properties of polygermanes are discussed.

b. Syntheses. i. Wurtz-type coupling. In analogy to the most common preparation of polysilanes, the first polygermane (I) was prepared by the reductive coupling of \( n\)-Bu\(_2\)GeCl\(_2\) with sodium metal ( Scheme 1). Poly(dibutyl)germane prepared by this method shows a bimodal broad molecular weight distribution and molecular weights higher than \( 7.7 \times 10^5 \) were obtained. Mochida and Chiba carried out Wurtz-type coupling reactions of a range of dichlorogermanes under various conditions ( Table 1).

The poly(dibutyl)germane, as obtained by heating at reflux in toluene a mixture of dibutylchlorogermaine and sodium metal dispersion as reducing agent, had a narrow molecular weight distribution, but was relatively low in molecular weight (entry 1). The addition of 18-crown-6 ether to the reaction mixture gave even lower yields and decreased molecular weights (entry 3). By adding the sodium metal dispersion to a
SCHEME 1. Wurtz-type coupling reaction of dialkyldichlorogermanes

\[
\begin{array}{c}
R_2\text{GeCl}_2 + \text{Na, toluene} \\
\rightarrow n \text{NaCl} \\
\text{R} = \text{alkyl}
\end{array}
\]

**TABLE 1.** Representative examples for the preparation of poly(dialkyl)germanes by Wurtz-type coupling\(^{31,32}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Precursor</th>
<th>Conditions</th>
<th>(M_w^{a} \times 10^3)</th>
<th>(M_n^{a} \times 10^3)</th>
<th>(M_w/M_n^{b})</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(n)-Bu(_2)GeCl(_2)</td>
<td>Na/toluene, reflux, 2 h</td>
<td>6.8</td>
<td>6.4</td>
<td>1.06</td>
<td>52.5</td>
</tr>
<tr>
<td>2</td>
<td>(n)-Bu(_2)GeCl(_2)</td>
<td>Na/toluene, reflux, 2 h, inverse addition(^c)</td>
<td>4.0</td>
<td>2.7</td>
<td>1.49</td>
<td>20.0</td>
</tr>
<tr>
<td>3</td>
<td>(n)-Bu(_2)GeCl(_2)</td>
<td>Na/18-c-6(^d)/toluene, reflux, 2 h</td>
<td>3.8</td>
<td>1.7</td>
<td>2.26</td>
<td>8.1</td>
</tr>
<tr>
<td>4</td>
<td>(n)-Bu(_2)GeCl(_2)</td>
<td>Na/toluene - HMPA, 50 °C, 2 h</td>
<td>3.6</td>
<td>2.1</td>
<td>1.69</td>
<td>40.9</td>
</tr>
<tr>
<td>5</td>
<td>(n)-Bu(_2)GeCl(_2)</td>
<td>Li/toluene, reflux, 2 h</td>
<td>3.6</td>
<td>2.5</td>
<td>1.47</td>
<td>5.0</td>
</tr>
<tr>
<td>6</td>
<td>(n)-Hex(_2)GeCl(_2)</td>
<td>Na/toluene, reflux, 2 h</td>
<td>15.1</td>
<td>10.4</td>
<td>1.45</td>
<td>20.0</td>
</tr>
<tr>
<td>7</td>
<td>(n)-Hex(_2)GeCl(_2)</td>
<td>Na-K/toluene, reflux, 2 h</td>
<td>11.5</td>
<td>7.8</td>
<td>1.49</td>
<td>8.5</td>
</tr>
<tr>
<td>8</td>
<td>(n)-Hex(_2)GeCl(_2)</td>
<td>Na/toluene, reflux, 2 h</td>
<td>976.7 (41%)</td>
<td>627.7</td>
<td>1.56</td>
<td>9.5</td>
</tr>
<tr>
<td>9</td>
<td>(n)-Hex(_2)GeCl(_2)</td>
<td>Na/toluene, reflux, 2 h, inverse addition</td>
<td>986(^e) (4%)</td>
<td>627.7</td>
<td>1.56</td>
<td>5.0</td>
</tr>
<tr>
<td>10</td>
<td>(n)-Hex(_2)GeCl(_2)</td>
<td>Na/toluene-diglyme (7 : 3), reflux, 2 h, inverse addition</td>
<td>5.01 (65%)</td>
<td>3.80</td>
<td>1.32</td>
<td>15.5</td>
</tr>
<tr>
<td>11</td>
<td>(n)-Hex(_2)GeBr(_2)</td>
<td>Na/toluene, reflux, 2 h</td>
<td>6.64 (85%)</td>
<td>5.35</td>
<td>1.24</td>
<td>23.0</td>
</tr>
<tr>
<td>12</td>
<td>(n)-Hex(_2)GeBr(_2)</td>
<td>Na/toluene, reflux, 2 h, inverse addition</td>
<td>5.70 (74%)</td>
<td>4.98</td>
<td>1.15</td>
<td>11.0</td>
</tr>
</tbody>
</table>

\(^a\)Molecular weight measured by GPC. Weight-average molecular mass is \(M_w = \sum n_i M_i^2 / \sum n_i M_i\). Number-average molecular mass is \(M_n = \sum n_i M_i / \sum n_i\).

\(^b\)Molecular weight distribution of isolated samples.

\(^c\)Inverse addition: The sodium is added to the dialkyldichlorogermane.

\(^d\)18-crown-6 ether.

\(^e\)An accurate molecular weight distribution was not determined.

toluene solution of \(n\)-Bu\(_2\)GeCl\(_2\) (inverse addition), lower yields of lower molecular weight polymers were obtained (entry 2). A similar observation was reported by Miller and Sooriyakumaran\(^{32}\). The addition of small amounts of HMPA as a co-solvent in the Wurtz-type coupling in toluene at 50 °C resulted in higher yields, but slightly decreased molecular weights (entry 4). Changing the reducing agent from sodium to lithium or sodium–potassium alloy gave very low yields. The use of lithium metal often resulted in cyclo-oligomerization rather than linear polymerization and sodium–potassium alloy induced degradation of the polymers. Polygermanes with higher molecular weights can
be produced from dialkylgermanium dichlorides containing long-chain alkyl substituents. Poly(dihexyl)germane was prepared using the classical Wurtz-type reaction conditions and was isolated in 20% yield with a molecular weight of $M_w = 15.1 \times 10^3$ and a molecular weight distribution $M_w/M_n = 1.45$ (entry 6). Miller and Sooriyakumaran reported much higher molecular weights for poly(dihexyl)germane as prepared by the Wurtz-type coupling of $n$-Hex$_2$GeCl$_2$, but the isolated yields were very low (entry 8). The condensation of $n$-Hex$_2$GeBr$_2$ produced polymers with a narrow molecular weight distribution, but they were relatively low in molecular weight and had poor film-forming properties (entry 11). The use of diglyme as a co-solvent did not significantly increase the yields of polymers and resulted in considerably lower molecular weights.

Despite the fact that the use of sodium–potassium alloy in the Wurtz-type coupling results in chain scission of linear polygermanes, it was used for the reduction of trichlorogermanes to prepare branched polygermanes$^{33,34}$. The polygermynes (PhGe)$_n$ and ($n$-BuGe)$_n$ were isolated in 41% and 11% yield, respectively. When conventional Wurtz-type coupling conditions with sodium as reducing agent were applied to prepare (PhGe)$_n$, only poor yields (6.3%) were obtained and the polyphenylgermylene$^{35}$ had a molecular weight of only $M_w = 1.7 \times 10^3$. The reduction of $n$-BuGeCl$_3$ and $n$-HexGeCl$_3$ with sodium gave the corresponding polygermynes in yields of 39% to 50% and with molecular weights of $M_w = 3.8 \times 10^3$ ($M_w/M_n = 1.2$) and $4.3 \times 10^3$ ($M_w/M_n = 1.2$), respectively. Bulky organic groups in monoorganogermanium trichlorides reduce the tendency to give high molecular weight polymers upon reduction of the corresponding RGeCl$_3$ and favour the formation of cyclic and polycyclic oligogermanes. The X-ray crystal structure analyses of some polycyclic oligogermanes$^{36-41}$, such as the octagermacubane$^{236}$ and the hexagermaprismane$^{337}$, were reported. The latter compound was prepared by the reaction of bis(trimethylsilyl)methylgermanium trichloride with lithium in 12% yield, and compound 2 was isolated in 3% yield after reduction of 2,6-diethylphenylgermanium trichloride with Mg/MgBr$_2$.

The properties of poly($n$-butyl)germyne, ($n$-BuGe)$_n$$^{35}$, as prepared in THF at room temperature by employing SmI$_2$ as reducing agent, were reported to be similar to those of ($n$-BuGe)$_n$ prepared by Wurtz-type coupling, although slightly lower yields were obtained. The synthesis of a linear polygermane (Et$_2$Ge)$_n$ from Et$_2$GeCl$_2$ and SmI$_2$ as reducing
agent was also reported. The advantage of SmI₂ over sodium or sodium–potassium alloy is the application of mild reaction conditions. In addition, the use of sodium metal or sodium–potassium alloy is much more hazardous and requires special safety precautions but, on the other hand, its use is significantly cheaper than that of SmI₂.

ii. Ligand substitution polymerization. Another approach to polygermanes is the ‘ligand substitution polymerization’, which is based on the tendency of diorganogermynes to give high molecular weight polymers by Ge–Ge bond formation. The stable inorganic germynes GeX₂ (X = Cl, I) react with Grignard or organolithium reagents to give intermediates of the type R₂Ge, which immediately polymerise to give linear polygermanes (4) or cyclic oligogermanes (Scheme 2). Stabilization of the diorganogermynes can be achieved through the use of bulky substituents and/or intramolecular coordination and thus the polymerization process is inhibited.

\[
\begin{align*}
n \text{GeX}_2 + 2n \text{RLi} & \underset{\text{Et}_2\text{O}}{\xrightarrow{-2n \text{LiX}}} \\
& \begin{array}{c}
\text{R} \\
\text{Ge} \\
\text{R}
\end{array} \\
& n
\end{align*}
\]

(Scheme 2. Polymerization of diorganogermynes)

The reaction of n-BuLi with GeCl₂ in Et₂O at −78 °C gave a bimodal molecular weight distribution (Table 2, entry 3) similar to the polygermanes formed by Wurtz-type coupling reactions. The same reaction when carried out at higher temperatures or with n-BuMgBr under reflux conditions gave only a low molecular weight fraction (Table 2, entries 4–7). The reaction of GeCl₂ with PhLi gave only low molecular weight oligomers and the reaction of Gel₂ with PhMgBr gave mainly (Ph₃Ge)₂ and Ph₄Ge (31).

iii. Electrochemical synthesis. Given the more or less drastic reaction conditions of the Wurtz-type coupling which requires high-standard safety precautions, there is increasing interest in the electrochemical synthesis of polygermanes and polygermane–polysilane copolymers. Electrochemical reactions proceed under mild conditions and usually require only simple setups. The effects of the nature of the electrodes (sacrificial anode and cathode) and of the solvent on the electroreductive coupling of n-Hex₂GeCl₂ to give poly(dihexyl)germane were investigated. The selection of the cathode material was reported to be very important for the outcome of the reactions. It was shown that polygermanes with phenyl groups or short alkyl substituents such as methyl, ethyl or propyl gave relatively low yields, low current efficiencies and low molecular weights. In contrast, poly(dibutyl)-, poly(dipentyl)- and poly(dihexyl)germanes were synthesised in high yields, with high current efficiencies and with molecular weights in the range of \( M_w = 10 \times 10^3 \) to \( 15 \times 10^3 \). Based on experimental observations such as variable-temperature UV spectra, no difference between poly(dihexyl)germane obtained by electrolysis and the same polygermane obtained by Wurtz-type coupling reactions was observed. However, the yields for \((n\text{-Hex}_2\text{Ge})_n\) obtained by electrochemical reduction are twice as high as those obtained by the Wurtz-type method using a sodium dispersion in toluene as reducing agent (Table 2, entries 2 and 9). The electrochemical synthesis of a three-dimensional network polysilane–polygermane copolymer \([(\text{cyclo-HexSi})_x(\text{PhGe})_y] \) \( x/y = 1.04 \) (5) was also reported (Scheme 3, Table 2, entry 10).
22. Organometallic polymers of germanium, tin and lead 1549

\[
\begin{align*}
\text{Ph} & \quad \text{Ge} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Si} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Si} & \quad \text{Cl} \\
\text{Cu electrode} & \quad -6 \text{CuCl} \\
\end{align*}
\]

(5)

For comparison, the copolymerization starting from the same precursors, i.e. PhGeCl₃ and cyclo-HexSiCl₃, was performed under Wurtz-type conditions. The polymodal molecular weight distribution of the product thus obtained is broader as compared with the polymer prepared electrochemically. The optical spectra of a similar copolymer \([(n-\text{HexSi})_x(n-\text{HexGe})_y]_n\) were also reported. Linear polysilane–polygermane and polygermane–polygermane copolymers of the types \([(n-\text{Hex}_2\text{Ge})_x(n-\text{Hex}_2\text{Si})_y]_n\), \([(n-\text{Bu}_2\text{Ge})_x(n-\text{Hex}_2\text{Ge})_y]_n\) and \([(\text{MePh}_2\text{Ge})_x(n-\text{Pen}_2\text{Ge})_y]_n\) were prepared electrochemically from the corresponding diorganodichlorogermandanes and diorganodichlorosilanes. In case of the germane–germane copolymers, the monomer-to-monomer ratio in the resulting copolymer is strongly influenced by the monomer-to-monomer ratio in the solution at the beginning of the reaction. In contrast, the silane-to-germane ratio in \([(n-\text{Hex}_2\text{Ge})_x(n-\text{Hex}_2\text{Si})_y]_n\) was almost constant at 1/3 germane to 2/3 silane, regardless of the diorganodichlorogermandane-to-diorganodichlorosilane ratio in the electrolyte solution.

Molecular weights of the copolymers were obtained in the range of 1.0 \times 10^3 to 4.5 \times 10^3 and were shown to be lower than in the corresponding homopolymers. It was concluded that random copolymerization took place in each case. In order to obtain a block-like copolymer, \((n-\text{Bu}_2\text{Ge})_n\) was added to an electrolyte solution of diphenylgermanium dibromide. A copolymer \([(n-\text{Bu}_2\text{Ge})_{76}(\text{Ph}_2\text{Ge})_{24}]_n\) with a molecular weight of \(M_w = 1.4 \times 10^3, (M_w/M_n = 2.7)\) was obtained. Furthermore, this experiment shows that reductive cleavage of germanium–germanium bonds in the polymer chains is induced electrochemically.

The preparation of the structure-controlled silane–germane copolymer \((\text{Me}_2\text{SiPh}_2\text{GeMe}_2\text{Si})_n\) at low temperature using ultrasound was achieved (Scheme 4)⁵₈.

\[
\begin{align*}
\text{Me} & \quad \text{Ph} & \quad \text{Me} & \quad \text{Me} & \quad \text{Ph} & \quad \text{Me} & \quad \text{Me} \\
\text{Cl} & \quad \text{Si} & \quad \text{Ge} & \quad \text{Si} & \quad \text{Cl} & \quad \text{THF, LiClO}_4 & \quad \text{ultrasound, } -10^\circ \text{C} \\
\text{Mg electrode} & \quad \text{Me} & \quad \text{Ph} & \quad \text{Me} \\
\end{align*}
\]

(6)

\[
\begin{align*}
\text{Me} & \quad \text{Ph} & \quad \text{Me} & \quad \text{Me} & \quad \text{Ph} & \quad \text{Me} & \quad \text{Me} \\
\text{Cl} & \quad \text{Si} & \quad \text{Ge} & \quad \text{Si} & \quad \text{Cl} & \quad \text{THF, LiClO}_4 & \quad \text{ultrasound, } -10^\circ \text{C} \\
\text{Mg electrode} & \quad \text{Me} & \quad \text{Ph} & \quad \text{Me} \\
\end{align*}
\]

(7)

SCHEME 4. Electrochemical synthesis of a silane–germane copolymer with a \(-\text{Si}–\text{Ge}–\text{Si}–\) sequence

The copolymer \((\text{Me}_2\text{SiPh}_2\text{GeMe}_2\text{Si})_n\) (7) had a molecular weight of \(M_w = 1.1 \times 10^3, (M_w/M_n = 1.31)\) and was isolated in 25% yield. The authors claim that the polymerizability of \(\alpha,\omega\)-dichlorooligosilanes under electrochemical conditions is mainly affected by the substituents at the chlorinated terminal silicon atoms, which provides interesting options for the design of copolymers with ordered sequences of silicon and germanium atoms.

iv. Catalytic routes. In contrast to the synthesis of polysilanes⁵¹,⁶²,⁶³, the number of catalytic routes to polygermanes is limited⁶⁴–⁶⁶. The catalytic dehydrogenative coupling
of Ph$_2$GeH$_2$ with dimethyltitanocene as catalyst predominantly gave the linear tetramer Ph$_2$HGe(Ph$_2$Ge)$_2$GeHPh$_2$ instead of (Ph$_2$Ge)$_n$. Phenylgermane PhGeH$_3$ was reported to give a polymer under similar reaction conditions, but its structure was not sufficiently determined. The dehydrogenative coupling of phenylgermane by zirconocene-based catalysts gave high molecular weight polyphenylgermanes with a partially three-dimensional network structure (Scheme 5).

\[
\text{Cp}_2\text{ZrCl}_2 \text{ or Cp}^*\text{CpZrCl}_2 \quad 2n-\text{BuLi, 25 °C, toluene} \quad \rightarrow \quad [(\text{PhGeH})(\text{PhGe})_m]_n
\]

**SCHEME 5.** A catalytic route to polygermanes

The polymerization after one day of PhGeH$_3$ using Cp$_2$ZrCl$_2$ gave a polymer, which displayed a trimodal molecular weight distribution with $M_w (M_w/M_n) = 7.3 \times 10^4$ (3.7), $3.1 \times 10^3$ (1.3) and $6.3 \times 10^2$ (1.0) in a 62/32/6 ratio (Table 2, entry 11). The pentamethylcyclopentadienyl-substituted catalyst Cp$^*$CpZrCl$_2$ appeared to be less active in promoting chain growth than Cp$_2$ZrCl$_2$.

A very efficient catalytic process for the high-yield preparation of permethylated polygermanes starting from trimethylgermane was reported by Berry and coworkers (Scheme 6, Table 2, entries 12 and 13). In the catalytic cycle, element–element bonds are produced and methane is eliminated. The proposed mechanism for the formation of linear and branched polygermanes is shown in Schemes 7 and 8.

Since the catalyst Ru(PMe$_3$)$_4$(GeMe$_3$)$_2$ is synthesised from HGeMe$_3$ and Ru(PMe$_3$)$_4$Me$_2$, the latter can be used as a precatalyst. The polygermane is isolated as a colourless gum in 80–90% yield. The molecular weight of the product is almost independent of both the amount and the type of the catalyst used. However, it was demonstrated that the measured molecular weights differ significantly when different methods for their determination were employed. The common method of refractive index detection and calibration against polystyrene standards gave molecular weights in the range of $M_w = 2 \times 10^4$ to $M_w = 8 \times 10^4$. The values obtained by the SEC/viscometry method were up to three times higher.

**c. Properties. i. Chemical properties.** Polygermanes exhibit unique electronic and optical properties arising from $\sigma$-electron delocalization through the germanium–germanium bonds, including a red shift of $\lambda_{\text{max}}$ with increasing chain length, narrow emission bands and semiconducting behaviour. Potential applications of such polymers as photoconductors, photoresists, and non-linear optical materials were suggested. The polygermanes are usually obtained as colourless solids, which are soluble in solvents such as chloroform, hexane, toluene and THF. They are thermally stable, fairly resistant towards oxidation and hydrolysis. Poly(dihexyl)germane was found to be stable in toluene at 100 °C. Thermogravimetric analyses of poly(alkyl, phenyl)germanes and polygermynes revealed that weight loss starts at temperatures around 230 to 285 °C, and their residue weights decreased around 50% upon heating to 500 °C. Poly(dialkyl)germanes were reported to be stable up to temperatures higher than 300 °C. Polygermanes should be handled under exclusion of light. The germanium–germanium backbone in polygermanes is an intense ultraviolet (UV) chromophore and photodegradation of Ge–Ge bonds takes place. Therefore, the polygermanes are attractive materials for applications as UV photoresists. The photodegradation process in
TABLE 2. Representative examples for the preparation of polygermanes using different methods

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>Method</th>
<th>$M_w^{a}$ ×10^3</th>
<th>$M_n^{a}$ ×10^3</th>
<th>$M_w/M_n$</th>
<th>Yield (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{(n-Bu}_2\text{Ge)}_n$</td>
<td>Na/toluene, reflux, 2 h</td>
<td>6.8</td>
<td>6.4</td>
<td>1.06</td>
<td>53</td>
<td>31</td>
</tr>
<tr>
<td>2</td>
<td>$\text{(n-Hex}_2\text{Ge)}_n$</td>
<td>Na/toluene, reflux, 2 h</td>
<td>15.1</td>
<td>10.4</td>
<td>1.45</td>
<td>20</td>
<td>31</td>
</tr>
<tr>
<td>3</td>
<td>$\text{(n-Bu}_2\text{Ge)}_n$</td>
<td>$\text{GeCl}_2/n$-$\text{BuLi/Et}_2\text{O}$, $-78^\circ\text{C}$, 1 h</td>
<td>17.9 (39%)</td>
<td>6.22 (61%)</td>
<td>2.88</td>
<td>98</td>
<td>43</td>
</tr>
<tr>
<td>4</td>
<td>$\text{(n-Bu}_2\text{Ge)}_n$</td>
<td>$\text{GeCl}_2/n$-$\text{BuLi/Et}_2\text{O}$, 0°C, 2 h</td>
<td>1.3</td>
<td>1.19</td>
<td>1.09</td>
<td>95</td>
<td>43</td>
</tr>
<tr>
<td>5</td>
<td>$\text{(n-Bu}_2\text{Ge)}_n$</td>
<td>$\text{GeI}_2/n$-$\text{BuLi/Et}_2\text{O}$, reflux, 3 h</td>
<td>2.2</td>
<td>1.7</td>
<td>1.28</td>
<td>52</td>
<td>31</td>
</tr>
<tr>
<td>6</td>
<td>$\text{(n-Bu}_2\text{Ge)}_n$</td>
<td>$\text{GeI}_2/n$-$\text{BuMgBr/Et}_2\text{O}$, reflux, 3 h</td>
<td>2.2</td>
<td>1.8</td>
<td>1.22</td>
<td>55</td>
<td>31</td>
</tr>
<tr>
<td>7</td>
<td>$\text{(Me}_2\text{Ge)}_n$</td>
<td>$\text{GeI}_2/\text{MeMgBr/Et}_2\text{O}$, reflux, 3 h</td>
<td>2.1</td>
<td>1.2</td>
<td>1.75</td>
<td>30</td>
<td>31</td>
</tr>
<tr>
<td>8</td>
<td>$\text{(n-Bu}_2\text{Ge)}_n$</td>
<td>electroreduction</td>
<td>14</td>
<td>2.0</td>
<td>7.1</td>
<td>31</td>
<td>55</td>
</tr>
<tr>
<td>9</td>
<td>$\text{(n-Hex}_2\text{Ge)}_n$</td>
<td>electroreduction</td>
<td>10</td>
<td>6.1</td>
<td>1.7</td>
<td>41</td>
<td>55</td>
</tr>
<tr>
<td>10</td>
<td>$\text{(c-HexSi)}_1.04(\text{PhGe)}_1.0$</td>
<td>electroreduction</td>
<td>6.2</td>
<td>3.1</td>
<td>2.0</td>
<td>23</td>
<td>56</td>
</tr>
<tr>
<td>11</td>
<td>$[(\text{GeHPh})/(\text{GePh})_n]$</td>
<td>$\text{PhGeH}_3/$catalyst</td>
<td>73 (62%)</td>
<td>19.7</td>
<td>3.7</td>
<td>b</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{C}_2\text{ZrCl}_2/n$-$\text{BuLi(1 : 2)}$/</td>
<td>toluene, 25°C, 24 h</td>
<td>3.1 (32%)</td>
<td>2.4</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.63 (6%)</td>
<td>0.6</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>$\text{H(Me}_2\text{Ge)}_n\text{Me}$</td>
<td>$\text{HGeMe}_3/$catalyst</td>
<td>66</td>
<td>18</td>
<td>3.7</td>
<td>97</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{Ru(PMe}_3)_4(\text{GeMe}_3)_2$</td>
<td>66</td>
<td>18</td>
<td>3.7</td>
<td>97</td>
<td>65</td>
</tr>
<tr>
<td>13</td>
<td>$\text{H(Me}_2\text{Ge)}_n\text{Me}$</td>
<td>$\text{HGeMe}_3/$catalyst</td>
<td>74</td>
<td>37</td>
<td>2.0</td>
<td>92</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{Me}_3\text{Ru(PMe}_3)_4$</td>
<td>74</td>
<td>37</td>
<td>2.0</td>
<td>92</td>
<td>65</td>
</tr>
</tbody>
</table>

$^a$Molecular weight measured by GPC (polystyrene standard). $M_w$ is weight-average molecular mass and $M_n$ is number-average molecular mass.

$^b$Not given.

SCHEME 6. Ruthenium-catalyzed demethanative coupling of trimethylgermane
SCHEME 7. Proposed mechanism for the demethanative coupling of HGeMe3 to give polygermanes.65

polygermanes was the topic of several recent reports. The analysis of photoproducts and laser flash photolysis of oligogermanes and high molecular weight polygermanes showed that in degassed cyclohexane solution both diorganogermylene extrusion and homolytic cleavage of the germanium–germanium bonds are competitive processes. The polygermyl radicals abstract a chlorine from polyhalomethanes to give the corresponding germanium chlorides and polyhalomethyl radicals. These radicals dimerise to give the corresponding polyhaloethanes. Furthermore, the polygermyl radicals add to 2,3-dimethyl-1,3-butadiene to give polyhalomethylchlorogermanes and add to 2,3-dimethyl-1,3-butadiene to give the corresponding germacyclopentene.

Poly(di-n-butyl)germane was decomposed to give low molecular weight oligomers after storage in THF for 2 h under exposure to daylight. Polygermane films, which have been deposited on quartz plates, are quite UV-light sensitive. Irradiation of the films with an 110-W low-pressure arc lamp (λ = 254 nm) for 1 min in air resulted in a tremendous decrease of the absorbance as a result of Ge–Ge bond cleavage. In the case of (MePhGe)$_n$ the molecular weight dropped from $M_w = 5.4 \times 10^3$ ($M_w/M_n = 1.4$) to $M_w = 2.9 \times 10^3$ ($M_w/M_n > 3.0$). The photodegradation process was also examined by X-ray photoelectron spectroscopy (XPS) and showed that the Ge–Ge bonds in films of polygermanes are almost quantitatively transformed into −Ge−O− sequences after 10 min of UV irradiation in air. Furthermore, laser flash photolysis was indicative for the formation of polygermyl radicals by homolytic Ge–Ge bond cleavage. In contrast to the results obtained for polygermanes in solution, no transient peaks assigned to diorganogermylenes in the absorption spectra were observed after laser flash photolysis. In conclusion, the key intermediates in the photodegradation of the polygermane films in air are polygermyl radicals generated by Ge–Ge bond cleavage. Polymers with −Ge−O−Ge−O− sequences in the backbone result from the oxygenation of polygermyl radicals.

### ii. Electronic properties

High molecular weight polygermanes show characteristic electronic absorption bands in the range of 300 to 360 nm (Table 3). The position of the absorption maxima depends on the nature of the substituents at germanium, the polymer phase, the molecular weight and the temperature. Furthermore, in polygermane–polysilane copolymers the Si-to-Ge ratio and the connectivity of germanium and silicon atoms in the polymer backbone also influence the electronic properties. Generally, the $\lambda_{max}$ values are shifted to higher wavelengths as the chain length of the alkyl groups increases. This trend may be explained by the difference in the chain conformation of linear polygermanes with larger alkyl substituents favouring a greater proportion of anti conformations over gauche conformations (Scheme 9).

Similarly, the replacement in polygermanes of alkyl substituents by phenyl groups results in significant red shifts of the absorption maxima (Table 3, entries 13–15). In contrast to several well-characterised poly(monoalkyl, monoaryl)germanes and poly(dialkyl)germane–poly(dialkyl)germane copolymers, reports on pure poly(diaryl)germanes were rare. The synthesis of poly(diphenyl)germane was reported, but as a result of its poor solubility in common organic solvents its characterization was insufficient.

Branched oligogermynes (RGe)$_n$ are yellow-coloured and exhibit an intense broad absorption from 200 nm tailing down into the visible region. The high extinction coefficients are attributed to an extension of the $\sigma$-conjugation effects in the branched germanium network.

In solution, the UV absorption characteristics of polygermanes may be different from those in the solid state. Poly(dihexyl)germane in solution has a $\lambda_{max}$ value of 327 nm, whereas the same polymer fraction deposited as a thin film on a quartz plate exhibits two
distinct $\lambda_{\text{max}}$ values at 317 and 339 nm$^{70}$ (entry 9). The $\lambda_{\text{max}}$ values of permethylated oligogermandes shift to higher wavelengths with increasing germanium chain length$^{25}$. It was suggested that the absorption maxima of polygermanes reach constant values as the number of germanium atoms becomes larger than approximately 20–30$^{31}$. In Table 3 some illustrative results for poly(dibutyl)germane are given (entries 3–6), which confirm this hypothesis. For \((n\text{-Bu}_2\text{Ge})_n\) the $\lambda_{\text{max}}$ value should be constant for molecular weights higher than approximately $5.8 \times 10^3$.

In solution, poly(dialkyl)germanes such as \((n\text{-Hex}_2\text{Ge})_n\), \((n\text{-Pen}_2\text{Ge})_n\) and \((n\text{-Bu}_2\text{Ge})_n\) show a distinct thermochromic behaviour$^{31,55}$. The $\lambda_{\text{max}}$ value of \((n\text{-Hex}_2\text{Ge})_n\) in pentane gradually shifts from $\lambda_{\text{max}} = 340$ nm at room temperature to $\lambda_{\text{max}} = 350$ nm at $-60$ °C.

![Scheme 9](image_url)

**Scheme 9.** Chain conformations in linear polygermane segments; *anti* and *gauche* conformation$^{77}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$M_w^a \times 10^3$</th>
<th>$M_w/M_n^b$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>((\text{Et}_2\text{Ge})_n)</td>
<td>293</td>
<td>0.86</td>
<td>4.0</td>
<td>55</td>
</tr>
<tr>
<td>2</td>
<td>((\text{Et}_2\text{Ge})_n)</td>
<td>305</td>
<td>3.4</td>
<td>1.21</td>
<td>31</td>
</tr>
<tr>
<td>3</td>
<td>((n\text{-Bu}_2\text{Ge})_n)</td>
<td>218</td>
<td>1.3</td>
<td>1.09</td>
<td>43</td>
</tr>
<tr>
<td>4</td>
<td>((n\text{-Bu}_2\text{Ge})_n)</td>
<td>290</td>
<td>2.2</td>
<td>1.22</td>
<td>31</td>
</tr>
<tr>
<td>5</td>
<td>((n\text{-Bu}_2\text{Ge})_n)</td>
<td>325</td>
<td>6.8</td>
<td>1.06</td>
<td>31</td>
</tr>
<tr>
<td>6</td>
<td>((n\text{-Bu}_2\text{Ge})_n)</td>
<td>325</td>
<td>14</td>
<td>7.1</td>
<td>55</td>
</tr>
<tr>
<td>7</td>
<td>((n\text{-Hex}_2\text{Ge})_n)</td>
<td>328</td>
<td>15.1</td>
<td>1.45</td>
<td>31</td>
</tr>
<tr>
<td>8</td>
<td>((n\text{-Hex}_2\text{Ge})_n)</td>
<td>340</td>
<td>&gt;300</td>
<td>\text{d}</td>
<td>32</td>
</tr>
<tr>
<td>9</td>
<td>((n\text{-Hex}_2\text{Ge})_n)</td>
<td>327; 339/317\text{c}</td>
<td>9.1</td>
<td>1.7</td>
<td>70</td>
</tr>
<tr>
<td>10</td>
<td>((n\text{-Hex}_2\text{Ge})_n)</td>
<td>345/325\text{c}</td>
<td>15.9</td>
<td>1.2</td>
<td>71</td>
</tr>
<tr>
<td>11</td>
<td>((n\text{-Oct}_2\text{Ge})_n)</td>
<td>342</td>
<td>&gt;300</td>
<td>\text{d}</td>
<td>32</td>
</tr>
<tr>
<td>12</td>
<td>((n\text{-HexMeGe})_n)</td>
<td>307</td>
<td>14.7</td>
<td>1.9</td>
<td>70</td>
</tr>
<tr>
<td>13</td>
<td>((\text{MePhGe})_n)</td>
<td>329</td>
<td>5.4</td>
<td>1.4</td>
<td>70</td>
</tr>
<tr>
<td>14</td>
<td>((n\text{-BuPhGe})_n)</td>
<td>337</td>
<td>3.9</td>
<td>2.5</td>
<td>55</td>
</tr>
<tr>
<td>15</td>
<td>((n\text{-HexPhGe})_n)</td>
<td>355</td>
<td>12.5</td>
<td>1.37</td>
<td>31</td>
</tr>
</tbody>
</table>

\text{a}Molecular weight measured by GPC. $M_w$ is weight-average molecular mass.

\text{b}Molecular weight distribution of isolated samples. $M_n$ is number-average molecular mass.

\text{c}Polymer film.

\text{d}Not given.
The change in the absorption maximum is reversible. In contrast, (MePhGe)$_n$, (Et$_2$Ge)$_n$ and (n-HexPhGe)$_n$ do not show significant thermochromic properties with the $\Delta \lambda_{\text{max}}$ values being in the range of zero to five nanometer. The thermochromic effect in solution is suggested to be the result of conformational changes of the germanium chains with the proportion of anti conformation (Scheme 9) increasing as the temperature is decreased. A similar thermochromic behaviour was observed for polygermanes in the solid state. For example, a thin film of the polymer (n-Hex$_2$Ge)$_n$ showed a single broad absorption at 337 nm, which significantly decreased in intensity and which was finally replaced by a sharper absorption at 370 nm upon rapid cooling to $-12^\circ$C. Differential scanning calorimetry (DSC) measurements showed a strong endothermic effect at 12.4 °C and a strong exothermic effect at $-1^\circ$C attributed to a crystallisation process, which is in agreement with the reversible thermochromic effect. Poly(diocytgermane) shows a similar thermochromic behaviour, whereas for poly(dipentyl)germane the effect is less distinctive. The thermochromic effect in the solid state is suggested to be a result of side-chain crystallisation, which locks the polymer backbone in a regular anti conformation (Scheme 9). Polygermanes with long alkyl chains show the most distinct thermochromic effect.

Typically, polygermane–polysilane copolymers have similar UV properties as compared with polygermane and polysilane homopolymers. The thermochromic behaviour of the copolymers depends on their monomer-to-monomer ratios in the polymer chain and on the identity of the alkyl substituents. In principle, the fine tuning of the absorption maximum can be achieved by a controlled copolymerization. Unfortunately, the copolymers reported so far often have relatively low molecular weights, which in turn results in the $\lambda_{\text{max}}$ values being even lower than those observed for high molecular weight polysilanes (Table 4).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>$n : m$</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$M_w^a$ $\times 10^3$</th>
<th>$M_w / M_n^b$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(n-Hex$_2$Ge)$_n$</td>
<td>100:0</td>
<td>325</td>
<td>10</td>
<td>1.7</td>
<td>57</td>
</tr>
<tr>
<td>2</td>
<td>(n-Hex$_2$Ge)$_n$(n-Hex$_2$Si)$_m$</td>
<td>30:70</td>
<td>304</td>
<td>1.7</td>
<td>1.9</td>
<td>57</td>
</tr>
<tr>
<td>3</td>
<td>(n-Hex$_2$Ge)$_n$(n-Hex$_2$Si)$_m$</td>
<td>36:64</td>
<td>305</td>
<td>1.1</td>
<td>1.7</td>
<td>57</td>
</tr>
<tr>
<td>4</td>
<td>(n-Hex$_2$Ge)$_n$(n-Hex$_2$Si)$_m$</td>
<td>32:68</td>
<td>313</td>
<td>2.0</td>
<td>1.8</td>
<td>57</td>
</tr>
<tr>
<td>5</td>
<td>(n-Hex$_2$Ge)$_n$(n-Hex$_2$Si)$_m$</td>
<td>c</td>
<td>316</td>
<td>112.8</td>
<td>1.24</td>
<td>31</td>
</tr>
<tr>
<td>6</td>
<td>(n-Hex$_2$Ge)$_n$(n-Hex$_2$Si)$_m$</td>
<td>38:62</td>
<td>322</td>
<td>c</td>
<td>(7.1)$^d$</td>
<td>32</td>
</tr>
<tr>
<td>7</td>
<td>(n-Hex$_2$Ge)$_n$(n-Hex$_2$Si)$_m$</td>
<td>65:35</td>
<td>326</td>
<td>c</td>
<td>c</td>
<td>32</td>
</tr>
<tr>
<td>8</td>
<td>(n-Hex$_2$Si)$_n$</td>
<td>0:100</td>
<td>314</td>
<td>19</td>
<td>4.6</td>
<td>57</td>
</tr>
</tbody>
</table>

$^a$Molecular weight measured by GPC. $M_w$ is weight-average molecular mass.
$^b$Molecular weight distribution of isolated samples. $M_n$ is number-average molecular mass.
$^c$Not determined.
$^d$High and low (in parentheses) polymer fraction.

2. Polystannanes

a. Introduction. Polystannanes have more diffuse bonding orbitals than polysilanes and polygermanes; this is associated with a more distinct $\sigma$-conjugation. As a result, a higher metallic character, a lower band gap, a lower photochemical resistance and a more distinct thermochromic behaviour than that in polygermanes are to be expected. The electronic structure of polystannane (SnH$_2$)$_n$ was calculated by the first principal local density functional method and compared with that of polysilane (SiH$_2$)$_n$ and polygermane.
(GeH$_2$)$_n$. The calculated band gaps for (SnH$_2$)$_n$, (GeH$_2$)$_n$ and (SiH$_2$)$_n$ in anti conformation (Scheme 9) were reported to be 2.80, 3.31 and 3.89 eV, respectively$^{20}$. Recently, the use of polystannanes for the fabrication of electroluminescent devices and lasers$^{78,79}$, electroconductive films$^{80}$, colour filters for liquid crystal displays$^{80}$ and of materials with third-order optical non-linearity$^{81}$ were suggested. Further examples envisaged for applications are the use of polystannanes in photoresist technology, in microlithography, as semiconductors and as precursors to tin-based semiconducting materials$^{82}$.

A variety of synthetic methods for the Sn–Sn bond formation are available to date, the most common of which are (i) the coupling of organotin halides R$_n$SnX$_{4-n}$ with organostannylmetal compounds, R$_3$SnM (M = Li, Na, MgBr, MgCl), (ii) the reductive coupling of organotin halides, R$_n$SnX$_{4-n}$, by metals or electrochemically, (iii) the condensation reactions of organotin hydrides, R$_n$SnH$_{4-n}$, with compounds of the type R$_n$SnY$_{4-n}$ (e.g. Y = NR$_2$, OSnR$_3$, OR'), (iv) the insertion of stannylenes R$_2$Sn into tin–element bonds such as Sn–H, Sn–C, Sn–Sn and Sn–Cl and (v) the elimination of dihydrogen from organotin hydrides, R$_n$SnH$_{4-n}$, catalysed by amines or transition metal compounds. These general methodologies have been reviewed by Davies$^{83}$ and more recently by Braunstein and Morise$^{84}$, who focused on the ‘dehydrogenative coupling of hydrostannanes catalysed by transition-metal complexes’. Despite the wide range of synthetic methods for the formation of Sn–Sn bonds, the controlled preparation of high molecular weight polystannanes still remains a challenging target. The preparation of polysilanes is much more easily achieved, the reason being the higher stability of the Si–Si bond [E(Si–Si) = 340 KJ mol$^{-1}$] in comparison with the rather weak Sn–Sn bond [E(Sn–Sn) = 151 KJ mol$^{-1}$]$^{85}$.

In this section we give a comparative overview on the recent developments in the preparation of polystannanes and discuss their properties.

b. Syntheses. i. Oligostannanes via stepwise synthesis. Linear oligostannanes can be viewed as model compounds for linear polystannanes and different sequences of oligostannanes with varying chain lengths were prepared to elucidate the relationship of structure and electronic properties$^{16–19,21–24}$. Adams and Dräger reported the reaction of Ph$_3$SnLi with 1–(t-Bu$_2$Sn)$_n$–I ($n = 2–4$, 10) to give mixtures of the linear oligostannanes Ph$_3$Sn(t-Bu$_2$Sn)$_n$SnPh$_3$ ($n = 1–4$, 11) depending on the reaction conditions employed (Scheme 10)$^{18}$. This experiment demonstrated the lability of the Sn–Sn bond and the tendency of oligo- and polystannanes to undergo equilibration processes in solution to give the thermodynamically most stable compounds.

$$\begin{align*}
2 \text{Ph}_3\text{SnLi} + 1–(\text{t-Bu}_2\text{Sn})_n–\text{I} \rightarrow & \text{Ph}_3\text{Sn}(\text{t-Bu}_2\text{Sn})_n\text{SnPh}_3 \\
& \text{n = 2–4, 10} \\
& \text{2 LiI} \rightarrow \text{n = 1–4, 11}
\end{align*}$$

SCHEME 10. Synthesis of oligostannanes via metal–halogen exchange

A stepwise construction of oligostannanes containing six tin atoms in the backbone is based on the tin–tin bond-forming hydrostannolysis reaction$^{86}$. To produce higher-order oligostannanes, the $\beta$-alkoxy substituent –CH$_2$CH$_2$OEt was used as protecting group at tin, which can easily be transformed into a Sn–H functionality by reaction with DIBAL-H ($i$-Bu$_2$AlH). The Sn–H bond serves as the site for extended chain growth of the polystannane skeleton$^{19}$ (Scheme 11). This approach is very tedious and oligostannanes (12) with up to a maximum of only six tin atoms in the backbone were prepared.
Bu$_3$Sn + RBu$_2$SnNMe$_2$ \( \rightarrow \) Bu$_3$SnSnBu$_2$R

i) $i$-Bu$_2$AH

\( -i$-Bu$_2$AlOEt

R = EtOCH$_2$CH$_2$

- C$_2$H$_4$

ii) RBu$_2$SnNMe$_2$

HNMe$_2$

i), ii) \((n-1)\) times

Bu$_3$Sn \( \rightarrow \) (SnBu$_2$)$_n$ \( \rightarrow \) SnBu$_2$R

Bu$_3$SnSnBu$_2$H

i) $i$-Bu$_2$AH

\( -i$-Bu$_2$AlOEt

R = EtOCH$_2$CH$_2$

- C$_2$H$_4$

ii) RBu$_2$SnNMe$_2$

HNMe$_2$

Bu$_3$SnSnBu$_2$H

SCHEME 11. Synthesis of oligostannanes

The development of this synthetic methodology has led to the preparation of oligostannanes with up to fifteen tin atoms in the linear chain

\((\text{Scheme 12})\) This was achieved by reaction of dibutyl(2-ethoxyethyl)stannane \((\text{13})\) with 0.2–0.3 equiv of lithium diisopropylamide (LDA) in THF to presumably generate an intermediate family of hydride-terminated oligostannanes \((\text{14})\), which were then reacted with dibutyl(dimethylamino)(2-ethoxyethyl)stannane \((\text{13})\) to give the final product \((\text{15})\). The formation of stannylenes, which insert into an Sn–H bond was proposed to explain the chain growth mechanism. However, small amounts of the cyclic oligomers \((\text{87})\) \(\text{cyclo-}(n$-$Bu$_2$Sn)$_5$\) and \(\text{cyclo-}(n$-$Bu$_2$Sn)$_6$\) were also formed and the short-chain oligomers predominate over oligomers with chain lengths of \(n > 10\).

RBu$_2$H

0.2–0.3 eq LiN(Pr-$i$)$_2$

\( \rightarrow \) HNMe$_2$

R = EtOCH$_2$CH$_2$

(13)

RBu$_2$SnLi \( \rightarrow \) Bu$_3$Sn

- LiOEt

- C$_2$H$_4$

RBu$_2$SnNMe$_2$

HNMe$_2$

RBu$_2$Sn (SnBu$_2$)$_n$ \( \rightarrow \) SnBu$_2$H

RBu$_2$SnBu$_2$H

n Bu$_2$Sn

(15) \(n = 0–12\)

SCHEME 12. Synthetic strategy to prepare oligostannanes with up to 15 tin atoms in the linear chain

Several cyclic and polycyclic oligostannanes with a rich structural diversity have been reported in the literature and it was concluded by Sita that the concepts and strategies established in organic chemistry can successfully be applied for the construction of polystannane frameworks as well. The polycyclic oligostannanes \((\text{16}–\text{19})\) are representative examples for this class of compounds.
\[ R = 2,6-\text{Et}_2\text{C}_6\text{H}_3 \]

**ii. Polystannanes via Wurtz-type coupling.** Early attempts to prepare high molecular weight polystannanes were directed towards the Wurtz-type coupling of diorganotin dichlorides\textsuperscript{86,88} because this method was known to be successful for the preparation of polysilanes\textsuperscript{13}. However, initially this method failed and only low molecular weight oligomers\textsuperscript{86} were formed. Nevertheless, in 1992 the first high molecular weight organotin polymer \( \text{H}(n\text{-Bu}_2\text{Sn})_n\text{H} \) (20) was reported, which was prepared by the Wurtz-type coupling of \( n\text{-Bu}_2\text{SnCl}_2 \) using sodium dispersion in toluene and the catalytic effect of 15-crown-5 ether (Table 5, Scheme 13)\textsuperscript{89}. However, following the above-mentioned experimental procedure for the preparation of 20\textsuperscript{89}, Tilley and coworkers\textsuperscript{82,90} failed to reproduce the results. The \(^{119}\text{Sn}\) NMR spectrum of the crude reaction mixture was consistent with the formation of small amounts of \( \text{H}(n\text{-Bu}_2\text{Sn})_n\text{H} \), but the major signals were assigned to the cyclic oligomers \( \text{cyclo}(n\text{-Bu}_2\text{Sn})_5 \) and \( \text{cyclo}(n\text{-Bu}_2\text{Sn})_6 \). A more detailed analysis of the reaction conditions used for the Wurtz-type coupling of \( n\text{-Bu}_2\text{SnCl}_2 \) in toluene at 60°C using a sodium dispersion and catalytic amounts of 15-crown-5 ether revealed a strong dependence of the polymer-to-oligomer ratio on the reaction conditions employed\textsuperscript{91}. During the first 2 h of the reaction, very little polymer is formed and most of the product is composed of low molecular weight cyclic oligomers. The maximum yield of high molecular weight polystannane (\( M_w \approx 7.7 \times 10^5 \)) was obtained after a reaction time of approximately 4 h. Prolonged reaction rapidly lead to chain scission and after 5.5 h the majority of polymer was reconverted into cyclic oligomers. The use of ultrasound had no influence on the degree of polymerization, but the time required to reach the optimal conditions was approximately halved.

To circumvent the problem of polystannane degradation by sodium-induced Sn\textendash{}Sn bond cleavage, a new synthetic procedure for the preparation of polystannanes under
### TABLE 5. Representative examples for the preparation of poly(dialkyl)stannanes by Wurtz-type coupling A, SmI$_2$-induced reduction B, electrochemical reduction C and dehydrogenative coupling D

<table>
<thead>
<tr>
<th>Entry</th>
<th>Method</th>
<th>Precursor</th>
<th>Conditions</th>
<th>$M_w$</th>
<th>$M_w/M_n$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>$n$-Bu$_2$SnCl$_2$</td>
<td>Na/15-crown-5 toluene/60 °C/14 h</td>
<td>ca 1.4</td>
<td>c</td>
<td>89</td>
</tr>
<tr>
<td>2</td>
<td>A</td>
<td>$n$-Bu$_2$SnCl$_2$</td>
<td>Na/15-crown-5 toluene/60 °C/14 h</td>
<td>0.24</td>
<td>2</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td>A</td>
<td>$n$-Bu$_2$SnCl$_2$</td>
<td>Na/15-crown-5 toluene/60 °C/4 h</td>
<td>109$^d$</td>
<td>1.4</td>
<td>91</td>
</tr>
<tr>
<td>4</td>
<td>B</td>
<td>Et$_2$SnCl$_2$</td>
<td>SmI$_2$/HMPA–THF 23 °C/24 h</td>
<td>0.48</td>
<td>1.2</td>
<td>42</td>
</tr>
<tr>
<td>5</td>
<td>B</td>
<td>$n$-Hex$_2$SnCl$_2$</td>
<td>SmI$_2$/HMPA–THF 23 °C/120 h</td>
<td>0.27</td>
<td>1.2</td>
<td>92</td>
</tr>
<tr>
<td>6</td>
<td>C</td>
<td>$n$-Bu$_2$SnCl$_2$</td>
<td>electrochemically in DME/Bu$_4$NClO$_4$</td>
<td>1.09</td>
<td>2.6</td>
<td>95</td>
</tr>
<tr>
<td>7</td>
<td>C</td>
<td>$n$-Oct$_2$SnCl$_2$</td>
<td>electrochemically in DME/Bu$_4$NClO$_4$</td>
<td>0.59</td>
<td>1.7</td>
<td>95</td>
</tr>
<tr>
<td>8</td>
<td>D</td>
<td>$n$-Bu$_2$SnH$_2$</td>
<td>neat monomer + cat.$^e$ 24 h</td>
<td>1.75</td>
<td>2.2</td>
<td>82</td>
</tr>
<tr>
<td>9</td>
<td>D</td>
<td>$n$-Bu$_2$SnH$_2$</td>
<td>neat monomer + cat. (CpCp$^\ast$ZrMe$_2$)/5 h</td>
<td>7.40</td>
<td>6.9</td>
<td>82</td>
</tr>
<tr>
<td>10</td>
<td>D</td>
<td>$n$-Bu$_2$SnH$_2$</td>
<td>neat monomer + cat. $^f$ 11 h</td>
<td>6.69</td>
<td>3.3</td>
<td>82</td>
</tr>
<tr>
<td>11</td>
<td>D</td>
<td>$n$-Bu$_2$SnH$_2$</td>
<td>neat monomer + cat. (Cp$_2$ZrMe$_2$)/5 h</td>
<td>4.60</td>
<td>3.3</td>
<td>82</td>
</tr>
<tr>
<td>12</td>
<td>D</td>
<td>$n$-Hex$_2$SnH$_2$</td>
<td>neat monomer + cat. $^e$ 23 h</td>
<td>3.68</td>
<td>2.4</td>
<td>82</td>
</tr>
<tr>
<td>13</td>
<td>D</td>
<td>$n$-Oct$_2$SnH$_2$</td>
<td>neat monomer + cat. $^e$ 15 h</td>
<td>9.57</td>
<td>6.7</td>
<td>82</td>
</tr>
<tr>
<td>14</td>
<td>D</td>
<td>$n$-Bu$_2$SnH$_2$</td>
<td>toluene/23 °C/13 h cat. HRh(CO)(PPh$_3$)$_3$</td>
<td>5.02</td>
<td>1.4</td>
<td>98</td>
</tr>
</tbody>
</table>

$^a$ Molecular weight measured by GPC. $M_w$ is weight-average molecular mass.
$^b$ Molecular weight distribution of isolated samples. $M_n$ is number-average molecular mass.
$^c$ Not reported.
$^d$ Crude reaction mixture, which contains 20% of cyclic oligomers. After 5.5 h the majority of polymer was reconverted to cyclic oligomers.
$^e$ CpCp$^\ast$Zr[Si(SiMe$_3$)$_3$]Me.
$^f$ Me$_2$C(η$^5$-C$_5$H$_4$)$_2$Zr[Si(SiMe$_3$)$_3$]Me.

Mild conditions using SmI$_2$ or alkali earth metal (Mg, Ca) vapor-solvent co-condensates was investigated$^{42,92}$. The resulting polystannanes (R$_2$Sn)$_n$ (R = Me, Et, n-Hex) showed narrow molecular weight distributions ($M_w/M_n = 1.2–1.5$), but only moderate molecular weights ($M_w = 1.1–4.8 \times 10^3$) were observed.

Using the Wurtz-type coupling reaction, Jones and coworkers reported the synthesis of a high molecular weight organostannane–organosilane copolymer (21)$^{93}$ starting from MePhSiCl$_2$ and $n$-Bu$_2$SnCl$_2$ in a 4 : 1 molar ratio (Scheme 14). The reaction was carried out with sodium metal, and MePhSiCl$_2$ was used as both reagent and solvent. After the work-up procedure, a product was obtained for which a Si : Sn ratio of 6.2 : 1 was estimated on the basis of the $^1$H NMR spectrum. The copolymer was isolated in 11% yield and had a molecular weight of $M_w = 15.1 \times 10^3$ and a molecular weight distribution of $M_w/M_n = 2.3$. The same reaction and work-up procedure was carried out using toluene,
resulting in the formation of a copolymer with a lower molecular weight \( (M_w = 3 \times 10^3, M_w/M_n = 1.5) \).

\[
n\text{Bu}_2\text{SnCl}_2 + \text{PhMeSiCl}_2 \xrightarrow{\text{Na, 120 °C}} \left[ \begin{array}{c} \text{Bu}^n \\ \text{Sn} \\ \text{Bu}^n \end{array} \right] + \left[ \begin{array}{c} \text{Ph} \\ \text{Si} \\ \text{Me} \end{array} \right]_m
\]

(21)


Matyjaszewski and coworkers\(^9^4\) reported the Wurtz-type synthesis of organostannane–organosilane copolymers under the influence of ultrasound starting from PhMeSiCl\(_2\) and Ph\(_2\)SnCl\(_2\). This approach resulted in the formation of low molecular weight copolymers with a broad molecular weight distribution \( (M_w = 4 \times 10^3, M_w/M_n = 3.7) \). The \(^1\)H NMR spectrum was indicative for a Si : Sn ratio of 1.4 : 1\(^9^4\).

iii. Polystannanes via electrochemical synthesis. Electrochemical reduction of diorganotin dihalides is expected to be the most important approach for the large-scale preparation of polystannanes\(^2^2\). However, so far only \((n-\text{Bu}_2\text{Sn})_n\) and \((n-\text{Oct}_2\text{Sn})_n\) were prepared by electrochemical synthesis\(^9^5\) (Table 5, Scheme 15). The reactions were carried out in 1,2-dimethoxyethane (DME) as solvent and with tetrabutylammonium perchlorate as supporting electrolyte. The yields reported were 40–60% for \((n-\text{Bu}_2\text{Sn})_n\) and 30–50% for \((n-\text{Oct}_2\text{Sn})_n\). The polystannane \((n-\text{Bu}_2\text{Sn})_n\) showed molecular weight distributions in the range of \( M_w/M_n = 2.1–2.6 \) and molecular weights of approximately \( M_w = 1.1 \times 10^4 \). The use of THF as solvent gave a narrower molecular weight distribution of \( M_w/M_n = 1.3 \), but also lower molecular weights of \( M_w = 0.64 \times 10^4 \), which is attributed to a polystannane degradation resulting from residual moisture in the THF solutions. For \((n-\text{Oct}_2\text{Sn})_n\) a molecular weight of \( M_w = 0.59 \times 10^4 (M_w/M_n = 1.7) \) was reported.

\[
n\text{Bu}_2\text{SnCl}_2 + 2\text{ne}^- \xrightarrow{-2n \text{Cl}^-} \left[ \begin{array}{c} \text{R} \\ \text{Sn} \\ \text{R} \end{array} \right]_n
\]

R = n-\text{Bu}, n-\text{Oct} (22)

SCHEME 15. Electrochemical synthesis of polystannanes

Electrochemical syntheses were used to prepare organostannane–organosilane and organostannane–organogermane copolymers\(^9^6\). Poly(dibutylstannylene-co-dibutylsilylene) and poly(dibutylstannylene-co-dibutylgermylene) were synthesised by the reduction of mixtures of dibutyl dichlorostannane and dibutyl dichlorosilane and dibutyl dichlorogermane, respectively, using tetrabutylammonium perchlorate as the supporting electrolyte and DME as solvent. The copolymers were isolated in low yields, had relatively high molecular weights but broad molecular weight distributions. For example, a copolymer \((n-\text{Bu}_2\text{Sn})_{0.47}(n-\text{Bu}_2\text{Si})_{0.57}\) was isolated in 11% yield from a reaction mixture containing
Organometallic polymers of germanium, tin and lead  

$n$-Bu$_2$SnCl$_2$ and $n$-Bu$_2$SiCl$_2$ in a one-to-one ratio. The copolymer had a molecular weight of $M_w = 1.26 \times 10^5$ and a molecular weight distribution of $M_w/M_n = 13$.

iv. Polystannanes via catalytic routes. The transition metal complex-catalysed dehydrogenative coupling of secondary stannanes R$_2$SnH$_2$ is a promising approach to high molecular weight polystannanes. The use of a variety of catalysts based on Ti, Zr, Hf, Sm, Rh, Cr, Mo, W and heterobimetallic Fe–Pd complexes was reported. The compounds 23–25 represent three examples of catalysts used for the dehydrogenative coupling of organostannanes.

The dehydropolymerization of $n$-Bu$_2$SnH$_2$ as catalysed by heterobimetallic Fe–Pd complexes gave mixtures of cyclic and linear polystannanes with the latter having a broad molecular weight distribution. On the basis of the relationship between the $\lambda_{max}$ value and the chain length for (R$_2$Sn)$_n$, the formation of high molecular weight polymers was suggested, but no molecular weight determination was reported. In case of the dehydropolymerization of Ph$_2$SnH$_2$ only the cyclic pentamer, cyclo-(Ph$_2$Sn)$_5$, and hexamer, cyclo-(Ph$_2$Sn)$_6$, were formed.

Metallocene-based catalysts were successfully used for the dehydropolymerization of secondary stannanes R$_2$SnH$_2$ (Table 5, Scheme 16). The syntheses of high molecular weight poly(dialkyl)stannanes (26) and poly(diarylstannanes (27) using different Cp$_2$ZrR$_2$ derivatives as catalysts were reported. The most active catalyst reported so far for the synthesis of high molecular weight poly(dibutyl)stannanes is Me$_2$C($\eta^5$-C$_5$H$_4$)$_2$Zr[Si(SiMe$_3$)$_3$]Me (24). It was claimed to produce H($n$-Bu$_2$Sn)$_n$H (26) with a molecular weight up to $M_w = 6.69 \times 10^4$ and a molecular weight distribution of $M_w/M_n = 3.30$. However, the polystannane was contaminated by ca 18% (by weight) of low molecular weight cyclic oligomers (28) with the cyclic pentamer cyclo-($n$-Bu$_2$Sn)$_5$ predominating. Usually, the polymerizations are initiated by addition under nitrogen of the neat monomer to the catalyst (2 mol%). The addition of small amounts of solvent (1 molar amount of toluene per monomer) significantly increased the molecular weights of the resulting polymers, but substantial dilution of the monomer predominantly lead to cyclization.

\[
\begin{align*}
R_2SnH_2 & \xrightarrow{[cat]} H \longrightarrow (R_2Sn)_n \longrightarrow H + cyclo-(R_2Sn)_n \\
(26) & \text{R = alkyl} \\
(27) & \text{R = aryl}
\end{align*}
\]

SCHEME 16. Catalytic dehydrogenative coupling of diorganotin dihydrides

Polymers with the highest molecular weights were obtained for secondary stannanes with long alkyl chains, e.g. a molecular weight of $M_w = 1.49 \times 10^5$ ($M_w/M_n = 8.76$) was observed for H($n$-Oct$_2$Sn)$_n$H$^{82}$. 

In case of the diorganostannanes Me₂SnH₂, PhMeSnH₂ and Ph₂SnH₂ only low molecular weight oligomers could be obtained, which is attributed to the low solubility of the corresponding oligostannanes. In order to circumvent this problem, monomeric diarylstannanes Ar₂SnH₂ with the solubilizing substituents \( \text{Ar} = p\text{-t-BuC₆H₄}, \ p\text{-n-HexC₆H₄}, \ o\text{-EtC₆H₄}, \ p\text{-n-BuOC₆H₄}, \ o\text{-Et}, p\text{-t-BuC₆H₃} \) and \( p\text-\text{(Me₃Si)₂NC₆H₄} \) were used in the \( \text{Cp₂ZrMe₂} \)-catalysed dehydropolymerization. At monomer concentrations in pentane above 0.09 M, relatively high molecular weight polymers \( \left[H(p\text{-t-BuC₆H₄})₂Sn\right]_nH \) were obtained (\( M_w = 5.4 \times 10^4; M_w/M_n = 3.6 \) for the linear fraction), whereas at low monomer concentrations (0.01–0.03 M) only low molecular weight oligomers were formed. The use of donor solvents such as pyridine inhibited the polymerization. A relatively narrow molecular weight distribution of \( M_w/M_n = 1.5 \) was observed when the dehydropolymerization of diaryltin dihydrides was carried out in the melt, but only moderate molecular weights \( M_w = 0.15 \times 10^4 \) were obtained together with a large fraction of cyclic oligomers. Notably, the dehydrogenative coupling of \( (p\text{-t-BuC₆H₄})₂SnH₂ \) predominantly gave the cyclic hexamer as by-product, whereas the cyclic pentamer was the major by-product in the polymerization of dialkylstannanes.

Hafnocenes are less active polymerization catalysts and metalocene chlorides are almost inactive. However, treatment of \( \text{[Cp₂MCl₂]} (\text{M} = \text{Zr}, \text{Hf}) \) with \( n\text{-BuLi} \) provided efficient catalysts for the dehydropolymerization of \( n\text{-Bu₂SnH₂} \). Mixtures of oligostannanes and cross-linked insoluble polystannanes were reported to be formed upon treatment of \( n\text{-Bu₂SnH₂} \) with \( \text{[Cp₂MCl₂]/Red-Al} (\text{M} = \text{Ti}, \text{Zr}, \text{Hf}) \) and \( \text{[M(CO)₆]/Red-Al} (\text{M} = \text{Cr}, \text{Mo}, \text{Wo}) \) as combination catalysts. The same catalysts were used in the dehydrogenative coupling of \( n\text{-Bu₃SnH} \) for which cross-linked polystannanes were observed as minor products. In both cases, the formation of cross-linked polystannanes is suggested to result from a combination of disproportionation and dehydrocoupling. The same combined processes were observed for the \( \text{[HRh(CO)(PPh₃)₂]-catalysed dehydropolymerization of n-Bu₂SnH₂} \). Interestingly, rapid addition of the catalyst to neat \( n\text{-Bu₂SnH₂} \) gave the cyclic pentamer and hexamer, whereas slow addition of the rhodium catalyst to a dilute solution of the monomer in toluene produced a highly branched, high molecular weight polystannane with a narrow molecular weight distribution (\( M_w = 5.02 \times 10^3; M_w/M_n = 1.43 \)).

Research on the optimization of reaction conditions and the elucidation of reaction mechanisms for the dehydrogenative polymerization of secondary stannanes is rather limited. In this context, Tilley and coworkers proposed a chain-grow mechanism (Scheme 17), which is similar to that proposed for the dehydropolymerization of organosilanes.

c. Properties. i. Chemical properties. The polystannanes reported to date are described as yellow- or orange-coloured viscous oils or solids. They are thermally stable at room temperature, but sensitive towards moisture and light. In air, solid samples decompose very slowly and poly(diaryl)stannanes are air-stable over at least several weeks in the dark. No decomposition of \( \text{H(n-Bu₂Sn)}_nH \) in pentane took place, even when oxygen was bubbled through its solution. It was concluded that polystannanes are stable towards oxygen but extremely reactive to moisture. In solution, poly(diaryl)stannanes as well as poly(dialky)stannanes photochemically degrade to give cyclic oligomers, predominantly the pentamer and the hexamer. Exposure of \( \text{H(p-t-BuC₆H₄)}_₂Sn\text{H}_n \) in THF to light for 30 min resulted in complete degradation to give a mixture of cyclic oligomers. Therefore, polystannanes should be handled under anaerobic conditions and exclusion of light. Only a few silane–stannane and germane–stannane copolymers were reported and their properties remain mainly unexplored. Okano and Watanabe
22. Organometallic polymers of germanium, tin and lead

\[
\begin{align*}
M & \longrightarrow H \\
H & \longrightarrow (R_2Sn)_m(R_2Sn)_n \longrightarrow H
\end{align*}
\]

**SCHEME 17.** Proposed mechanism for the transition metal catalysed dehydropolymerization of organostannanes

demonstrated that an increase of the \(n\)-Bu\(_2\)Si content in polystannane–polysilane copolymers \([(n\mbox{-}Bu_2Si)_m(n\mbox{-}Bu_2Sn)_n]\) results in a substantial lower tendency for decomposition of the copolymers, but also results in absorption peaks at shorter wavelengths compared with that of \((n\mbox{-}Bu_2Sn)_n\) at \(\lambda_{\text{max}} = 380\) nm. The same tendency was observed in the corresponding poly(dibutyl)stannane–poly(dibutyl)germane copolymers, but in addition the absorption peak of a copolymer with a Sn : Ge ratio of 32 : 68 was observed at \(\lambda_{\text{max}} = 315\) nm, which is at an even shorter wavelength than that of poly(dibutyl)germane itself (\(\lambda_{\text{max}} = 324\) nm)\(^{96}\).

Thermogravimetric analyses (TGA) of poly(dialkyl)stannanes under nitrogen showed onset temperatures for thermal decomposition in the temperature range of 250–280°C, which is close to the values for related polydialkysilanes\(^ {82}\). The TGA analyses of poly(diaryl)stannanes\(^ {100}\) show onset temperatures for the decomposition in the range of 203–327°C. Thermal decomposition of polystannanes leads to tin and tin oxide, and thus application of these materials for the preparation of conductors or coatings in semiconductors may be envisaged. It is worth noting that electronic conductivities of about 0.01–0.3 S cm\(^{-1}\) were observed for thin films of the polystannanes after exposure to SbF\(_5\) vapor as an oxidant\(^ {82}\).

Polystannanes are routinely characterised by gel permeation chromatography (GPC, polystyrene standard), UV spectroscopy, thermal gravimetric analysis (TGA) and \(^1\text{H}\) and \(^{119}\text{Sn}\) NMR spectroscopy. Especially, \(^{119}\text{Sn}\) NMR in solution is a powerful tool to determine the ratio of high molecular weight polymers to cyclic oligomers. The signals assigned to the cyclic oligomers are usually low-frequency shifted compared with the signals of the corresponding polystannane. Thus, the hexamer cyclo-\([(p-t\mbox{-}BuC_6H_4)_2Sn]_6\) has a \(^{119}\text{Sn}\) NMR chemical shift \(\delta = 221\), which is quite different from the chemical shift \(\delta = 197\) of the linear polymer \(H[(p-t\mbox{-}BuC_6H_4)_2Sn]_nH\). \(^{119}\text{Sn}\) NMR chemical shifts of some representative polystannanes and cyclic oligomers are given in Table 6. \(^1\text{H}\) NMR spectroscopy was used to determine the ratio of cyclic oligomers to linear polymers in the case of the polymerization of \(n\mbox{-}Bu_2\text{SnH}_2\) and \(n\mbox{-}Hex_2\text{SnH}_2\). The terminal methyl groups give rise to distinct triplets which are well separated for the linear and the cyclic compounds. For poly(diocetyl)stannane and the related cyclic diocetylstannanes, however, the \(^1\text{H}\) NMR spectra are very similar and consequently, these compounds could not be distinguished by this method\(^ {82}\).
TABLE 6. $^{119}$Sn NMR chemical shifts (in ppm) of polystannanes and cyclic oligostannanes\textsuperscript{82,97,100} in benzene-$d_6$

<table>
<thead>
<tr>
<th>Poly- and cyclic oligo-</th>
<th>$\delta$($^{119}$Sn)</th>
<th>Poly- and cyclic oligo-</th>
<th>$\delta$($^{119}$Sn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(dialkyl)stannanes</td>
<td></td>
<td>(diaryl)stannanes</td>
<td></td>
</tr>
<tr>
<td>H($\text{n-Bu}_2\text{Sn}$)$_n$</td>
<td>$\text{H}$</td>
<td>H($\text{p-t-ButC}_6\text{H}_4$)$_2\text{Sn}$</td>
<td>$\text{H}$</td>
</tr>
<tr>
<td>H($\text{p-t-ButC}_6\text{H}_4$)$_2\text{Sn}$</td>
<td>$\text{H}$</td>
<td>H($\text{p-n-HexC}_6\text{H}_4$)$_2\text{Sn}$</td>
<td>$\text{H}$</td>
</tr>
<tr>
<td>cyclo($\text{n-Bu}_2\text{Sn}$)$_n$</td>
<td>$\text{H}$</td>
<td>H($\text{p-t-ButC}_6\text{H}_4$)$_2\text{Sn}$</td>
<td>$\text{H}$</td>
</tr>
<tr>
<td>H($\text{p-n-HexC}_6\text{H}_4$)$_2\text{Sn}$</td>
<td>$\text{H}$</td>
<td>H($\text{p-t-ButC}_6\text{H}_4$)$_2\text{Sn}$</td>
<td>$\text{H}$</td>
</tr>
<tr>
<td>cyclo($\text{n-Hex}_2\text{Sn}$)$_n$</td>
<td>$\text{H}$</td>
<td>H($\text{o-Et-p-n-BuOC}_6\text{H}_4$)$_2\text{Sn}$</td>
<td>$\text{H}$</td>
</tr>
<tr>
<td>H($\text{o-Et-p-n-BuOC}_6\text{H}_4$)$_2\text{Sn}$</td>
<td>$\text{H}$</td>
<td>H($\text{o-Et-p-n-BuOC}_6\text{H}_4$)$_2\text{Sn}$</td>
<td>$\text{H}$</td>
</tr>
</tbody>
</table>

\textit{ii. Electronic properties.} The UV-visible spectroscopic properties of oligostannanes\textsuperscript{18,19,22,30}, polystannanes\textsuperscript{42,82,90–92,95,97,98,100} and organosilane–organostannane copolymers\textsuperscript{93,96} have attracted great interest. Concerning the electronic spectra of oligostannanes, homologous series of linear oligostannanes show red-shifting of the lowest energy transition with increasing chain length reaching a plateau value. The specific positions and magnitudes of these transitions are strongly influenced by the nature of the substituents at tin.

All soluble high molecular weight polystannane derivatives absorb strongly in the UV. In Table 7, the $\lambda_{\text{max}}$ values of some representative homopolymers are given. Extinction coefficients $\varepsilon_{\text{max}}$ in the range of $4.2 \times 10^3$ to $6.3 \times 10^4$ were reported\textsuperscript{82}. At room temperature, high molecular weight poly(dialkyl)stannanes exhibit $\lambda_{\text{max}}$ values in the range of 380–400 nm. The actual value observed may vary depending upon the percentage of cyclic oligomers present, the temperature and the polymer phase (e.g. solid vs solution). For comparison, the $\lambda_{\text{max}}$ values for Et(SnEt$_2$)$_6$Et (Sn$_6$)$_3$\textsuperscript{30}, [EtO(CH$_2$)$_2$-$\text{n-Bu}_2\text{Sn}$]$_2$Sn(Bu-t)$_2$ (Sn$_9$)$_2$\textsuperscript{23} and [EtO(CH$_2$)$_2$-$\text{n-Bu}_2\text{Sn}$($\text{n-Bu}_2\text{Sn}$)$_6$]$_2$Sn(Bu-n)$_2$ (Sn$_{15}$)$_2$\textsuperscript{22}.

TABLE 7. Absorption characteristics of representative polystannanes in solution

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$M_w$\textsuperscript{a} $\times 10^4$</th>
<th>$M_w/M_n$\textsuperscript{b}</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(Et$_2$Sn)$_n$</td>
<td>368</td>
<td>0.48</td>
<td>1.2</td>
<td>42</td>
</tr>
<tr>
<td>2</td>
<td>($\text{n-Bu}_2\text{Sn}$)$_n$</td>
<td>390</td>
<td>4.12</td>
<td>3.0</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td>(n-Bu$_2$Sn)$_n$</td>
<td>382</td>
<td>1.75</td>
<td>2.2</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>(n-Bu$_2$Sn)$_n$</td>
<td>381</td>
<td>1.09</td>
<td>2.6</td>
<td>95</td>
</tr>
<tr>
<td>5</td>
<td>(n-Bu$_2$Sn)$_n$</td>
<td>380</td>
<td>ca 100</td>
<td>ca 1.4</td>
<td>91</td>
</tr>
<tr>
<td>6</td>
<td>(n-Hex$_2$Sn)$_n$</td>
<td>384</td>
<td>&gt;1</td>
<td>e</td>
<td>82</td>
</tr>
<tr>
<td>7</td>
<td>(n-Oct$_2$Sn)$_n$</td>
<td>388</td>
<td>&gt;1</td>
<td>e</td>
<td>82</td>
</tr>
<tr>
<td>8</td>
<td>(n-Oct$_2$Sn)$_n$</td>
<td>378</td>
<td>0.59</td>
<td>1.7</td>
<td>95</td>
</tr>
<tr>
<td>9</td>
<td>(Ph$_2$Sn)$_n$</td>
<td>402</td>
<td>&lt;1</td>
<td>e</td>
<td>82</td>
</tr>
<tr>
<td>10</td>
<td>[($\text{p-t-ButC}_6\text{H}_4$)$_2$Sn]$_n$</td>
<td>432</td>
<td>5.60</td>
<td>3.4</td>
<td>100</td>
</tr>
<tr>
<td>11</td>
<td>[($\text{p-n-HexC}_6\text{H}_4$)$_2$Sn]$_n$</td>
<td>436</td>
<td>4.82</td>
<td>2.4</td>
<td>100</td>
</tr>
<tr>
<td>12</td>
<td>[($\text{p-n-ButOC}_6\text{H}_4$)$_2$Sn]$_n$</td>
<td>448</td>
<td>1.20</td>
<td>1.7</td>
<td>100</td>
</tr>
<tr>
<td>13</td>
<td>[($\text{o-Et-p-n-BuOC}_6\text{H}_4$)$_2$Sn]$_n$</td>
<td>450</td>
<td>0.42</td>
<td>1.1</td>
<td>100</td>
</tr>
<tr>
<td>14</td>
<td>[($\text{o-Et-p-n-ButOC}_6\text{H}_4$)$_2$Sn]$_n$</td>
<td>506</td>
<td>0.44</td>
<td>1.1</td>
<td>100</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Molecular weight measured by GPC. $M_w$ is weight-average molecular mass.

\textsuperscript{b}Molecular weight distribution. $M_n$ is number-average molecular mass.

\textsuperscript{c}Not given.
are 325 nm, 342 nm and 362 nm, respectively. A sample of H\(\text{Bu}_2\text{Sn})_n\text{H} (M_w = 4.12 \times 10^4, M_w/M_n = 2.96)\) displayed a transition at 390 nm in pentane, whereas the corresponding polysilane \(\text{Bu}_2\text{Si})_n\text{H}\) and polygermane \(\text{Bu}_2\text{Ge})_n\) have limiting \(\lambda_{\text{max}}\) values of 314 and 333 nm, respectively. Thus, the \(\sigma \rightarrow \sigma^*\) transitions for polystannanes are red-shifted by ca 70 nm with respect to comparable polysilanes and by ca 50 nm with respect to comparable polygermanes.

Polystannanes exhibit \(\lambda_{\text{max}}\) values attributed to the \(\sigma \rightarrow \sigma^*\) transitions in the range of 430–506 nm. A significant \(\sigma \rightarrow \pi\) interaction was suggested to occur in these polymers, which lowers the band gaps with respect to those for related poly(dialkyl)-stannanes. A sample of H\(\text{Et}_{\text{p}}\text{Bu}_2\text{Sn})_n\text{H}\) with a molecular weight of \(M_w < 5 \times 10^3\) exhibited a band gap of ca 2.3 eV, the smallest band gap reported for \(\sigma\)-conjugated linear polymers so far. There is an approximately linear correlation for the poly(diaryl)stannanes between the polymer band gap (as indicated by the \(\lambda_{\text{max}}\) values) and the \(\text{Sn}^\text{119}\) NMR chemical shifts, with the \(\text{Sn}^\text{119}\) NMR resonances shifting to higher frequencies as the band gap is narrowed.

The hyperbranched polymer, as obtained by the dehydropolymerization of \(\text{Bu}_2\text{SnH}_2\) with a rhodium catalyst, has a \(\lambda_{\text{max}}\) value of 394 nm, which is slightly red-shifted with respect to high molecular weight poly(dibutyl)stannane (Table 7, entries 2–5).

Poly(diocetyl)stannane and poly(dihexyl)stannane exhibit a reversible thermochromic behaviour as a result of a phase transition at ca 40 °C. A discolouration of the polymers was observed upon slightly warming above room temperature and variable-temperature UV-vis spectrometry showed a reduction of the \(\lambda_{\text{max}}\) values of \((\text{Oct}_2\text{Sn})_n\) in toluene solution from 384 to 369 nm and of \((\text{Hex}_2\text{Sn})_n\) from 398 to 382 nm. On the other hand, however, poly(dibutyl)stannane and poly(diaryl)stannane do not exhibit thermochromic behaviour in the temperature range between −10 to 90 °C and −20 to 90 °C, respectively.

**B. Polymers Containing Germanium in the Backbone**

**i. Germanium containing \(\sigma\text{-}\pi\)-conjugated linear chain polymers.** Polygermanes show interesting physical properties as a result of the \(\sigma\)-conjugation in the germanium backbone, whereas unsaturated organic polymers exhibit conductivity as a result of \(\pi\)-conjugation in the linear carbon chain. The combination of \(\sigma\) and \(\pi\)-conjugated structure fragments was expected to give access to a new class of polymers. A theoretical investigation on silicon- and germanium-containing linear chain polymers of the type \(29^{106}\) showed that the electronic properties of the germanium-containing polymers are close to those of the silicon-containing analogues.

\[
\left[ \text{MR}_2 \underset{n}{\cdots} \text{MR}_2 \underset{n}{\cdots} \text{Z} \right]
\]

(29)

\(\text{M} = \text{Ge, Si} \)
\(\text{R} = \text{H, Me, F} \)
\(\text{Z} = \text{CH=CH} \cdots, \text{C} \equiv \text{C} \cdots, \)

The calculated band gaps for \([\text{GeH}_2\text{GeH}_2\text{CH=CH}]_n\), \([\text{GeMe}_2\text{GeMe}_2\text{CH=CH}]_n\) and \([\text{GeF}_2\text{GeF}_2\text{CH=CH}]_n\) were estimated to amount to 3.22 eV, 3.06 eV and 2.93 eV,
respectively. For comparison, the calculated band gap for \[(\text{SiH}_2)_2\text{CH}═\text{CH}\] \(n\) was reported to be 3.07 eV. In polymers of the general formula \([\text{MR}_2-\text{MR}'_2-Z]_n\) (\(E = \text{Ge}, \text{Si}; R, R' = \text{H}, \text{CH}_3, p-\text{Tol}, \text{F}; Z = -\text{CH}═\text{CH}, -\text{C}≡\text{C}, -2,5-\text{C}_4\text{H}_2\text{S}\)) the highest-energy occupied band corresponds to a delocalised \(\sigma\) interaction along the polymer skeleton and the lowest-energy unoccupied band is related to a \(\text{C}−\text{C} \pi^*\) antibonding interaction. Some thiophene-based polymers with germanium in the backbone were prepared in order to study possible \(\sigma\)-\(\pi\)-conjugation along the polymer skeleton\(^{107−110}\). Compounds 30 and 31 represent two examples, in which alternating dialkylgermanium moieties and thiophene units build up the polymer skeleton\(^{109,110}\).

\[
\begin{align*}
\begin{array}{c}
\text{S} & \text{GeMe}_2 \\
\end{array} & \quad \begin{array}{c}
\text{S} & \text{GeBu}_2 \\
\end{array}
\end{align*}
\]

(30) \hspace{2cm} (31)

Wurtz-type coupling reactions of bis(halodiorganogermanium)-ethene, -thiophene and -benzene derivatives 32 were reported to give soluble polymers 33\(^{108}\) with molecular weights in the range of \(M_w = 2.1\) to \(3.3 \times 10^4\) (Scheme 18).

\[
\begin{align*}
\begin{array}{c}
\text{Me} & \text{Ge} & \text{Me} \\
\text{Cl} & \text{R} & \text{Cl} \\
\end{array} & \quad \begin{array}{c}
\text{Me} & \text{Ge} & \text{Me} \\
\text{R} & \text{R} & \text{Cl} \\
\end{array} & \quad \begin{array}{c}
\text{Me} & \text{Ge} & \text{Me} \\
\text{R} & \text{R} & \text{n} \\
\end{array}
\end{align*}
\]

(32) \hspace{2cm} (33) \hspace{2cm} R = \text{Me, Ph}

\[
\begin{align*}
\text{Ge} & \text{Ge} \\
\end{align*}
\]

SCHEME 18. Wurtz-type coupling of bis(halodiorganogermanium) derivatives

In a similar manner, digermanylene polymers 34 were prepared by the treatment of di-Grignard reagents with 1,2-dichlorotetramethyldigermane (Scheme 19)\(^{107}\). The molecular weights (\(M_w = 2.6\) to \(4.7 \times 10^3\)) of the polymers 34 were significantly lower compared with those of the digermanylene polymers 33\(^{108}\).

The molecular weights of the digermanylene polymers do not significantly influence the absorption properties of the polymers. The absorption spectra show \(\lambda_{\text{max}}\) values in the range of 244–260 nm depending on the \(\pi\)-electron system bridging the organogermanium moieties. These values are relatively low compared with \(\lambda_{\text{max}}\) values of 300–335 nm reported for polygermanes. In general, polymers composed of alternating digermanylene units and \(\pi\)-electron systems are insulators. Upon doping with an electron acceptor, the polymers can be switched from their neutral insulating state to a doped conducting state. For instance, upon doping with \(\text{SbF}_5\) or \(\text{I}_2\), the digermanylene polymers 33 and 34 show conductivities in the range of \(10^{-4} \, \text{S cm}^{-1}\). The polymers are light-sensitive,
which was demonstrated by the decrease in the intensity of the absorbance of a thin \([-\text{GeMe}_2-1,4-\text{C}_6\text{H}_4-\text{GeMe}_2-]\)_n film upon irradiation (\(\lambda = 254\ \text{nm}\)) at room temperature in air\(^{107}\). The decrease in the absorbance intensity was attributed to Ge–Ge bond cleavage and the formation of Ge–O–Ge fragments.

Poly[(germylene)diacetylenes] contain alternating \(-\text{GeR}_2-\) and diyne units in the polymer backbone. The reactions of dilithiobutadiyne or the corresponding di-Grignard reagent with diorganogermanium dibromides gave \([-\text{GeRR'}\equiv\text{C}≡\text{C}≡\text{C}]-\)_n (\(R, R' = \text{Me, Et, Ph}\) \(^{35}\)) in isolated yields of 50–87\% (Scheme 20).

The polymers \(^{35}\) are cream-coloured solids, which are soluble in common organic solvents. In contrast to pure organic polynes, the poly[(germylene) diacetylenes] \(^{35}\) are quite stable at higher temperatures. Thermally induced degradation reactions were observed only at temperatures above 150°\(C\). Weight-average molecular weights in the range of \(M_w = 2.3–3.1 \times 10^3\) were determined by gel permeation chromatography (GPC). These relatively low molecular weights correspond to degrees of polymerization in the range of \(n_w = 8–15\), depending on the substituents at germanium. The poly[(germylene)diacetylenes] \(^{35}\) were reported to be insulators, with conductivities in the range of \(10^{-12}–10^{-15}\ \text{S cm}^{-1}\). Upon doping with FeCl\(_3\) the conductivities increased to \(10^{-4}–10^{-5}\ \text{S cm}^{-1}\), which is comparable with conductivity values of conjugated organic polymers.

The pyrolysis of poly[(germylene)diacetylenes] \(^{35}\) under argon was studied\(^{112}\). At relatively low temperatures (150–250°\(C\)) cross polymerization through the triple bonds was observed and further heating to temperatures up to 1200°\(C\) provided crystalline
germanium clusters, together with a large amount of free carbon (40–61%). When the poly[(germylene)diacetylenes] were pyrolysed under an atmosphere of ammonia at 750 °C, germanium nitride, Ge₃N₄, and metallic germanium were formed. Another type of conjugated polymers, in which germole rings are incorporated into the polymer backbone, was recently reported by Tilley and coworkers. They prepared bis-p-halophenyl-2,5-germole monomers, which were polymerised via nickel-catalysed coupling to give oligo- and poly-2,5-diphenylgermoles of type (Scheme 21). The high molecular weight polymer (Mₘ = 2 × 10⁴) shows an absorption at λ_max of 442 nm, which is red-shifted with respect to that of (λ_max = 376 nm) and poly(diphenyl-1,4-cis-dienylene) (λ_max = 396 nm). It was suggested that the increased λ_max value of compared with the latter organic polymer results either from a decrease in the steric interactions along the polymer chain allowing better orbital overlap, or from a lowering of the LUMO level in the π-system by incorporation of the germole ring. Compound shows photoemission properties, suggesting potential applications in light-emitting devices.

ii. Polyferrocenylgermanes. Thermal ring-opening polymerization (ROP) was used to prepare high molecular weight poly(ferrocenyl)germanes (Scheme 22). This new class of polymers shows thermal stabilities, morphologies and electrochemical properties similar to those of poly(ferrocenyl)silanes, which have been reported earlier. In the thermal ROP process, the germanium bridged [1]ferrocenophanes are simply heated under vacuum to induce the polymerization. In comparison with ferrocene, the cyclopentadienyl rings in [1]dialkylgermaferrocenophanes are tilted against each other. The release of the steric strain by the polymerization process was reported to be the driving force to give linear polymers of the type [Fe(η⁵-C₅H₃R')₂GeR₂]ₙ (R' = H, SiMe₃). The temperature required for the polymerization largely depends on the substituent pattern at germanium and the organic substituents R at the cyclopentadienyl ring, e.g. Fe(η⁵-C₅H₄)₂GeMe₂ polymerises at 90 °C and Fe(η⁵-C₅H₄)₂GePh₂ at 230 °C. The molecular weights of polyferrocenylgermanes as determined by gel permeation chromatography (GPC) are usually in the range of 5.0 × 10⁴–2.0 × 10⁶ with varying polydispersities. It is noteworthy that GPC seems to underestimate the absolute molecular weight. Light scattering measurements on [Fe(η⁵-C₅H₄)₂GeMe₂]ₙ gave a value of M_w = 3.3 × 10⁶ for the absolute molecular weight, whereas that obtained from GPC measurements was M_w = 8.2 × 10⁵. The underestimation of the molecular weight by the use of GPC was also reported for high molecular weight polygermanes. Starting from [1]germaferrocenophane, Fe(η⁵-C₅H₄)₂GeMe₂ (41) and the corresponding [1]silaferrocenophane, Fe(η⁵-C₅H₄)₂SiMe₂ (40), the random poly(ferrocenyl)dime-thylsilane–poly(ferrocenyl)dime-thylgermane copolymer was prepared by thermal ROP as well as by transition metal-catalysed polymerization (Scheme 23). Virtually the same silane–germane copolymer was reported by Tanaka and coworkers, who studied the influence of different palladium and platinum catalysts on the transition metal-catalysed homo- and copolymerization of Fe(η⁵-C₅H₄)₂GeMe₂ and Fe(η⁵-C₅H₄)₂SiMe₂ under mild conditions.

A one-pot synthesis of homo- and copolymers of ferrocenyl-dialkylgermanes starting from dilithioferrocene and the corresponding dichlorogermanes R₂GeCl₂ (R = Me, Et, n-Bu) was reported by Pannell and coworkers. The [1]germaferrocenophanes thus formed were heated at 140 °C without isolation prior to the thermal treatment. The polymers thus obtained had molecular weights lower than those reported for polyferrocenylgermanes prepared from purified [1]germaferrocenophanes.

Glass transition temperatures (T_g) for the poly(ferrocenyl)germanes are in a wide range of −7 to +124 °C and were found to depend on the nature of the substituents at germanium and the substituents at the cyclopentadienyl rings. Cyclovoltammetric measurements of
SCHEME 21. Synthesis of a poly(2,5-diphenylgermole)
the polymers show two oxidation waves, which is consistent with an electronic coupling of the iron centres. In contrast, poly(vinylferrocene) does not show any coupling of the ferrocenyl moieties. The UV-vis spectra of poly(ferrocenyl)germanes in solution showed $\lambda_{\text{max}}$ values of approximately 448 nm for both the homopolymers containing unsubstituted cyclopentadienyl rings and the germane–silane copolymer. The $\lambda_{\text{max}}$ values are close to those of ferrocene ($\lambda_{\text{max}} = 440$) and bis(trimethylgermyl)ferrocene ($\lambda_{\text{max}} = 444$ nm). The ferroenophane $[\text{Fe}(\eta^5-C_5H_4SiMe_3)_2\text{GeMe}_2]_n$ shows a bathochromic shift to $\lambda_{\text{max}} = 474$ nm, which is near the value observed for tetrakis(trimethylsilyl)ferrocene ($\lambda_{\text{max}} = 484$ nm).
iii. Synthesis of germanium containing copolymers by ‘oxidation–reduction copolymerization’. An alternative route to the conventional methods for the preparation of germanium-containing polymers, which is based on an oxidation–reduction process starting from stable germylenes, was introduced by Kobayashi and coworkers. Diorganogermylenes containing substituents such as methyl, ethyl or phenyl polymerise spontaneously to give polygermanes. Thermally stable, monomeric germylenes are accessible by the use of bulky substituents, which prevent the self-oligomerisation and/or polymerization. The appropriate choice of the substituents at germanium allows the corresponding germylene to act as a reducing species which copolymerises with various oxidizing monomers such as aldehydes, p-benzoquinone derivatives, cyclic α,β-unsaturated ketones and cyclic sulphides to give high molecular weight polymers (43–46) ($M_w > 10^5$) containing the germanium atoms in the main chain. The reactions proceed smoothly under mild conditions and usually give one-to-one periodic polymers. A two-to-one periodic polymer (45) was obtained by the reaction of cyclic bis-amidogermylenes and p-benzoquinone derivatives. The reaction of germylenes with benzoquinones or cyclic sulphides proceeds without the use of any catalyst, acid scavenger or dehydrating agent. The polymerization of α,β-unsaturated ketones with germylenes is catalysed by various lithium salts, but not by sodium salts or radical initiators such as tetramethylpiperidinyloxyl (TEMPO) or 2,2-azobis-iso-butyronitrile (AIBN).

![Chemical structures](#)

Compounds 43–46 are representative examples of the polymers prepared by the ‘oxidation–reduction copolymerization route’.

All polymers exhibit a periodic rather than a random distribution of the starting monomers in the polymer backbone. Nevertheless, for each class of these polymers a different reaction mechanism was proposed. In case of the reaction
of bis[bis(trimethylsilyl)amido]germanium with benzoquinone derivatives, a biradical propagation mechanism was established\textsuperscript{124}. In the copolymerization, polymeric germyl radicals were detected by ESR spectroscopy and were quenched with the radical scavenger TEMPO.

The copolymers \textit{43} obtained by the reaction of bis[bis(trimethylsilyl)amido]germanium with benzoquinone derivatives are thermally stable and melt without decomposition. However, generally they undergo hydrolysis in a THF–water solution. An exception is the 2,5-di-\textit{t}-butylhydroquinone copolymer, which is stable towards hydrolysis\textsuperscript{124}. A totally different mechanism was proposed for the copolymerization of bis[bis(trimethylsilyl)amido]germanium with cyclic propylene sulphide\textsuperscript{128} (Scheme 24). The first step is an oxidative insertion of the germylene into a C−S bond to give a germathietane \textit{47}, which is converted to germathione \textit{48} by a loss of propylene. The germathione \textit{48} is unstable and reacts via ring-opening with the episulphide to give the zwitterion \textit{49}. The propagation proceeds via successive combination among the zwitterions to give the regular one-to-one copolymer \textit{50} with a S−Ge−S sequence.

\begin{equation}
\begin{align*}
R & \quad \text{Ge} \quad + \quad \text{Me} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \quad \text{Me} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \\
\quad \text{R} & \quad \text{R} \quad \text{Ge} \quad \text{S} \\
\quad \text{Me} & \quad \text{S} \end{align*}
\end{equation}

SCHEME 24. Proposed mechanism for the copolymerization of a propylene sulphide and bis[bis(trimethylsilyl)amido]germanium

The mechanism is only valid for systems which are capable of a propylene release. In contrast, the reactions of germynes with thietane gave regular one-to-one copolymers \textit{51} with a C−Ge−S sequence\textsuperscript{127} (Scheme 25).
The reaction mechanism proposed for the lithium-catalysed copolymerization of germylenes with cyclic ketones is based on the formation of germyl anions, which were formed by the coordination of the anion of the lithium salt to the germylene (Scheme 26). The germyl anion reacts with the ketone via a Michael-type addition to give an enolate anion. The latter enolate regenerates a germyl anion by reaction with the germylene. Alternating propagation leads to the regular one-to-one copolymer 52\textsuperscript{126,129}.

\[ \text{Ge} + \text{LiX} \rightarrow \text{Ge}^- \text{Li}^+ \]

\[ \text{Ge}^- \text{Li}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Ge} \text{Li}^+ \]

\[ \rightarrow \text{Ge} \text{Li}^+ \]

\[ \text{Ge} + \text{LiX} \rightarrow \text{Ge}^- \text{Li}^+ \]

\[ \text{Ge}^- \text{Li}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Ge} \text{Li}^+ \]

\[ \rightarrow \text{Ge} \text{Li}^+ \]

\[ \text{Ge} + \text{LiX} \rightarrow \text{Ge}^- \text{Li}^+ \]

\[ \text{Ge}^- \text{Li}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Ge} \text{Li}^+ \]

\[ \rightarrow \text{Ge} \text{Li}^+ \]

\[ \text{Ge} + \text{LiX} \rightarrow \text{Ge}^- \text{Li}^+ \]

\[ \text{Ge}^- \text{Li}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Ge} \text{Li}^+ \]

\[ \rightarrow \text{Ge} \text{Li}^+ \]

\[ \text{Ge} + \text{LiX} \rightarrow \text{Ge}^- \text{Li}^+ \]

\[ \text{Ge}^- \text{Li}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Ge} \text{Li}^+ \]

\[ \rightarrow \text{Ge} \text{Li}^+ \]

\[ \text{Ge} + \text{LiX} \rightarrow \text{Ge}^- \text{Li}^+ \]

\[ \text{Ge}^- \text{Li}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Ge} \text{Li}^+ \]

\[ \rightarrow \text{Ge} \text{Li}^+ \]

\[ \text{Ge} + \text{LiX} \rightarrow \text{Ge}^- \text{Li}^+ \]

\[ \text{Ge}^- \text{Li}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Ge} \text{Li}^+ \]

\[ \rightarrow \text{Ge} \text{Li}^+ \]

\[ \text{Ge} + \text{LiX} \rightarrow \text{Ge}^- \text{Li}^+ \]

\[ \text{Ge}^- \text{Li}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Ge} \text{Li}^+ \]

\[ \rightarrow \text{Ge} \text{Li}^+ \]

\[ \text{Ge} + \text{LiX} \rightarrow \text{Ge}^- \text{Li}^+ \]

\[ \text{Ge}^- \text{Li}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Ge} \text{Li}^+ \]

\[ \rightarrow \text{Ge} \text{Li}^+ \]

\[ \text{Ge} + \text{LiX} \rightarrow \text{Ge}^- \text{Li}^+ \]

\[ \text{Ge}^- \text{Li}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Ge} \text{Li}^+ \]

\[ \rightarrow \text{Ge} \text{Li}^+ \]

\[ \text{Ge} + \text{LiX} \rightarrow \text{Ge}^- \text{Li}^+ \]

\[ \text{Ge}^- \text{Li}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Ge} \text{Li}^+ \]

\[ \rightarrow \text{Ge} \text{Li}^+ \]

\[ \text{Ge} + \text{LiX} \rightarrow \text{Ge}^- \text{Li}^+ \]

\[ \text{Ge}^- \text{Li}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Ge} \text{Li}^+ \]

\[ \rightarrow \text{Ge} \text{Li}^+ \]

\[ \text{Ge} + \text{LiX} \rightarrow \text{Ge}^- \text{Li}^+ \]

\[ \text{Ge}^- \text{Li}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Ge} \text{Li}^+ \]

\[ \rightarrow \text{Ge} \text{Li}^+ \]

\[ \text{Ge} + \text{LiX} \rightarrow \text{Ge}^- \text{Li}^+ \]

\[ \text{Ge}^- \text{Li}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Ge} \text{Li}^+ \]

\[ \rightarrow \text{Ge} \text{Li}^+ \]

\[ \text{Ge} + \text{LiX} \rightarrow \text{Ge}^- \text{Li}^+ \]

\[ \text{Ge}^- \text{Li}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Ge} \text{Li}^+ \]

\[ \rightarrow \text{Ge} \text{Li}^+ \]

\[ \text{Ge} + \text{LiX} \rightarrow \text{Ge}^- \text{Li}^+ \]

\[ \text{Ge}^- \text{Li}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Ge} \text{Li}^+ \]

\[ \rightarrow \text{Ge} \text{Li}^+ \]

\[ \text{Ge} + \text{LiX} \rightarrow \text{Ge}^- \text{Li}^+ \]

\[ \text{Ge}^- \text{Li}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Ge} \text{Li}^+ \]

\[ \rightarrow \text{Ge} \text{Li}^+ \]

\[ \text{Ge} + \text{LiX} \rightarrow \text{Ge}^- \text{Li}^+ \]

\[ \text{Ge}^- \text{Li}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Ge} \text{Li}^+ \]

\[ \rightarrow \text{Ge} \text{Li}^+ \]

\[ \text{Ge} + \text{LiX} \rightarrow \text{Ge}^- \text{Li}^+ \]

\[ \text{Ge}^- \text{Li}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Ge} \text{Li}^+ \]

\[ \rightarrow \text{Ge} \text{Li}^+ \]

\[ \text{Ge} + \text{LiX} \rightarrow \text{Ge}^- \text{Li}^+ \]

\[ \text{Ge}^- \text{Li}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Ge} \text{Li}^+ \]

\[ \rightarrow \text{Ge} \text{Li}^+ \]

\[ \text{Ge} + \text{LiX} \rightarrow \text{Ge}^- \text{Li}^+ \]

\[ \text{Ge}^- \text{Li}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Ge} \text{Li}^+ \]

\[ \rightarrow \text{Ge} \text{Li}^+ \]

\[ \text{Ge} + \text{LiX} \rightarrow \text{Ge}^- \text{Li}^+ \]

\[ \text{Ge}^- \text{Li}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Ge} \text{Li}^+ \]

\[ \rightarrow \text{Ge} \text{Li}^+ \]

\[ \text{Ge} + \text{LiX} \rightarrow \text{Ge}^- \text{Li}^+ \]

\[ \text{Ge}^- \text{Li}^+ + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Ge} \text{Li}^+ \]

\[ \rightarrow \text{Ge} \text{Li}^+ \]
Polycarbogermane and polycarbostannane block copolymers \(56^{134}\) were prepared by pyrolysis of the organogermanium and organotin bridged \(p\)-cyclophanes \(55\) followed by deposition polymerization of the \(p\)-xylene monomers thus produced (Scheme 29).

C. Polymers Containing Tin in the Backbone

i. Polyferrocenylstannanes. In 1996, the synthesis of the first high molecular weight poly(ferrocenyl)stannane \([\text{Fe}(\eta^5-C_5H_4)_2\text{Sn(}t\text{-Bu})_2]_n\) \((58a)\) was reported by Manners and coworkers\(^{135}\). The polymer was obtained by ring-opening polymerization (ROP) of the \([1]\)stannaferrocenophane \(\text{Fe}(\eta^5-C_5H_4)_2\text{Sn(}t\text{-Bu})_2\) \((57a)\) (Scheme 30). Similarly, \([\text{Fe}(\eta^5-C_5H_4)_2\text{Sn(}2,4,6-(CH_3)_3C_6H_2)_2]_n\) \((58b)\) was prepared starting from the corresponding \([1]\)stannaferrocenophane \(57b^{136}\).

In principle, \([1]\)stannaferrocenophanes are promising candidates for ROP, although, as a result of the bigger covalent radius of tin, the ring strain is expected to be lower than in related silicon-containing derivatives. For \(57a\) the ring strain energy was estimated to be \(36(\pm 9) \text{ kJ mol}^{-1}\), which is approximately half of the value reported for organosilicon-bridged \([1]\)ferrocenophanes\(^{136}\). On the other hand, the bond between tin and the \textit{ipso}-carbon of the cyclopentadienyl ligand is weaker than in the corresponding \([1]\)silaferrocenophanes. High molecular weight polymers \(58a\) were obtained by thermally induced polymerization in the solid state \((M_w = 1.3 \times 10^5; M_w/M_n = 1.6)\) as well as in toluene solution at room temperature \((M_w = 9 \times 10^5; M_w/M_n = 1.6)\). The polymerization of \(57b\) proceeds significantly slower in comparison with the \(t\)-Bu2Sn-bridged analogue \(57a\), which can be explained by a lower ring strain energy of \(18(\pm 9) \text{ kJ mol}^{-1}\).
22. Organometallic polymers of germanium, tin and lead

Scheme 29. Polycarbogermane and polycarbostannane block copolymers

Scheme 30. Synthesis of poly(ferrocenyI)stannanes
of the former. Room-temperature ROP in benzene of 57b gave a high molecular weight polymer \( M_w = 1.35 \times 10^6 \); \( M_w/M_n = 1.3 \), but after 15 days only 50% of the monomers were converted. Thermal polymerization in the solid state of 57b quantitatively gave a lower molecular weight polymer \( M_w = 1.55 \times 10^5 \); \( M_w/M_n = 1.9 \). The [1]stannaferrocenophanes 57a and 57b both gave high yields of the cyclic dimer 59 when the ROP was carried out in CHCl₃.

![Diagram](image)

To date, the synthesis of strained [1]stannaferrocenophanes as precursors for ROP is restricted to compounds with bulky substituents at tin. Previous attempts to prepare tin-bridged ferrocenophanes by the reaction of dilithioferrocene with diorganotin dichlorides, \( \text{R}_2\text{SnCl}_2 \), containing less bulky substituents (\( \text{R} = \text{Me, Et, n-Bu, Ph} \)) resulted in the isolation of oligomers \( (M_n < 4.6 \times 10^3) \) and cyclic dimers. The crystal structure analyses of the [2]distannaferrocenophane 60 and the [3]tristannaferrocenophane 61, which are essentially unstrained, were also reported.

### ii. Homo- and heterobimetallic polycarbostannanes

Homometallic polycarbostannanes 63 were prepared starting from di(\( n \)-butyl)-di(4-pentenyl)stannane (62) via an acyclic diene metathesis reaction using both a molybdenum-alkylidene and an aryloxo tungsten catalyst (Scheme 31). Regardless of the catalyst, the polymerization proceeds smoothly and produces polymers with molecular weights of \( M_n = 1.6 \times 10^4 \) g mol\(^{-1} \). When the tungsten chloride catalyst is used, the organotin monomer simultaneously serves as cocatalyst and polymer precursor.

Similar to the synthesis of a germanium-containing poly(\( p \)-xylene) (PPX), the tin-containing block copolymer of unsubstituted PPX and a diorganotin bridged PPX were prepared (Scheme 29).

A heterobimetallic polycarbostannane 64 was obtained from the reaction of the bidentate \( \text{[Fe(CO)}_2\text{Cp–X–Cp(CO)}_2\text{Fe]}^{2–} \) \( (X = -\text{CHNM}_2\text{CHNM}_2{=}–) \) with \( \text{Ph}_2\text{SnCl}_2 \). The molecular weight as determined by osmometry was \( M_n = 8.5 \times 10^3 \) g mol\(^{-1} \), indicating relatively short chains. The reaction of the methylene-substituted dianionic...
iii. Organotin oxides. It is well established that diorganotin oxides (R₂SnO)ₙ, monooorganotin oxides (RSnO₁.₅)ₙ, and monooorganotin hydroxide oxides [RSn(OH)O]ₙ, containing small organic groups R such as Me, Et and n-Bu are polymeric, whereas bulky substituents stabilise oligomeric compounds. The polymeric stannoxanes are high-melting, insoluble, amorphous powders, the detailed structures of which are not known. On the basis of Mössbauer spectroscopy and solid state ¹¹⁹Sn NMR spectroscopy, the formation of cross-linked polymers containing five- and/or six-coordinate tin atoms was assumed.

iv. Polystannasiloxanes. Although metallasiloxanes containing Si–O–M linkages (M = main group as well as transition metals) are well known, reports on
polystannasiloxanes\textsuperscript{147–151} are rare. The synthesis of stannasiloxane block copolymers\textsuperscript{66} from sodium metasilicate $\text{Na}_2\text{SiO}_3$ and diorganotin compounds, such as di-$n$-butyltin oxide ($n$-$\text{Bu}_2\text{SnO}$), di-$n$-butyltin dimethoxide [$n$-$\text{Bu}_2\text{Sn(OMe)}_2$] and di-$n$-butyltin dichloride, were reported\textsuperscript{148} (Scheme 32). The silicon-to-tin ratio in the insoluble silicagel-like polymers varies in the range of 0.7–1.2 depending on the reaction conditions employed. On the basis of IR-spectroscopic measurements, the polymers were proposed to contain $\text{Si}–\text{O}–\text{Si}$, $\text{Si}–\text{O}–\text{Sn}$ and $\text{Sn}–\text{O}–\text{Sn}$ sequences.

\[
\text{Na}_2\text{SiO}_3 + n\text{-Bu}_2\text{SnX}_2 \rightarrow \begin{array}{c}
\text{Si} \begin{array}{c}O \\
\text{Sn} \begin{array}{c}O \\
\text{n-Bu} \\
\text{n-Bu}
\end{array}
\end{array}
\end{array}
\]

(Scheme 32. Synthesis of stannasiloxane block copolymers)

The first well-defined linear polystannasiloxane was reported in 1997. The reaction of $[\text{Ph}_2(\text{HO})\text{Si}]_2\text{O}$ with $t$-$\text{Bu}_2\text{SnCl}_2$ gave $[t$-$\text{Bu}_2\text{SnOSiPh}_2\text{OsiPh}_2\text{O}]_n$\textsuperscript{67} in high yield.

\[
[\text{Ph}_2(\text{HO})\text{Si}]_2\text{N} + t\text{-Bu}_2\text{SnCl}_2 \xrightarrow{\text{Et}_3\text{N}} 1/n[t\text{-Bu}_2\text{SnOSiPh}_2\text{OsiPh}_2\text{O}]_n
\]

A single crystal X-ray crystal structure analysis established a linear chain structure with both tin and silicon having tetrahedral configuration. In contrast to the polymeric structure found in the solid state, the stannasiloxane\textsuperscript{67} forms a six-membered ring in solution (Scheme 33).

\[
[t\text{-Bu}_2\text{SnOSiPh}_2\text{OsiPh}_2\text{O}]_n \rightarrow 1/n\begin{array}{c}
\text{Si} \begin{array}{c}O \\
\text{Sn} \begin{array}{c}O \\
\text{Ph} \\
\text{Ph}
\end{array}
\end{array}
\end{array}
\]

(Scheme 33. Structures of\textsuperscript{67} in the solid state and in solution)

III. POLYMER-SUPPORTED ORGANOTIN AND ORGANOGERMANIUM COMPOUNDS

Organotin compounds have become widely used reagents in organic syntheses\textsuperscript{83,86,88,152} which is a result of the special character of the tin–element bonds. For instance, tin–hydrogen, tin–oxygen and tin–carbon bonds are stable in air at room temperature but can be selectively cleaved under specific reaction conditions. Especially, organotin hydrides have become very popular reducing agents. Nevertheless, in recent years the toxicity of organotin and especially triorganotin compounds has been demonstrated\textsuperscript{153} which hampers the use of organotin reagents in the pharmaceutical industry and in
products which are potentially released into the environment. These drawbacks have initiated numerous attempts to prepare insoluble polymer-supported organotin reagents. The major advantage of these polymeric reagents is their easy separation from the reaction products. Thus, these compounds can be recovered and reconverted to the active tin species and their release to the environment is reduced to a minimum. A drawback of the heterogenous reaction is often the longer reaction time required compared with the analogous homogenous reaction. Furthermore, the structural characterization of the active tin sites inside the polymer is difficult to achieve.

Inorganic matrices and insoluble as well as soluble organic polymers are used as polymer supports (P). Recently, the applications of insoluble polymer-supported organotin reagents in organic synthesis have been reviewed\[154]. Other potential applications of polymer-supported organotin compounds include antifouling reagents, modifiers for rubbers used in tyre manufacturing and precursors for SnO₂. In contrast to organotin compounds, polymer-supported organogermainium compounds have attracted less attention and we are not aware of polymer-supported organolead compounds.

In this section new advances and novel synthetic methods, potential applications and structure elucidation techniques in the field of polymer-supported organotin and organogermainium compounds are presented.

**A. Polymer-supported Organotin Compounds**

1. **Syntheses**
   
   **i. Inorganic solid supports.** A promising approach to preparing insoluble organotin reagents which can easily be recovered by filtration is the anchoring of functionalised organotin compounds to inorganic matrices. The immobilised organotin reagents \[68\] and \[69\] were prepared starting from aluminium oxide and silica gel\[155,156\].

   \[
   \text{Si(OMe)_2(CH}_2 \text{)_5 SnBu}_2 \text{HOSiO}_2 \tag{69}
   \]

   \[
   \text{Si(OCH}_2 \text{)}_3 \text{SnBu}_2 \text{HOSiO}_2 \tag{68}
   \]

   The amount of active organotin hydride species in the \(\text{Al}_2\text{O}_3\) matrix (\[68\]), as determined by reaction with \(\text{CH}_3\text{I}\), was only 0.17 mmol g\(^{-1}\) \(\text{Al}_2\text{O}_3\) support\[155\]. Nevertheless, 1,1-dichloro-2,2-diphenylcyclopropane was almost quantitatively reduced to 1,1-diphenylcyclopropane. After recovering and reconveting the polymer-supported organotin halide into the corresponding organotin hydride \[68\] by reaction with diisobutyl aluminium hydride, the activity is almost halved with respect to the starting material. The silica-linked polymer \[69\] efficiently functions as an in situ prepared hydride transfer reagent for the reduction of carbonyl compounds using polymethylhydrosiloxane (PMHS) as hydrogen source\[156\]. After use and recovery of the polymer-supported organotin compound, no significant loss of activity was observed.

   **ii. The polymer resin functionalization route.** In contrast to the rather limited work on inorganic matrices as supports, the functionalization of a prebuild polymer was widely investigated. Usually, a cross-linked polystyrene is used as starting material and the organotin species are linked to the aryl groups of the polymer either directly or via alkyl spacers (Scheme 34).
An early example for the direct coupling of a tin reagent to Amberlite XE 305, a macroporous polystyrene, was reported by Crosby and coworkers\textsuperscript{157}. The synthetic route is shown in Scheme 35. Reaction of the polymer-supported diorganotin dihydride \textsuperscript{70} with iodoctane to give octane indicated a minimum content of 2 mmol tin hydride per gram of the polymer.

The polymer-supported organotin dihydride \textsuperscript{70} was shown to be an efficient reducing agent for aldehydes and ketones, but substantial loss of activity was observed after regeneration. More recently, various polymer-supported butyltin reagents (\textsuperscript{71}, \textsuperscript{72}) were studied as reagents for the acetylation of sucrose\textsuperscript{158}.

The polymer-supported butyltin dichloride was shown to catalyse the acetylation of sucrose to give 6-\textit{O}-acetyl sucrose in 59\% yield. The yield obtained was close to that previously reported for the same synthesis using (\textit{n}-Bu\textsubscript{2}SnO\textsubscript{n}) as catalyst\textsuperscript{159}. The polymer-supported organotin catalyst was regenerated without significant loss of activity by reaction with acetyl chloride. In contrast to (\textit{n}-Bu\textsubscript{2}SnO\textsubscript{n}) no regioselectivity towards acetylation of sucrose at the C-6 position was observed.

In polymer-supported organotin compounds the −CH\textsubscript{2}CH\textsubscript{2}− spacer has been widely used for the anchoring of active tin moieties to the polymer support. In contrast, the −CH\textsubscript{2}− spacer proved to be unsuitable, since the C−Sn bond of a stannyl group in the benzyl position is easily cleaved\textsuperscript{160−166}. A general method for the preparation of P−CH\textsubscript{2}CH\textsubscript{2}−SnBu\textsubscript{2}H starts from Amberlite XE 305, which is converted to P−CH\textsubscript{2}Cl

\[ \text{Scheme 34. Organotin-functionalised polystyrene} \]

\[ \text{Scheme 35. Synthesis of a polymer-supported diorganotin dihydride starting from Amberlite XE 305} \]
by chloromethylation. Wittig-type vinylation was used to prepare \( \text{P-CH=CH}_2 \), followed by hydrostannation with Bu\(_2\)SnHCl to give \( \text{P-CH}_2\text{CH}_2\text{SnBu}_2\text{Cl} \). The tin chloride was transformed to \( \text{P-CH}_2\text{CH}_2\text{SnBu}_2\text{H} \) by reaction with LiAlH\(_4\). This rather specific route is limited to the \(-\text{CH}_2\text{CH}_2-\) spacer and therefore a more convenient and general reaction sequence was developed by Dumartin and coworkers\(^{167,168}\) (Scheme 36). They prepared polymer-supported organotin hydrides in which the stannyl group is linked to the polymer via methylene spacers of various lengths. The functionalised polystyrenes were prepared from lithiated Amberlite XE 305, which was reacted either with Br(CH\(_2\))\(_n\)Cl \((n = 3, 4)\) or with ethylene oxide \((n = 2)\), followed by halogenation with PPh\(_3\)/CCl\(_4\) or Me\(_3\)SiCl/NaI. The polymer-supported halogenoalkanes \(73\) were transformed into the polymer-supported tin hydrides \(75\) by reaction with Bu\(_2\)SnHLi. An alternative route is the reaction of \(73\) with (i) Bu\(_2\)SnPhLi and (ii) I\(_2\) to give the polymer-supported tin iodide \(74\), which in turn reacts with NaBH\(_4\) to give \(75\).

\[
\begin{align*}
\text{Amberlite XE 305} & \quad \xrightarrow{\text{BuLi, TMEDA}} \quad \text{P} \quad \xrightarrow{\text{Li}} \quad \text{P} \\
\text{Br(CH\(_2\))\(_n\)Cl} & \quad \xrightarrow{n = 3,4} \quad \text{P} \quad \xrightarrow{\text{i) PPh\(_3\)/CCl\(_4\)}} \quad \text{P} \\
\text{P} \quad \xrightarrow{(\text{CH\(_2\)))\(_n\)SnBu\(_2\)H} & \quad \xrightarrow{\text{Bu\(_2\)SnHLi}} \quad \text{P} \\
\text{NaBH\(_4\)/EtOH} & \quad \xrightarrow{\text{i) Bu\(_2\)SnPhLi}} \quad \text{P} \\
\text{P} \quad \xrightarrow{(\text{CH\(_2\)))\(_n\)SnBu\(_2\)I} & \quad \xrightarrow{\text{ii) I\(_2\)}} \quad \text{P} \\
\end{align*}
\]

**SCHEME 36. Synthesis of polymer-supported tin hydrides**

The minimal tin loadings of the polymer supported tin hydrides \(75\) were found to be in the range of 0.9–1.4 mmol SnH g\(^{-1}\), which is comparable with the activity of the polymer-supported and \(-\text{CH}_2\text{CH}_2-\) linked dibutyltin hydride reported by Neumann and coworkers\(^{160,169}\). The advantage of the use of alkyl sequences longer than the \(-\text{CH}_2\text{CH}_2-\) spacer is the prevention of \(\beta\)-elimination in free-radical processes.

**iii. The monomer polymerization route.** Compared with the resin-functionalization route, the homo- and copolymerization of organotin-containing monomers permits one to influence the polymer resin structure to a greater extent. In principle, it is possible to prepare gel-type, macroporous, microporous or nonporous polymers. The pore structure, tin loading, solubility and other factors which influence the reactivity of the polymer-supported organotin reagents can be controlled by appropriate
copolymorization processes of carefully chosen monomers. Thus, physical properties of organotin-containing polymers, being important for materials applications, can be fine-tuned. In order to mimic the properties of commercial macroporous polystyrenes such as Amberlite XE 305, the copolymerization of monomeric tin-containing styrene derivatives and divinylbenzene were carried out. Neumann and coworkers copolymerised [(2-vinylphenyl)ethyl]dibutyltin chloride and divinylbenzene (ca 10%) to prepare the macroporous cross-linked polymer, which was converted into the polymer-supported tin hydride by using di-n-butylaluminium hydride. A tin-loading of 1.55 mmol SnH g$^{-1}$ was obtained for the polymer. The copolymerisation of [(2-vinylphenyl)ethyl]triphenyltin with vinyl-containing comonomers in the presence of divinylbenzene was also reported. The triphenyltin-containing polymer was chemically modified to give functionalised polymer-supported organotin compounds of type $\text{P(}\text{CH}_2\text{)}_2\text{SnBu}_2\text{X}$

<table>
<thead>
<tr>
<th>$\text{X}$</th>
<th>$\text{Y}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>(76)</td>
</tr>
<tr>
<td>H</td>
<td>(77)</td>
</tr>
<tr>
<td>Ph, Br, OMe</td>
<td>(78)</td>
</tr>
<tr>
<td>OMe, Y = Cl, Br</td>
<td></td>
</tr>
</tbody>
</table>

A mixture of $m$- and $p$-substituted [(2-di-n-butylchlorostannyl)ethyl]styrene was copolymerised with different amounts of styrene and a mixture of $m$- and $p$-substituted divinylbenzene (Scheme 37). The copolymers are granular colourless solids, which are insoluble but swellable in both protic and aprotic solvents. The proportions of the organotin monomer used in the starting reaction mixtures corresponded to 94, 73 and 25 wt%. The values of the monomeric units in the polymers as estimated by argentometric titration (Cl/g polymer) were lower than expected and were found to be 68, 46 and 10 wt% (yield 50–75 wt%). Under the reaction conditions employed, the organotin monomer is not quantitatively incorporated into the polymer matrix. Deleuze and coworkers examined the copolymerization of the same system, but used pure isomers of $p$-[(2-di-n-butylchlorostannyl)ethyl]styrene and $p$-divinylbenzene or $m$-divinylbenzene instead. The resulting tin-loading of the polymer was much closer to the monomer ratio in the reaction mixtures than that reported for the copolymerization of mixed isomers. The high permanent porosity of the supports obtained enable the polymer-supported organotin chlorides to reduce 1-bromoadamantane using NaBH₄ as hydride source. The reactivity of the polymer-supported organotin chloride is comparable with that of tributyltin chloride. The polymer-supported organotin chloride exhibits a relative high intrinsic stability, as was shown by several uses without loss of activity and without need of regeneration.

The polymer was reacted with sodium hydroxide in EtOH/H₂O to give a mixture of stannol and distannoxane moieties in ratios depending on the tin-loading capacities of the starting polymers. The ratio was not changed upon heating at reflux the polymer in a benzene/water mixture. The trend of decreasing distannoxane-to-stannol ratio with decreasing tin-loading capacity is in accordance with a lower ‘effective concentration’ of the tin monomers in the copolymer as a result of dilution with styrene. Two stannol moieties, which are close to one another, can form distannoxanes by a condensation reaction, whereas isolated stannols remain unchanged. The reaction of the polymer-supported di-n-butyltin chloride with sodium 4-methylbenzoate was also reported. The resulting tethered carboxylate displayed poor stability and reacted under protic conditions to give 4-methylbenzoic acid. Tributyltin-3-$p$-vinylphenylpropionate (TBTSP)
SCHEME 37. A monomer polymerization route to polymer-supported organotin reagents

(83) was homo- and copolymerised with styrene, affording polymer-supported organotin compounds in which a tributyltin moiety is linked via a carboxylate group to a polystyrenic support.
The homopolymerization of 83 gave a soluble polymer of relatively low molecular mass \( M_n = 8.4 \times 10^3 \), but the average molecular weight increased with increasing content of styrene co-units in the copolymer. For a TBTSP-to-styrene ratio of one-to-four, a polymer with \( M_n = 1.5 \times 10^4 \) was obtained.

Other trialkyltin-containing monomers such as 3-tributyltinstyrene (84), tributyltin methacrylate (85) and \{4-[bis(trimethylstannyl)methyl]styrene\} (86) were also reported to homo- and copolymerise with styrene under radical conditions. In addition, 3-tributyltinstyrene (84) was copolymerised under radical conditions with ethyl acrylate, methyl methacrylate, vinyl acetate and acrylonitrile. A functional methacrylate-based polymer was prepared by the copolymerization of the triorganotin methacrylate monomer 87 with styrene and divinylbenzene.

In order to prepare non-styrenic polymer-supported organotin chlorides, which are expected to show physical properties such as mechanical strength, polarity and porosity different from those of polystyrene-based supports, Deleuze and coworkers copolymerised dibutyl[3-(allyloxy)propyl]tin chloride with N-phenylmaleimide (PMI) and 1,1′-(methylene-4,1-phenylene)bismaleimide (MPBMI) to prepare the polymers 88a and 88b.

\[
\begin{align*}
\text{(84)} & \quad \text{(85)} \\
\includegraphics[width=0.2\textwidth]{84.png} & \quad \includegraphics[width=0.2\textwidth]{85.png}
\end{align*}
\]

\[
\begin{align*}
\text{(86)} & \quad \text{(87)} \\
\includegraphics[width=0.2\textwidth]{86.png} & \quad \includegraphics[width=0.2\textwidth]{87.png}
\end{align*}
\]

\[
\begin{align*}
\text{(88a)} & \quad \text{(88b)} \\
\includegraphics[width=0.2\textwidth]{88a.png} & \quad \includegraphics[width=0.2\textwidth]{88b.png}
\end{align*}
\]
It turned out that the insertion of the organotin compound into the polymer 88a did not exceed 16 mol%, regardless of the monomer feed. Various insoluble polymers 88b were prepared by the radical copolymerization of dibutyl[3-(allyloxy)propyl]tin chloride, PMI, as a chain diluent, and MPBMI as cross-linking agent. These polymers exhibited higher swelling capacities in toluene than those of macroporous organotin-functionalised polystyrene resins\textsuperscript{174}. The rather low specific surface areas as determined by BET analyses were in the range of 3–23 m\textsuperscript{2} g\textsuperscript{−1} indicating the polymer structure to be more gel-type than expected, which in turn is the result of the poor cross-linking ability of the bismaleimide under the polymerization conditions employed. The activity of the polymer-supported organotin chloride 88b was demonstrated in the reduction of 1-bromoadamantane using NaBH\textsubscript{4} as primary hydride source. The polymer could be recycled and used several times without significant loss of activity. A drawback was the relatively high extent of tin-leaching during the reduction process (ca 0.5–0.8% per run), which was attributed to the high reaction temperatures of 95 °C.

\textit{iv. Anionic polymerization.} Anionic oligomerization of ethylene or styrene followed by electrophilic substitution of the resulting anionic polymer with tin halides such as tin tetrachloride, \textit{n}-butyltin trichloride, \textit{di}-\textit{n}-butyltin dichloride and diphenyltin dichloride, respectively, was reported\textsuperscript{181}. The resulting linear macromolecules which are soluble in common organic solvents contain organotin moieties at one chain end. In a typical synthetic procedure, the oligomerization of ethylene with \textit{n}-butyllithium as initiator was followed by treatment of the resulting suspension of living polyethylene with \textit{di}-\textit{n}-butyltin dichloride at −78 °C. The product was separated from any insoluble by-products by extraction with hot toluene. Similarly, tin-containing polybutadiene and polystyrene–polybutadiene copolymers were prepared by anionic polymerization and with trialkyltin chlorides as end-capping reagents, giving tin-modified rubbers which are used for tyre manufacturing\textsuperscript{182–186}. 

(88b)
2. Applications

i. Organic synthesis. As a result of both the economical and ecological considerations mentioned before, organic syntheses on solid phases have become an established method for synthetic organic transformations\textsuperscript{187}. Polymer-supported organotin reagents were shown to be as efficient as their soluble counterparts in various organic transformations. The advantages of the polymer-supported reagents are that (i) the amount of toxic organotin species released into the environment is minimised and (ii) the reagents can easily be separated from the reaction mixtures and regenerated for repeated use. On the other hand, depending on the nature of the support, longer reaction times are often required as a result of diffusion-controlled reactions. The most common reaction to test the practical value of polymer-supported organotin hydride reagents is the dehalogenation of alkyl halides. The results are compared with those obtained by the use of Bu$_3$SnH as a soluble hydride transfer reagent. After the reaction, the polymer is recovered, regenerated and used again in the same standard reaction\textsuperscript{154,167–169,174,180} (Scheme 38).

\[ \text{Scheme 38. Test for multiple use of polymer-supported organotin hydrides} \]

A variety of other alkyl and aryl halides were successfully dehalogenated by polymer-supported organotin hydrides even in the presence of functional groups\textsuperscript{155,157,160,168,169,181,188}. Two representative examples are shown in Scheme 39.

\[ \text{Scheme 39. Dehalogenations using a polystyrene-supported tin hydride (P-SnH)\textsuperscript{169}} \]
The dehalogenations of 3-bromocamphor and 1-bromoadamantane were reported to be efficient both by using a triorganotin hydride which is linked to the polymer support via a \(-\text{CH}_2\text{CH}_2-\) spacer\(^{169}\), and by using a diorganotin dihydride, which is directly bound to the support\(^{157}\). The latter reagent showed significant loss of activity (40%) after regeneration whereas the former was used repeatedly without loss of activity. The polymer-supported diorganotin dihydride was also shown to reduce aldehydes and ketones. For example, benzaldehyde was converted into benzyl alcohol in a 91% yield. However, in this case the regeneration appeared to be even worse as compared with the reduction process of organic halides. Only 30% of the diorganotin dihydride content was regenerated and decomposition of the polymer-supported tin compound was observed\(^{157}\).

Polystyrene-supported organotin hydrides were successfully used in the dehydroxylation of various secondary alcohols according to the Barton-type reaction\(^{160,169,189}\). The secondary hydroxyl group is transformed into a thiono group, which in turn is reduced by the organotin hydride reagent in a free-radical chain reaction to give the corresponding alkane. The synthesis of 5-cholestene is given as an example in Scheme 40. The polymer-supported organotin hydride \(\text{P-CH}_2\text{CH}_2-\text{SnBu}_2\text{H}\) is an excellent substitute for the Bu\(_3\)SnH usually used in such reactions.

The same polymer-supported organotin reagent was also used in the Barton-type deoxygenation of steroid derivatives, sugar derivatives and diols\(^{160}\). Furthermore, the radical deamination of secondary and tertiary amines via the corresponding isocyanides was also reported\(^{160,169}\).

The search for other reactions in which a polymer-supported organotin hydride is capable of substituting Bu\(_3\)SnH as radical source has led to the application of \(\text{P-CH}_2\text{CH}_2-\text{SnBu}_2\text{H}\) for the ring enlargement of dichloromethylcyclohexadienones. Two out of twelve examples\(^{190}\) for the preparation of tropone ring systems are shown in Scheme 41.

The Giese-type reaction is another example for a free-radical reaction in which Bu\(_3\)SnH was replaced by a polymer-supported organotin hydride. The free-radical chain coupling of alkyl and aryl radicals with electron-deficient olefins requires a low stationary concentration of the organotin hydride. The carbon–carbon coupling reaction of cyclohexyl halides with acrylonitrile was carried out to give cycloC\(_6\)H\(_{11}\)(CH\(_2\))\(_2\)CN, being almost free of tin by-products\(^{165}\), but the conversion rates were rather low when compared with conventional methods using Bu\(_3\)SnH. The best results were obtained when the polymer-supported organotin hydride was generated \textit{in situ} and in a low steady-state concentration from the corresponding polymer-supported organotin chloride and NaBH\(_4\). The \textit{in situ} preparation of polymer-supported organotin hydrides starting from the corresponding organotin chloride and sodium borohydride was also applied for the reduction of 1-bromoadamantane (activity test)\(^{174}\) and for the synthesis of 2-alkoxytetrahydrofuranes\(^{178,179}\). The latter synthesis started from bromoacetals and the intramolecular radical cyclization gave tetrahydrofuran derivatives, which in turn are precursors for \(\gamma\)-butyrolactones (Scheme 42).

Organotin hydrides are used to generate stannyl radicals, which in turn initiate radical chain reactions. However, the presence of high contents of organotin hydrides in the reaction mixture can be disadvantageous since tin hydrides are known to be strong radical scavengers. Neumann and coworkers suggested the use of polymer-supported distannanes\(^{164,166}\) as radical source to circumvent this problem. Polymer-supported distannanes \(\text{90}\) with tin loadings of 0.95–1.13 mmol g\(^{-1}\) were prepared by treatment of the organotin halide resins \(\text{89}\) with lithium naphthalenide and sodium naphthalenide\(^{166}\).
SCHEME 40. Barton-type deoxygenation using a polymer-supported organotin hydride
SCHEME 41. Ring enlargement of dichloromethylcyclohexadienones using a polymer-supported organotin reagent

SCHEME 42. Intramolecular radical carbocyclisations to give furan derivatives

respectively (Scheme 43). These reducing agents proved to be superior to the initially used magnesium-anthracene. The polymer-supported distannane was used as a source of stannyl radicals in several radical cyclization reactions, such as the photochemical radical chain addition of \( t \)-butyl iodide to acetylenes yielding the \( Z/E \) mixture of alkenes or the photochemical cyclization of citronellyl bromide to give menthane in high yields (Scheme 44).

The one-step preparation of \( \gamma \)-butyrolactones starting from an acyclic \( \alpha \)-iodo ester was also investigated by using the polymer-supported distannane as radical source. The \( \gamma \)-butyrolactone was formed in 35% yield and contained 61% of the reduced \( \alpha \)-haloester (Scheme 45).

The palladium-catalysed carbon–carbon cross-coupling reaction of organotin reagents with a variety of organic electrophiles has found various synthetic applications (the Stille reaction). Usually, only one organic group from the tetraorganotin reagent is
SCHEME 43. Preparation of the polymer-supported distannane 90

SCHEME 44. Polymer-supported distannane 90 as radical source in organic reactions

SCHEME 45. Polymer-supported distannane 90 for the synthesis of γ-butyrolactones
transferred since compounds of the type $R_3SnX$ are quite unreactive under the reaction conditions employed (Scheme 46).

$$R_3Sn \rightarrow R' + R'' \xrightarrow{\text{Pd-cat.}} X \rightarrow R' + R'' \rightarrow R_3SnX$$

$X = \text{Cl, Br, I, Tf}$

$R = \text{alkyl}$

$R' = \text{alkyl, vinyl, aryl, alkynyl}$

$R'' = \text{allyl, vinyl, aryl}$

**SCHEME 46.** The Stille-type reaction

A major drawback of this reaction is the formation of equimolar amounts of rather toxic trialkyltin by-products. Kuhn and Neumann investigated polystyrene-supported tin reagents for the Stille-type reaction\textsuperscript{163}. Therefore, immobilised organotin chlorides ($91a$) and hydrides ($91b$) were transformed to polymer-supported Stille-type reagents by reaction of the polymer-supported organotin chlorides $91$ with various Grignard reagents or by hydrostannation reactions of the polymer-supported organotin hydrides with terminal alkynes, respectively (Scheme 47). The polymer-supported reagents $92$ and $93$ were used successfully in the Stille-type coupling with electrophiles such as acyl chlorides, vinyl iodides and vinyl triflates\textsuperscript{163}.

**SCHEME 47.** Polymer-supported Stille-type reagents

A polymer-supported allyltin derivative was also reported to undergo a Lewis-acid-catalysed addition to benzaldehydes to give products such as 1-phenylbut-3-en-1-ol and 1-($p$-bromophenyl)but-3-en-1-ol\textsuperscript{154}.

The polymer-supported random stannol/stannoxane copolymer $94$ was shown to catalyse the lactonisation of hydroxycarboxylic acids\textsuperscript{170}. 

$$\text{P} - \xrightarrow{(CH_2)_2} \text{Sn} \rightarrow \text{Bu}$$

a: $X = \text{Cl}$

b: $X = \text{H}$

$$\text{P} - \xrightarrow{(CH_2)_2} \text{Sn} \rightarrow \text{R} \rightarrow \text{Bu}$$

$$\text{P} - \xrightarrow{(CH_2)_2} \text{Sn} \rightarrow \text{CH} = \text{CH} \rightarrow \text{R}' \rightarrow \text{Bu}$$

$R = \text{C} \equiv \text{CPh}, \text{CH} = \text{CH}_2, \text{CH} \equiv \text{CHCH}_3$

$R' = \text{CO}_2\text{Me}, \text{CO}_2\text{H}$
While the optimal yields of the isolated lactones were comparable with the yields obtained using conventional tin-based catalysts such as hexa–n-butyldistannoxane, n-dibutyltin oxide, tri–n-butylcholorostannane or tri–n-butylmethoxystannane, the solid phase reaction offers the advantage of a simplified purification procedure\(^{170}\). The catalytic trans-esterification using solid polymer-supported organotin alkoxides was also reported\(^{171}\). The catalyst could be recovered without significant loss of activity or leaching of organotin compounds from the polymers.

**ii. Radiopharmaceuticals.** Radiopharmaceuticals are drugs which contain unstable nuclei emitting particles or photons. They are used as imaging agents for diagnostic purpose and in radiotherapy of various diseases. Triorganotinal and -vinyl compounds are selectively cleaved by iodine to give iodoaryls and iodoxynils under fairly mild conditions, making organotin reagents promising precursors to prepare pharmaceuticals containing radioactive iodine isotopes. However, the complete removal of the toxic triorganotin by-products from the pharmaceutical product is a serious problem difficult to overcome by conventional separation techniques. Therefore, the use of polymer-supported organotin reagents as intermediates in the synthesis of radiopharmaceuticals was examined\(^{154,192–198}\). In principle, the organic precursor is anchored to the polymer support via the triorganotin moiety and in a subsequent step the radiopharmaceutical is released into solution by tin–carbon bond cleavage. Radioiodinated vinyl iodides were prepared by reaction of the polymer-supported organotin hydride \(\text{P}–\text{CH}_2\text{CH}_2–\text{SnBu}_2\text{H}\) with terminal alkynes to give the polymer-supported tin vinyl compounds \(\text{P}–\text{CH}_2\text{CH}_2–\text{SnBu}_2\text{Vinyl}\), subsequently followed by radio-demetallation of the latter with \(\text{Na}^{125}\text{I}\) and chloramine T as oxidant\(^{197}\). Similarly, the polymer-supported organotin hydride \(\text{P}–(\text{CH}_2)_4–\text{SnBu}_2\text{H}\) was used in reaction sequences to study the iodo-demetallation reaction of polymer-bound pharmaceuticals\(^{152,154,193}\). Four representative examples of radioactive substances prepared via polymer-supported organotin compounds are given below.

Hunter and coworkers started from the polymer-supported organotin chloride \(^{95}\), which was reacted with aryllithium compounds to give precursors for radioiodinated pharmaceuticals\(^{192,195,196,198}\).

The syntheses of \(^{123}\text{I}-\) and \(^{131}\text{I}-\)labelled \(\text{N}\)-isopropyl-4-idoamphetamine and \(^{123}\text{I}\)-labelled \(\text{m}\)-iodobenzylguanidinium, \([^{123}\text{I}]{\text{MIBG}}\), were reported. The synthesis of \([^{123}\text{I}]{\text{MIBG}}\) \(^{192}\), which has found application in nuclear medicine either as an imaging agent for diagnosis or as a therapeutic agent for neutral crest tumors, is shown in Scheme 48.

**iii. Applications in tyre manufacturing.** Two important properties of tyres are the so-called rolling resistance and the wet grip, which both depend on the physical characteristics
of the polymeric material used in the manufacturing process. The properties of some organotin-containing polymers have recently been investigated, since the incorporation of organotin groups changes the performance characteristics of elastomers used for tyres. Among these polymers, tin-containing polybutadiene and styrene–butadiene copolymers have attracted most attention\(^\text{182–186,199}\), but in addition derivatives such as polyisoprene and \(\alpha\)-methylstyrene were also investigated\(^\text{182}\). In a typical synthetic procedure, living anionic polymerization of 1,3-butadiene or 1,3-butadiene/styrene mixtures was followed by the addition of various tin chlorides. Tributyltin chloride was added in order to end-cap the polymer chains, whereas the addition of tin tetrachloride provided star-shaped polymer structures. The latter process was followed either by addition of trialkyltin chlorides to end-cap the polymers with trialkyltin groups or by addition of an antioxidant to terminate the polymerization and to end-cap the polymers with methyl groups\(^\text{182}\). One-dimensional \(^{119}\)Sn NMR and \(^1\)H/\(^{13}\)C/\(^{119}\)Sn triple-resonance three-dimensional NMR studies of organotin-containing polybutadienes were carried out to provide information on the microstructure of the organotin-containing polymers\(^\text{183,184,199}\).

**iv. Tin dioxide formation.** Tin dioxide, \(\text{SnO}_2\), is a promising material for light-transmitting electrodes in optoelectronic devices as a result of its optical transparency and its electronic conductivity. Furthermore, the high chemical stability of \(\text{SnO}_2\) makes it a valuable coating material. On the other hand, its high chemical stability prevents patterning of \(\text{SnO}_2\) thin films by wet etching. Starting from various precursors, dip-coating followed by hydrolysis, chemical vapour deposition, spray pyrolysis and sputtering are suitable methods for the preparation of \(\text{SnO}_2\) thin films. Alternatively, soluble organotin polymers are promising precursors for the preparation of \(\text{SnO}_2\) thin films and their use was suggested to solve the problem of patterning by lithographic techniques\(^\text{177,200–202}\). For example, a thin film of poly\{4-[(trimethylstannyl)methyl]styrene (96)\} was spincoated on quartz plates from its toluene solution, dried, irradiated and pyrolysed to give a \(\text{SnO}_2\) thin film without any cracks or peeling\(^\text{202}\). In contrast, pyrolysis of the same polystyrene derivative without irradiation did not give \(\text{SnO}_2\), but low molecular weight organotin compounds which escaped from the quartz plate by evaporation.
SCHEME 48. Synthesis of $^{[131]}$MIBG via the polymer-supported organotin chloride.
It was suggested that the irradiation causes homolytic cleavage of the benzylic Sn−C bonds in 96 giving rise to formation of a cross-linked organic network. This network is insoluble and tin species are thought to be trapped in it. Upon heating, the cross-linked polymer film functions as a matrix for the organotin precursors of SnO₂ and is completely removed after pyrolysis (Scheme 49).

\[
\text{SnMe}_3 \xrightarrow{\Delta} \text{SnO}_2 + \text{cross-linked network + tin species}
\]

SCHEME 49. Preparation of SnO₂ via poly[4-[(trimethylstannyl)methyl]styrene (96)

3. Leaching of organotin compounds

As mentioned before, the toxicity of organotin compounds is the major drawback of organotin reagents and, despite its synthetic utility, it prevents its entry to the pharmaceutical industry and questions the application of organotin compounds in products from which they can be released into the environment. Polymer-supported organotin reagents are suggested to reduce the tin contamination of the final products almost to zero. Without any doubt, the tin contamination of products prepared by using immobilised organotin reagents is very low when compared with the same product prepared by the use of a soluble organotin reagent, e.g. the reduction of 3-iodocholestene (1.45 mmol) with Bu₃SnH gave 5-cholestene in 75% isolated yield after one recrystallization. The 5-cholestene was highly contaminated with tin (7000 ppm). In order to reduce this contamination to 45 ppm, four recrystallization cycles were needed. Using the polymer supported tin hydride \( P-(CH_2)_4-SnBu_2H \) instead, 5-cholestene was isolated in 60% yield with a residual tin contamination of approximately 45 ppm without the need of recrystallization. Junggebauer and Neumann reported the photochemically initiated cyclization of acyclic \( \alpha \)-haloester to give \( \gamma \)-butyrolactones using the polymer-supported distannane 90 in which the distannane units function as radical source. The tin contamination of the cyclization products was evaluated by Atomic Absorption Spectroscopy (AAS). Depending on the temperature and the time of irradiation with UV light, tin contaminations in the range of 150–1100 ppm were detected, which is much too high for applications under the purity standards required for pharmaceutical products. Nevertheless, photochemical reactions using Bu₆Sn₂ gave even significantly higher values of tin contamination.

The non-styrenic macroporous polymer-supported organotin chloride 88b showed good activity in the catalytic reduction of 1-bromoadamantane with sodium borohydride as primary hydride source. The reagent was used several times and showed substantial tin leaching, which was estimated by AAS to be 0.3–1.2% of the initial tin content per run. The leaching of tin increased with increasing temperature.
polymer-supported organotin halides $\text{P}−(\text{CH}_2)_4−\text{SnBu}_2\text{I}$ and $\text{P}−(\text{CH}_2)_2−\text{SnBu}_2\text{Cl}$\textsuperscript{204}. The $\text{P}−(\text{CH}_2)_4−\text{SnBu}_2\text{I}/\text{NaBH}_4$ system was the most efficient one when the amount of halide was kept in the range of 0.2–0.9 equivalents, and isolated yields of adamantane of about 90\% were obtained. Very low levels of tin pollution (<35 ppm) in the adamantane were observed by ICP-MS measurements, reaching values which were identical to blank experiments for low tin halide-to-$\text{NaBH}_4$ ratios. The residual tin contamination in adamantane which was prepared with the system $\text{P}−(\text{CH}_2)_2−\text{SnBu}_2\text{Cl}/\text{NaBH}_4$ was significantly higher (1975 ppm). The highest tin contamination of adamantane was observed when the $\text{Bu}_3\text{SnCl}/\text{NaBH}_4$ system was used. Even after purification of the adamantane by flash chromatography or treatment with potassium fluoride solution, a residual tin content of about $10^5$ ppm was detected.

In addition to the chemical degradation of polymer-supported organotin reagents, the mechanical abrasion of the polymer beads is another origin of organotin contamination of the products. It is also possible that the polymer resin contains organotin compounds which were incorporated during the synthesis of the polymer-supported reagent and which were not completely separated from the polymer resin despite careful purification. The preparation of non-polluting organotin reagents for applications in organic syntheses remains a challenging target.

4. Characterization

To date, several applications of polymer-supported organotin compounds were reported but for further developments it is essential to get a better insight into the microstructure of the polymers and the nature of the organotin functionalities anchored to the polymer. The elemental analysis is still a standard and essential method to elucidate the composition of the polymer. In addition, energy-dispersive X-ray analysis (EDX) was performed on polymer-supported organotin chlorides in order to determine the tin-to-chloride ratio. Mainly gel permeation chromatography (GPC) was used to determine the average molecular weights of soluble polymer-supported organotin compounds\textsuperscript{172,177,182,185,186,201,202}. An alternative method to estimate the average molecular weight of polymers is the measurement of intrinsic viscosities\textsuperscript{176}. The thermal behaviour of polymers, which is a crucial property for applications in materials science, was investigated by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)\textsuperscript{172,175−177,182,185,186,201,202}. Polymer-supported reagents containing functional organotin moieties such as $\text{Sn}−\text{H}$ or $\text{Sn}−\text{OOCR}$ were characterised by infrared spectroscopy (IR)\textsuperscript{157,167,168,172,205}. For $\text{Sn}−\text{H}$ containing polymer-supported reagents, the tin hydride loading of the polymer was determined by test reactions with haloalkanes such as methyl iodide, 1-bromoadamantane or 1-bromoocane\textsuperscript{155,157,162,167,168,205}. Determination of the quantity of the alkanes thus formed is an indirect measure for the minimum tin hydride content of the polymer, provided that the reaction is quantitative. The effective tin hydride loading usually differs from the total tin loading and even from the real tin hydride loading. The latter can be higher than the value determined by the test reaction. This divergence is a result of the tin hydride sites being located in the polymer matrix and hence being not accessible because of diffusion problems. The specific surface area as estimated by the Brunauer, Emmet and Teller (BET) nitrogen adsorption method is valuable to provide information on the pore structure of the polymer and the potential accessibility of functional groups inside the polymer network\textsuperscript{174,180}.

One-dimensional $^{119}\text{Sn}$ NMR spectroscopy in solution was used to characterise soluble polymer-supported organotin compounds\textsuperscript{181,199}. To get a more detailed understanding of the microstructure of tin-containing polymers, $^1\text{H}/^{13}\text{C}/^{119}\text{Sn}$ triple resonance 3D NMR
experiments of polybutadienes containing tributyltin groups at the chain ends were carried out\(^{183,184}\). The combination of 1D, 2D and 3D NMR experiments allowed a detailed assignment of all \(^1H\), \(^{13}C\) and \(^{119}Sn\) NMR signals of the different structures observed. Based on the chemical shift assignment it was possible to quantify the amount of each structure. After the identification of the atomic connectivity patterns, the chain end monomer distribution can be extracted from quantitative \(^{13}C\) NMR spectra. It was pointed out that this 3D NMR technique is applicable to the structural characterization of organotin compounds, even when isotopic labelling is not possible for compounds having nuclei of low natural abundance and despite the extremely low concentration of the species in a polymer matrix.

One-dimensional solid state \(^{117}Sn\) and \(^{119}Sn\) NMR were used to get qualitative information on the organotin functionalities anchored to insoluble polymers\(^{170,172,205}\). Under certain conditions also quantitative information was deduced from solid state \(^{117}Sn\) NMR. However, this required a careful choice and setting of the acquisition conditions\(^{205}\). The quantification of relative amounts of different tin species in a polymer matrix was reliable within 10%. For example, the polymer \(P-(\text{CH}_2)_6-SnBu_2H\) was prepared from the corresponding tin iodide \(P-(\text{CH}_2)_6-SnBu_2I\) by reduction with NaBH\(_4\). From the integrals of the \(^{117}Sn\) NMR signals assigned to the Sn–H and Sn–O–Sn functionalities, the SnH-to-Sn\(_{\text{total}}\) ratio was estimated to be approximately 58\%. To check this result, the total amount of tin was determined by elemental analysis and the tin hydride content was estimated by a test reaction with 1-bromodecane. The resulting SnH-to-Sn\(_{\text{total}}\) ratio of 54\% was in good agreement with the ratio estimated from the \(^{117}Sn\) NMR CP-MAS spectra.

Further developments in the field of insoluble polymer-supported organotin compounds will be accompanied by the expansion of solid state tin NMR data and the development of new NMR techniques. In Table 8, some representative examples of \(^{117}Sn\) and \(^{119}Sn\) NMR chemical shifts of polymer-supported organotin compounds are given.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>(\delta) (ppm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(P-(\text{CH}_2)_4-SnBu_2Cl)</td>
<td>+146</td>
<td>205</td>
</tr>
<tr>
<td>2</td>
<td>(P-(\text{CH}_2)_4-SnBu_2Br)</td>
<td>+128</td>
<td>205</td>
</tr>
<tr>
<td>3</td>
<td>(P-(\text{CH}_2)_4-SnBu_2I)</td>
<td>+82</td>
<td>205</td>
</tr>
<tr>
<td>4</td>
<td>(P-(\text{CH}_2)_4-SnBu_2H)</td>
<td>−90</td>
<td>205</td>
</tr>
<tr>
<td>5</td>
<td>(P-(\text{CH}_2)_4-SnBu_2Ph)</td>
<td>−43</td>
<td>205</td>
</tr>
<tr>
<td>6</td>
<td>(P-(\text{CH}_2)_4-SnBu_2OSnR^3)</td>
<td>ca +84</td>
<td>205</td>
</tr>
<tr>
<td>7</td>
<td>(P-(\text{CH}_2)_4-SnBu_2SnR^3)</td>
<td>ca −82</td>
<td>205</td>
</tr>
<tr>
<td>8</td>
<td>(P-(\text{CH}_2)_4-SnBu_2R^a)</td>
<td>ca −12</td>
<td>205</td>
</tr>
<tr>
<td>9</td>
<td>(P-(\text{CH}_2)_6-SnBu_2H)</td>
<td>−92</td>
<td>205</td>
</tr>
<tr>
<td>10</td>
<td>(P-(\text{CH}_2)_6-SnBu_2Ph)</td>
<td>−43</td>
<td>205</td>
</tr>
<tr>
<td>11</td>
<td>(P-(\text{CH}_2)_2-SnBu_2Cl)</td>
<td>+148 to +150(^b)</td>
<td>170</td>
</tr>
<tr>
<td>12</td>
<td>(P-(\text{CH}_2)_2-SnBu_2OH)</td>
<td>+101 to +103(^b)</td>
<td>170</td>
</tr>
<tr>
<td>13</td>
<td>(P-(\text{CH}_2)_2-SnBu_2_2)</td>
<td>+91 to +92(^b)</td>
<td>170</td>
</tr>
<tr>
<td>14</td>
<td>(P-(\text{CH}_2)_2-SnBu_2OOCAr)</td>
<td>+104</td>
<td>170</td>
</tr>
<tr>
<td>15</td>
<td>(P-(\text{CH}_2)_2-\text{COOSnBu}_3)</td>
<td>+92 to +95, −45(^b, d)</td>
<td>172</td>
</tr>
</tbody>
</table>

\(^a\) R = alkyl groups similar to the \(n\)-Bu group, but not defined in the original publication.

\(^b\) Slightly different chemical shifts were observed depending on the nature of the polymer support.

\(^c\) Ar = \(p\)-CH\(_3\)C\(_6\)H\(_4\).

\(^d\) Two signals were observed as a result of tetra- and pentacoordinated tin atoms in the polymer matrix.
B. Polymer-supported Organogermanium Compounds

1. Polymer-supported reagents

Organogermanium compounds are known to be non-toxic, which makes them attractive as reagents in organic syntheses. However, the high price of germanium is a disadvantage and consequently reactions involving organogermanium reagents are only economic if the latter can be completely recovered from the reaction mixtures. A promising strategy to address this problem is the development of polymer-supported germanium reagents. Thus, the use of polymer-supported organogermanium hydrides as substitutes for polymer-supported organotin hydrides as reducing agents for organic halides was suggested. Three examples of polymer-supported germanium hydrides are presented in Scheme 50.

\[
\text{P} \quad \text{i) BuLi/TMEDA} \\
\text{Et}_2\text{GeCl}_2 \\
\text{iii) LiAlH}_4 \\
\]

\[
\text{P} \quad \text{i) BuLi/TMEDA} \\
\text{Et}_2\text{GeCl}_2 \\
\text{iii) LiAlH}_4 \\
\]

\[
\text{Et}_2\text{GeCl}_2 \\
\text{AIBN} \\
\text{(CH}_2\text{)}_2 \quad \text{GeEt}_2\text{Cl} \\
\]

\[
\text{Et}_2\text{GeCl}_2 \\
\text{AIBN} \\
\text{(CH}_2\text{)}_2 \quad \text{GeEt}_2\text{Cl} \\
\]

SCHEME 50. Synthesis of polymer-supported organogermanium hydrides

The polystyrene-supported organogermanium hydrides were characterised by solid state NMR, IR (\(\nu\ \text{Ge}--\text{H} 2000–2018\ \text{cm}^{-1}\)) and X-ray photoelectron spectroscopy (XPS) (Ge content 3.8–4.0 mmol g\(^{-1}\); degree of functionalization 0.28–0.30)\(^{206}\). Several octyl and phenyl halides were reduced by the polymer-supported organogermanium reagents simply by heating the corresponding reaction mixtures with free-radical initiators. The reactivity of the germanium hydrides increased with increasing chain length of the \((\text{CH}_2)_n\)-spacer. The best results were obtained for the reduction of 1-octyl bromide and 1-octyl iodide with P–(CH\(_2\))\(_2\)–GeEt\(_2\)H (99). Gas chromatography indicated that octane was formed in 60% yield. In addition, polyhalobenzenes were reduced stepwise, e.g. 1-bromo-2-chlorobenzene was reduced to 1-chlorobenzene in 22% yield using P–(CH\(_2\))\(_2\)–GeEt\(_2\)H (99). The polymer-supported organogermanium hydrides were used several times and recycled, and their efficiency was only reduced to 90% when compared with the first run.
2. Germanium-based linkers for solid-phase synthesis

The solid-phase synthesis of organic compounds requires a linkage element which acts as a tether to the polymeric support. In a multi-step synthesis the linker must be stable towards all reaction conditions used, but should easily and quantitatively be cleaved to release the target molecule without any degradation of the latter.

Recently, organogermanium compounds were used as novel linkers for the immobilization of organic compounds on polymer supports\textsuperscript{207,208}. Monoaryltrialkyl germanium compounds display a high stability towards bases and nucleophiles, but the germanium–aryl bond is readily cleaved by a variety of electrophilic reagents. Though germanium compounds are relatively expensive, they are promising candidates for the traceless linkage strategy of aromatic products. Compared with their silicon-containing analogues, they offer the advantage of the germanium–aryl bond to be more easily cleaved than the aryl–silicon bond. In organotin compounds the tin–aryl bond is even more easily cleaved but, as mentioned before, the organogermanium compounds are less toxic.

In Scheme 51, an example for the immobilization of the germanium-based precursor 100 to Argogel\textsuperscript{TM} polymer is shown\textsuperscript{208}. The clean release of several biaryl compounds from the polymer 101 was achieved by electrophilic degermylation with various reagents (i–iv) (Scheme 51).

![Scheme 51](image)

SCHEME 51. Immobilization of 4-methoxybiphenyl to Argogel\textsuperscript{TM} and release of the products by electrophilic degermylation

A linkage strategy was used for the solid-phase synthesis of a range of 1,4-benzodiazepine derivatives\textsuperscript{207}. It was demonstrated that the germanium route is superior to the silicon route because numerous functional groups are tolerated and the demetallation using trifluoroacetic acid or bromine is easier for germanium compounds. In Scheme 52
SCHEME 52. Solid-phase synthetic strategy for 1,4-benzodiazepine derivatives using a germanium linker strategy: i) polymer support linkage, ii) solid-phase synthesis, iii) product release

the general synthetic strategy, which was used for the solid-phase synthesis of eight 1, 4-benzodiazepine derivatives, is shown.

3. Germanium-containing polyacetylenes

Organic and organometallic substituents linked to a polyacetylene backbone influence the physical and chemical properties of the organic polymer. To study the effects of organogermanium moieties, the germanium-containing polyacetylenes 102–106 were prepared and their properties investigated. The polymerization of the dipropargylgermanium compounds \( R_2\text{Ge}(\text{CH}_2\text{C}≡\text{CH})_2 \) (\( R = \text{Me}, \text{Ph} \)) as catalysed by MoCl\(_5\)- and WCl\(_6\)-based catalysts gave the polymers 102, which have a polyene structure.
with recurring germanium-containing heterocycles. The soluble polymers had a $\lambda_{\text{max}}$ value of 430 nm and a number-average molecular weight of $M_n = 1.2 \times 10^4$.

\[
\begin{align*}
(102) & \quad R = \text{Me, Ph} \\
(103) & \quad R = \text{Me, } R' = \text{Me}_3\text{Ge} \\
(104) & \quad R = \text{Ph, } R' = o-\text{Me}_3\text{GeC}_6\text{H}_4 \\
(105) & \quad R = \text{Ph, } R' = p-\text{Me}_3\text{GeC}_6\text{H}_4 \\
(106) & \quad R = \text{H, } R' = o-\text{Me}_3\text{GeC}_6\text{H}_4
\end{align*}
\]

The polymers 104 and 105 were prepared from the corresponding acetylenes with a TaCl$_5$-based cocatalyst. The weight-average molecular weights were higher than $M_w = 1 \times 10^6$ as determined by GPC. In contrast, unsubstituted phenylacetylene yielded only relatively low molecular weight polymers with number-average molecular weights of $M_n \approx 1 \times 10^4$. The yellow trimethylgermyl-containing polymers 104 and 105 are thermally stable up to temperatures of ca 400°C. Poly(1-phenyl-2-o- trimethylgermylphenyl)acetylene (104) shows two absorption maxima at $\lambda_{\text{max}} = 380$ nm and 440 nm in the UV-visible spectrum and has an oxygen permeability coefficient which is about twice as high as that of poly(dimethylsiloxane). In contrast to its $p$-substituted analogue 105, the former polymer is also soluble in non-polar solvents. The structurally similar polymer 106 is also soluble in common organic solvents but differs significantly in its properties from 104 and 105. The dark purple solid ($\lambda_{\text{max}} = 551$ nm) has an onset temperature of weight loss at 230°C (TGA) and its oxygen permeability coefficient is ten times lower than that of 104.

**IV. COORDINATION POLYMERS OF ORGANOTIN AND ORGANOLEAD COMPOUNDS**

### A. Organotin Polymers

The high Lewis acidity of organotin derivatives having electron-withdrawing substituents bound to tin often results in a donor–acceptor complex formation with Lewis basic functionalities. To date, far more than 1000 crystal structure analyses of monomeric intra- and intermolecular coordinated compounds have been reported and even more complexes have been studied in solution. In addition, more than 300 oligomeric and polymeric organotin compounds have been studied by X-ray crystal structure analysis. In this Section, progress in the chemistry of tin-based coordination polymers covering the literature between 1995 and 2000 is reported, but selected results reported earlier and which we believe to be valuable for a better understanding of the matter are also included. The formation of oligomeric or polymeric organotin compounds can be achieved by the choice of suitable bidentate, tridentate or multidentate ligands. The coordination number at tin is increased to five or six resulting in tin-containing chain structures, layered compounds or three-dimensional networks. To date, the highest nuclearity observed in oligomeric organotin compounds is twelve. Several derivatives of the isostructural fragment $[(\text{RSn})_{12}(\mu_3-O)_{14}(\mu-OH)_6]^{2+}$ ($R = n$-Bu, $i$-Pr, $\text{Me}_3\text{SiCH}_2$) (107)
have been reported\textsuperscript{215–224}. A similar structural motif was observed in the cation \(([i-PrSn]_{12}(O)_{4}(OH)_{24})^{4+}\), which additionally encapsulates a Na\textsuperscript{+} ion in the organotin oxide core\textsuperscript{225}. The novel cluster \(([\text{Sn(CH}_{2})_{3}\text{Sn}]_{6}(\text{ClCH}_{2}\text{CO}_{2})_{14}(\text{OH})_{2}\text{O}_{10})\)\textsuperscript{226} was prepared starting from Cl\textsubscript{3}Sn(CH\textsubscript{2})\textsubscript{3}SnCl\textsubscript{3} and Cl\textsubscript{3}CH\textsubscript{2}COOH under the influence of air moisture.

\begin{equation}
\text{(107)} \quad \left[\text{(RSn)}_{12}\text{O}_{14}(\text{OH})_{6}\right]^{2+}
\end{equation}

\text{R} = n\text{-Bu, } i\text{-Pr, CH}_{2}\text{SiMe}_{3}

Only one diorganotin-based supramolecular compound with twelve tin atoms, namely \([\text{Me}_{3}\text{SiCH}_{2}(\text{Cl})\text{Sn(CH}_{2})_{3}\text{Sn(Cl)}(\text{CH}_{2})_{3}\text{Sn(Cl)}\text{CH}_{2}\text{SiMe}_{3}]\text{O}_{1.5}\)\textsuperscript{4} (108)\textsuperscript{227}, has been reported so far. The structure consists of three almost planar Sn\textsubscript{4}Cl\textsubscript{4}O\textsubscript{2} layers. Each layer is connected to the next layer by four trimethylene chains to give a triple ladder structure.

\begin{equation}
\text{(108)} \quad \text{R} = \text{CH}_{2}\text{SiMe}_{3}
\end{equation}

1. \textit{Intermolecular organotin–halide coordination}

Organotin fluorides\textsuperscript{214,228} show a strong tendency to associate in the solid state, unless bulky organic ligands or intramolecular donor coordination precludes the intermolecular
association. Examples of monomeric triorganotin fluorides 109a are the sterically overcrowded compounds Sn[C(SiMe2Ph)3]Me2F and Sn[C(SiMe3)3]Ph2F219, and the intramolecularly coordinated N(CH2CH2CH2)3SnF230 and [Me2N(CH2)3]2SnF2231. In polymeric chains of triorganotin fluorides, the tin atom is five-coordinate and has a trigonal bipyramidal configuration with the fluorine atoms in axial positions.

A symmetrical linear structure 109b with two identical Sn–F distances of 2.146(1) Å was reported for Ph3SnF232. In contrast, an unsymmetrical structure 109c with Sn–F distances of 2.051(10) Å and 2.303(10) Å was reported for the polymeric tricyclohexyltin fluoride233. For comparison, the Sn–F single bond distance in monomeric Sn[C(SiMe3)3]Ph2F amounts to 1.965(2) Å229.

\[ \text{monomeric} \quad \overset{\text{polymeric, linear}}{\text{polymeric, bent}} \]

\[
\begin{align*}
\text{(109a)} & \quad \text{X} = \text{F, Cl} & \text{(109b)} & \text{(109c)}
\end{align*}
\]

A particular behaviour was observed for the unsymmetrically substituted triorganotin fluoride Me2PhSnF234. In the solid state the tin fluoride adopts a 109c-type structure with only slightly different Sn–F distances of 2.162(1) and 2.179(1) Å, and Sn–F–Sn and F–Sn–F angles of 172.6(1) and 179.4(1)°, respectively. Depending on the concentration, the solvent and the temperature, in solution oligomers (Me2PhSnF)\(n\) up to an association degree of \(n = 50\) were observed. In addition, electrospray mass spectrometry proved the existence of species \([\text{Me2PhSn})_n\text{F}_{n-1}]^+\) with \(n = 1–5\).

Although Sn–Cl–Sn bridges are weaker than Sn–F–Sn bridges, they are strong enough to give self-organised polymeric organotin chlorides in the solid state83,214. A recent example of a triorganotin chloride crystallizing as a linear chain polymer of type 109b is tribenzyltin chloride, (PhCH2)3SnCl235, in which one short Sn–Cl distance of 2.387(2) Å and one long Sn–Cl distance of 3.531(2) Å were observed. In contrast, trimethyltin chloride236 forms a zigzag chain of type 109c, with Sn–Cl distances of 2.430(2) and 2.692(2) Å, and an Sn–Cl–Sn angle of 150.5°, whereas Ph3SnCl237 does not associate in the solid state and consists of discrete tetrahedral molecules of type 109a. Recently, the isostructural palladium and platinum complexes, \{MCl2[Ph2CH2CH2SnClMe2]3\}\(n\) (M = Pd, Pt) \(\text{(110, 111)}\)238, containing both organotin chloride and phosphine moieties, were reported. In the solid state the tin atoms adopt a distorted trigonal–bipyramidal configuration (110). Short intramolecular Sn–Cl distances in the range of 2.440(2)–2.679(2) Å (Pd) and 2.436(2)–2.682(2) Å (Pt), respectively, are accompanied by intermolecular Sn–Cl distances of 3.232(2)/3.234(2) Å (Pd) and 3.248(2)/3.223(3) Å (Pt), giving rise to formation of an infinite chain polymer. Both compounds were found to be monomeric in solution and, on the basis of heteronuclear NMR experiments, structure 111 was postulated.

The spacer-bridged ditin compound MeCl2Sn(CH2)3SnCl2Me239 was reported to contain, in the solid state, hexacoordinated tin atoms as a result of strongly unsymmetrical intermolecular Sn–Cl–Sn bridges with Sn–Cl distances in the range of 2.381(1)–3.484(1) Å, giving rise to the formation of a sheet-like polymer.
A two-dimensional sheet-like polymer was also observed in the solid state for the chloride complex \( \{ \text{Cl}_2\text{Sn}[(\text{CH}_2)_3\text{Sn}\text{Cl}_2\text{Me}]_2\}\text{Cl}^-\ [\text{Cl}_3\text{P}_2\text{N}]^{2-} \). As a result of the chloride complexation as well as of unsymmetrical intermolecular Sn–Cl–Sn bridges, the compound contains both penta- and hexacoordinated tin atoms. The dimethylene-bridged triorganotin bromide (Ph\(_2\)BrSnCH\(_2\))\(_2\)\(^{240}\) and the methylene- and dimethylene-bridged diorganotin dibromides (PhBr\(_2\)Sn\(_2\)(CH\(_2\))\(_2\)\(^{241}\) and (PhBr\(_2\)Sn\(_2\)(CH\(_2\))\(_2\)\(^{242}\), respectively, are rare examples for coordination polymers realised by unsymmetrical intermolecular Sn–Br–Sn bridges with Sn–Br distances in the range of 2.483–3.724(2) Å. An early example of this type of coordination polymers is Et\(_2\)SnBr\(_2\)\(^{243}\), which forms a polymer chain with tin atoms in a distorted octahedral coordination environment. The Sn–Br distances were found to be 2.505(4) and 3.777(4) Å.

A recent attempt to prepare an organotantalum fluoride starting from Me\(_3\)SiCH\(_2\)TaCl\(_4\) and excess Me\(_3\)SnF afforded the crystalline compound (Me\(_3\)SnCl·Me\(_3\)SnF·TaF\(_5\))\(_n\)\(^{113}\) containing octahedrally configurated tantalum and trigonal bipyramidally configurated tin atoms. The linear chain in \(^{113}\) was reported to consist of the unit [Sn–Cl–Sn–F–Ta–F–] with Sn–Cl distances of 2.555(3) and 2.562(2) Å and Sn–F distances of 2.514(7) and 2.54(9) Å. In addition, weak Sn–F contacts of 3.59(3) Å link the chains to give a two-dimensional layer.
22. Organometallic polymers of germanium, tin and lead

Long tin–fluorine interatomic distances, which are only slightly shorter than the tin–fluorine van der Waals distance of 3.64 Å, were reported for 1,4-[Me3SnOC-(CF3)2]2C6F4245. Fluorine atoms of both the CF3 and C6F4 groups are involved in intermolecular Sn–F interactions [3.462(11), 3.442(10) Å] giving rise to formation of a sheet-like polymer. This example illustrates that even very weak such interactions can be structure-directing in organotin chemistry.

Recently, a layered structure was reported for [(Me3Sn)3O]Cl (114)246. The oxonium salt was prepared by simply heating at reflux (Me3Sn)2O and Me3SnCl in THF (equation 1).

\[
\text{(Me}_3\text{Sn)}_2\text{O} + \text{Me}_3\text{SnCl} \xrightarrow{\text{thf, reflux}} \left[\text{(Me}_3\text{Sn)}_3\text{O}\right]\text{Cl}
\]

In the crystal lattice, the oxonium ion is trigonal planar coordinated by three Me3Sn groups. The two-dimensional structure is built up by a hexagonal AB layer with interlayer distances of 6.32 Å. Each hexagon consists of 12-membered Sn6Cl3O3 rings.

The single crystal X-ray structure analysis of the trimethyltin-substituted ammonium salt [H2N(SnMe3)2][SnMe3Cl2] (115)247 was also reported. In compound 115 the anion
[SnMe_3Cl_2]^- forms a trigonal bipyramid with the chlorine atoms in the axial positions. In the crystal lattice a chain structure is formed as the result of weak interionic tin–chlorine interactions [Sn···Cl 3.223(3), 3.182(3) Å] bridging the chlorine atoms of the anion and the tin atoms of the cation [H_2N(SnMe_3)_2]^+.

2. Intermolecular organotin–oxygen coordination

i. Intermolecular Sn–OR (R = H, alkyl) interactions. Usually, organotin hydroxides are associated by strong intermolecular tin–oxygen bonds and divers oligomeric and polymeric structures are known. The triorganotin hydroxides Et_3SnOH (116), Ph_3SnOH (117), BzMe_2SnOH (118) and Me_2Si(CH_2SnMe_2OH) (119) were fully characterised. They crystallise in a zigzag chain structure with the tin atoms being pentacoordinated. The hydroxide groups are located in the axial positions and the structures are bent at the oxygen. The Sn–O–Sn bridges are slightly unsymmetrical with Sn–O distances ranging from 2.15 to 2.29 Å. In contrast, the sterically overcrowded trimesityl tin hydroxide is monomeric in the solid state and the tin–oxygen bond length amounts to 1.999(6) Å.

Simple organotin alkoxides as well as the cyclic dioxaostannolanes are also suggested to associate in solution and in the solid state. The degree of association depends on
22. Organometallic polymers of germanium, tin and lead

both the steric requirements of the alkyl groups bound to tin as well as on the alkoxy groups. Trimethyltin methoxide, Me₃SnOMe (120)²⁵³, forms polymeric zigzag chains similar to Et₃SnOH (116) with the Sn—O—Sn bridge being again slightly unsymmetrical [Sn—O 2.20(2)/2.26(2) Å]. In dioxastannolane derivatives, relatively weak intermolecular tin–oxygen interactions were observed in the solid state and, for example, 2,2-di-n-butyl-1,3,2-dioxastannolane (121)²⁵⁴ forms a ribbon-type polymer with six-coordinate tin in a highly distorted octahedral arrangement. The intra- and intermolecular Sn—O bond lengths within the central Sn₂O₄ ring amount to 2.04(1) and 2.51(1) Å, respectively. The degree of association decreases in the sterically more crowded 2,2-di-t-butyl-1,3,2-dioxastannolane (122)²⁵⁵, for which dimers with pentacoordinated tin atoms were observed both in the solid state and in solution. The crystal structure analysis of 122 revealed two similar but structurally independent molecules with Sn—O bond lengths of 2.049(6)–2.253(7) Å.

\[ \text{polymer} \]

\[ \text{dimer} \]

(121) \( R = n\text{-Bu} \)

(122) \( R = t\text{-Bu} \)

The solution- and solid-state coordination behaviour of \( \omega \)-trichlorostannyl alcohols Cl₃Sn(CH₂)ₙOH (\( n = 3–5 \))²⁵⁶ were investigated by means of multinuclear NMR spectroscopy and, in the case of \( n = 5 \), by single crystal X-ray structure analysis. The latter revealed a polymeric structure for Cl₃Sn(CH₂)₅OH, which results from significant intermolecular HO—Sn interactions of 2.356(6) Å. The five-coordinate tin atoms exist in a distorted trigonal–bipyramidal geometry with the oxygen and one of the chlorine atoms occupying the axial positions (123a). It was suggested that Cl₃Sn(CH₂)₃OH and Cl₃Sn(CH₂)₄OH do not show intermolecular but intramolecular OH—Sn coordination, to give five- and six-membered rings (123b), respectively, both in CD₂Cl₂ solution and in the solid state.

\[ \text{(123a)} \]

\[ \text{(123b)} \]

*ii. Organotin carboxylates.* Organotin carboxylates have been the subject of numerous investigations and more than 300 X-ray crystal structure analyses have been reported to date²⁵⁷. The structural chemistry of organotin carboxylates was thoroughly reviewed by Tiekink²⁵⁸. In this section we focus on some representative examples of polymeric organotin carboxylates.
The tin–oxygen interatomic distances present in organotin carboxylates were classified in terms of primary Sn–O covalent bonds (ca. 2.0 Å), slightly longer dative Sn–O bonds (ca. 2.2–2.3 Å) and Sn···O secondary interactions (>2.5 Å).214 Triorganotin carboxylates can adopt the three idealised structure types 124a–c.

In 124a, the carboxylate is essentially monodentate resulting in tetrahedrally configured tin atoms. In 124b, the carboxylate is intramolecularly bidentate giving rise to a distorted trigonal–bipyramidal coordination geometry at tin with one oxygen and one carbon atom in the axial positions. In 124c, a linear polymer is formed as a result of unsymmetrically bridging carboxylate groups connecting trigonal bipyramidally configured tin centres. No example for the ideal structure 124a has been reported so far, since at least weak secondary interactions can be discussed in the molecular structures of triorganotin carboxylates.258 Structure 124b was only observed with aromatic carboxylic acids or with bulky substituents at tin. Recent examples are the triphenyltin derivatives of p-ethoxybenzoic acid, acetylsalicylic acid and phthalic acid.259 In the solid state, the structures of most of the triorganotin carboxylates approximate to the infinite chain polymer of type 124c in which the oxygen atoms occupy the axial positions of the trigonal bipyramid.258,260–271 The carboxylate groups not only bridge two tin centres, but in many structures an additional secondary intramolecular tin–oxygen interaction of approximately 3.0 Å was observed resulting in distortions of the trigonal–bipyramidal geometries. Very often, this effect was neglected in the discussion of crystal structure determinations. On the basis of the crystal structure analyses of seventeen polymeric triorganotin carboxylates, it was demonstrated that the tin–tin repeat distance in the polymers was approximately constant at 5.19 ± 0.21 Å, regardless of both the identity of the substituents at the carboxylic acids and the substituents at tin.261 A similar tin–tin repeat distance of 5.155 Å was reported for the polymeric diorganotin compound diethyl[3-(2-pyridyl)-2-sulfanylpropenato]tin, [Et₂Sn(pyspa)] (H₂pyspa = HOOC–C(SH)=CH–2-pyridine), which adopts a zigzag chain polymer structure similar to that of type 124c.

The crystal structure analyses of tin-containing dicarboxylates were also reported. Depending on the carboxylates used, linear infinite chain structures, two-dimensional, supramolecular layered structures and three-dimensional networks were observed. A chain polymer was reported for methylphenylammonium tributyl(pyridine-2,6-dicarboxylato)stannate (125), in which the tributyltin moieties are linked via the pyridine-2,6-dicarboxylate. The carboxylate groups form hydrogen bonds to the ammonium salt and thus no additional C=O···Sn interaction was observed. The coordination geometry at tin is again trigonal–bipyramidal with the oxygens in the axial positions [Sn–O 2.275(2), 2.279(2) Å].
Poly\[trans\]-bis(trimethyltin)-2,2'-bipyridyl-4,4'-dicarboxylate, Me$_3$SnOOC(2,2'-bipy)-COOSnMe$_3$ (126), forms a two-dimensional polymer. Each carboxylate group binds two trimethyltin moieties in a bridging bidentate fashion giving a layered structure. The tin atoms show a slightly distorted trigonal–bipyramidal configuration with two essentially different axial Sn−O bond lengths of 2.145(2) and 2.519(2) Å.

Bis(trimethyltin)malonate, Me$_3$SnOOCCH$_2$COOSnMe$_3$ (127), is an intriguing example of a three-dimensional network built up by pentacoordinated organotin moieties with the oxygens in the axial positions of a trigonal bipyramid [Sn−O 2.19(1), 2.17(1), 2.44(2), 2.46(2) Å] and malonate units as tetradentate spacers. The basic three-dimensional structure consists of four helices which are interconnected by O−Sn−O bridges resulting in 24-membered macrocycles.

A donor atom-containing substituent in the alkyl or aryl group R' in carboxylic esters of the type R'COOSnR$_3$ makes possible an alternative bonding to carboxylate bridging. A range of substituted carboxylic acids having an additional donor group was reported to give polymeric triorganotin compounds in the solid state. Among the earliest examples
was trimethyltin glycinate (128)\textsuperscript{279} whose X-ray single crystal structure analysis revealed a polymeric network as a result of tin–nitrogen interactions with Sn–N bond lengths of 2.46(2) Å. In addition, the carboxylate group is involved in O···H–N hydrogen bonding. A more recent example for a triorganotin ester with additional Sn–N linkage is triphenyltin-3-pyridylcarboxylate [Sn–N 2.568(7) Å] (129)\textsuperscript{280}.

Mössbauer and infrared spectroscopic data in the solid state of tributyltin 2-benzoylbenzoate (130a) and triphenyltin 2-benzoylbenzoate (130b) were indicative for
a trans-$\text{C}_3\text{SnO}_2$ trigonal–bipyramidal geometry at tin. A single crystal X-ray structure analysis confirmed this assumption and revealed a polymeric chain structure as a result of ketonic oxygen–tin bridges for both compounds. The tin–ketonic oxygen distances in 130a and 130b amount to 2.675(10) Å and 2.880(4) Å, respectively. Analogously, triphenyltin derivatives of pyridylcarboxylic acid N-oxides crystallise as N-oxide bridged chains with pentacoordinated tin atoms and monodentate carboxylate groups.

The solid state structures of heteroatom-substituted carboxylic triorganotin esters are difficult to predict. In some cases the heteroatom indeed functions as a bridge between the tin centres, but often the polymeric nature of the compound results from bidentate carboxylate ligands giving the general trans-$\text{R}_3\text{SnO}_2$ structure-type. For example, in 130 the heteroatom represents the linking functionality, whereas in catena-poly[trimethyltin-µ-(3-benzoyl-α-methylbenzeneacetato-O1,O1)] and dithiocarbamoylacetato-triphenyltin derivatives, the heteroatoms are not involved in coordinative bonds to tin.
The synthesis and characterization of a series of triphenyltin derivatives of \(N\)-2-hydroxynaphthylidene-\(\omega\)-amino acids, 2-HOC\(_{10}H_6\)CH=NC\((CH_2)\)\(n\)COOH, and \(n\)-salicylidene-\(\omega\)-amino acids, 2-HOC\(_6\)H\(_4\)CH=NC\((CH_2)\)\(n\)COOH (\(n = 1, 2, 3\) and 5)\(^{285}\), were reported. The X-ray crystal structure analysis of 2-HOC\(_6\)H\(_4\)CH=NC\((CH_2)\)\(5\)COOSnPh\(_3\) (133) showed the phenolic hydroxyl groups to be involved in the O(H)–Sn coordination with a Sn–O bond length of 2.328(4) Å. The tin atom is five-coordinate with the phenolic oxygen and one oxygen of the carboxylic group [Sn–O 2.148(4) Å] in the axial positions of a trigonal bipyramid. In addition, a weak Sn–O interaction [Sn–O 2.973(5) Å] involving the second oxygen of the carboxylic group causing a distortion of the trigonal bipyramid was observed. It was suggested that the other compounds of the series have a similar structural arrangement.

![Chemical structure of 133](image)

By appropriate choice of the reactants and the reaction conditions, a phenol-substituted carboxylic acid may react with an organotin compound to give both an organotin ester and an organotin aryl oxide within the same molecule. The reaction of trimethyltin chloride with 4-hydroxy-3-methoxybenzoic acid (HVAH) in the presence of water and pyridine at 130°C in a sealed tube gave the unique two-dimensional coordination polymer 134 (equation 2)\(^{286}\).

\[
\text{HO} \text{COOH} + \text{Me}_3\text{SnCl} \xrightarrow{\text{pyridine/H}_2\text{O}} \left\{[(\text{Me}_2\text{Sn(VA)}_{0.5})_2\text{O}]_2 \text{2H}_2\text{O}\right\}_n
\]

The molecular structure of 134 exhibits a two-dimensional rhombohedral grid\(^{286}\) in which the corners are composed of a ladder-type arrangement which is typical for tetraorganodistannoxanes\(^{258,287}\). The endocyclic tin atoms of the basic ladder fragment are connected by two oxygens to give the central almost planar Sn\(_2\)O\(_2\) ring. Each tin atom has a trigonal–bipyramidal geometry. The axial positions are occupied by an oxygen of a phenolato group and an oxygen of a carboxylate from different VA\(^{2-}\) moieties. Thus, each VA\(^{2-}\) ligand uses one phenolate oxygen and one carboxylate oxygen to function as a spacer connecting the ladders, to give a two-dimensional rhombic grid. Two water molecules are located in the rhombic cavity of 134 as a result of hydrogen bonds between water and a carboxylate group. In addition, the two water molecules form hydrogen bonds between each other.

One-dimensional polymeric tetraorganodistannoxanes based on a typical ladder arrangement \(L_4R_8\text{Sn}_4\text{O}_2\) (\(L = \text{ligand, e.g. halogen, carboxylate; R = alkyl, aryl}\) were
reported, but their polymeric structures are quite different from that of 134. In $\text{Me}_2\text{Sn(OOCMe)}_2\text{O}_2$ (135) a polymeric chain of the basic ladder structure entity results from an intermolecular interaction of an exocyclic tin atom and an oxygen of a monodentate carboxylate group [Sn–O 2.56(1) Å]. The covalent Sn–O bond length of the monodentate carboxylate amounts to 2.26(1) Å with an additional weak intramolecular tin-oxygen interaction of 2.89(1) Å.

A quite different bonding situation was observed in the crystal structure of bis{dimethyl[trans-3-(2-thiophenyl)-2-propenato]tin}oxide $\text{Me}_2\text{Sn(OOC\text{=CHC}_4\text{H}_3\text{-S})}_2\text{O}_2$ (136), in which two additional weak intermolecular interactions of carboxylate oxygens of two monodentate carboxylate groups to adjacent tins (Sn–O 2.953 Å) result in a one-dimensional coordination polymer. In addition, the same carboxylate oxygen chelates the tin atom to which the ligand is bound (Sn–O 2.850 Å).

Different synthetic routes were developed to prepare distannoxane carboxylates. Two methods commonly used are (i) the reaction of diorganotin oxides with carboxylic acids under azeotropic removal of water and (ii) the hydrolysis of diorganotin dicarboxylates. Diorganotin dicarboxylates are highly moisture-sensitive.
and the few compounds which are structurally characterised show diverse structure types. Dimethyltin diacetate, $\text{Me}_2\text{Sn(OOCMe)}_2$\textsuperscript{290}, is monomeric, di-$n$-butyl(1,1-cyclobutanedicarboxylato)tin, [\(n\)-Bu\(n\)-Bu\(n\)-Sn(OOC\(n\)-C\(_6\)H\(_6\)COO)]\(_n\)\textsuperscript{291}, is a one-dimensional polymer with a zigzag chain, bis(formato)dimethyltin, [\(\text{Me}_2\text{Sn(OOCH)}_2\)]\(_n\)\textsuperscript{292}, is a sheet-like polymer with linear Me\(_2\)Sn moieties nearly symmetrically bridged by formate anions and bis(trifluoroacetato)dimethyltin, [\(\text{Me}_2\text{Sn(OOCFCF}_3\)]\(_n\)\textsuperscript{290}, crystallises in a three-dimensional network formed by bridging trifluoroacetate groups around octahedrally coordinated tin atoms.

The behaviour in solution of dimethyltin(IV) complexes containing different aminopolycarboxylic acids were also investigated\textsuperscript{293,294}. The X-ray crystal structure analyses of the tin complexes with \(N\)-methyliminodiacetate (mida), pyridine-2,6-dicarboxylate (pdc) and ethylenediamine-$N,N'$-diacetate (edda) revealed dimeric structures for the first two compounds and a monomeric structure for the complex dimethyltin (edda). In contrast, the dimethyltin(IV) complex (137) with ethylenediamine-$N,N,N',N'$-tetraacetate (edta) and water is a polymer in which each tin atom adopts a distorted pentagonal–bipyramidal configuration with the two methyl groups in axial positions.

\(\text{Sn} \rightarrow \text{O(ketone)}\) interactions. 1,4-dimethylpiperazine-2,5-dione is the simplest cyclic peptide, which was used to study adducts with SnCl\(_4\), BuSnCl\(_3\), Me\(_2\)SnCl\(_2\) and Ph\(_2\)SnCl\(_2\) by \(^{119}\)Sn Mössbauer and IR spectroscopy\textsuperscript{295}. The crystal structure analysis of the 1:1 complex of Ph\(_2\)SnCl\(_2\) and 1,4-dimethylpiperazine-2,5-dione (138) revealed an infinite polymeric zigzag chain, in which the octahedrally coordinated tin atoms are
bridged by ketonic oxygen atoms \( [Sn-O 2.379(6), 2.468(6) \text{ Å}] \). The phenyl groups are in mutual \textit{trans} position and both the chlorine atoms as well as the oxygens are \textit{cis}.

Both the \( N\)-mono- and \( N,N\)-bis(trimethylstannyl)acetamides, \( \text{MeC(O)NMe(SnMe}_3) \) \((139a)\) and \( \text{MeC(O)N(SnMe}_3)_2 \) \((139b)\) form polymeric chain-like arrays with pentacoordinated tin atoms in the solid state.\(^{296}\) In \(139a\) and \(139b\) the intermolecular \(Sn-O\) distances amount to \(2.564(4) \text{ Å}\) and \(2.672(3) \text{ Å}\), respectively and the \(Sn-N\) distances to \(2.173(3) \text{ Å}(139a)\) and \(2.098(3)/2.155(3) \text{ Å}(139b)\). A similar structure was also reported for \(N\)-(trimethylstannyl)-\(N\)-nitromethylamine, \(\text{Me}_3\text{SnN(Me)NO}_2\) \(^{297}\), which is build up by infinite \(\text{SnMe}_3-N(\text{Me})-N(\text{O})-O-\)chains. The oxygen and the nitrogen atoms occupy the axial positions in the trigonal bipyramid with \(Sn-O\) and \(Sn-N\) distances of \(2.39(5)\) and \(2.33(4) \text{ Å}\), respectively.

![Structure](image)

\((139a)\) \(R = \text{Me}\)
\((139b)\) \(R = \text{SnMe}_3\)

iv. \textit{Intermolecular Sn–O=S and Sn–O=Se interactions}. Organotin compounds with intermolecular \(Sn-O=S\) or \(Sn-O=Se\) interactions are relatively rare and only a few single crystal X-ray structure analyses have been reported. Early examples of coordination polymers are the trimethyltin sulphinates \(\text{Me}_3\text{SnO}_2\text{SR} (R = \text{Me}, \text{CH}_2\text{C≡CH})\)\(^{298–300}\) and the corresponding selenates \(\text{R}_3\text{SnO}_2\text{SeR} (R = \text{Me}, \text{Ph})\)\(^{301,302}\). The synthesis and solid state structure determination of the organotin selenite derivative \((\text{Me}_3\text{Sn})_2\text{O}_3\text{SeH}_2\text{O}\) \((140)\)\(^{303}\) was also reported. One of the tin atoms is part of a polymeric chain in which the tin centres are bridged by two oxygens of the tridentate ligand \([Sn-O 2.263(6), 2.293(6) \text{ Å}]\), while the second tin is pendant to the chain linked via the third oxygen of the \(\text{SeO}_3^{3–}\) group \([Sn-O 2.139(6) \text{ Å}]\). The latter tin atom is coordinated by a water molecule \([Sn-O 2.660(7) \text{ Å}]\), which itself forms hydrogen bonds to the selenite group. The overall structure is that of a three-dimensional network composed of pentacoordinated tin atoms. A similar structure was reported for bis(triphenylstannyl)sulphite, \([\text{(Ph}_3\text{Sn})_2\text{O}_3\text{S}]_n\) \((141)\)\(^{304}\), which crystallised without water, with the consequence that \(141\) contains pentacoordinated tin atoms. In the case of the pentacoordinated tin atoms, the axial \(Sn-O\) bond lengths amount to \(2.264(3)\) and \(2.252(3) \text{ Å}\), which are significantly longer than the \(Sn-O\) bond length for the tetracoordinated tin \([Sn-O 2.032(2) \text{ Å}]\).

A two-dimensional polymeric sheet-like structure was reported for \(\text{Me}_2\text{Sn(SO}_3\text{F)}_2\) \(^{305}\) and a polymeric zigzag chain for chlorotris(\(p\)-methylsulphonylphenyl)tin, \([\text{SnCl(C}_6\text{H}_4-\text{SO}_2\text{CH}_3-p)]_n\) \((142)\)\(^{306}\). In \(142\), the tin atoms are pentacoordinated as a result of a weak intermolecular \(Sn-O\) interaction of \(3.046(5) \text{ Å}\). Only one out of the three \(p\)-methyl-sulphonylphenyl groups is involved in coordinative oxygen–tin bonds.
Similar to the structure of compound 142, trigonal–bipyramidal tin centres with weak sulphoxide oxygen–tin interactions were observed in the polymeric chain structures of compounds 143–146\(^{307,308}\). The Sn–O lengths were reported to be in the range of 2.82 to 3.14 Å.

In diorganotin dihalide complexes with sulphoxide-containing ligands, the coordination number at tin is increased to six and the sulphoxide oxygen–tin distances are significantly shortened as compared with 142–145. In poly[cis-dichloro-trans-dimethyltin-\(\mu\)-meso-1,2-bis(phenylsulphinyl)ethane-O:O\] (146a) and poly[cis-dichloro-trans-dimethyltin-\(\mu\)-meso-1,2-bis(propylsulphinyl)ethane-O:O\] (146b), Sn–O distances of 2.397(3) and 2.404(3) Å, and 2.316(3) and 2.320(3) Å, respectively, were observed\(^{309,310}\). The disulphoxide ligands bridge the hexacoordinated tin centres to give infinite chains in the solid state.
(143)

(144)

(145)

(146a) R = Ph

(146b) R = Pr
v. Intermolecular Sn–O=P interactions. Attempts to prepare organotin derivatives of phosphorus acids usually resulted in amorphous powders unsuitable for X-ray diffraction. However, the crystal structure analysis of one representative, namely (Me₂Sn)₃(PO₄)₂·8H₂O, was reported. The organotin phosphate is build up by fused eight-membered Sn₂O₄P₂ rings with alternating Me₂Sn and PO₄ groups leading to infinite ribbons. Coordination of water molecules to tin and extensive hydrogen bonding results in a complex three-dimensional network. Organotin derivatives of organophosphorus acids show a higher solubility and a series of complex oligomeric structures including drums, cubes, oxygen-capped clusters, butterfly formations, crowns and polymers were characterised by X-ray crystallography. These compounds were prepared by (i) azeotropic dehydration of a mixture of an organotin hydroxide or organotin oxide, respectively, and the acid, (ii) by salt elimination from an organotin halide and the salt of the phosphorus-containing acid, or (iii) by treating a tin alkoxide or tin amide with the corresponding acid. Based on NMR and ¹¹⁹Sn Mössbauer spectroscopic investigations it was concluded that tributyltin phosphate, (Bu₃SnO)₃P(O), tributyltin phenylphosphonate, (Bu₃SnO)₂P(O)Ph, and tributyltin diphenylphosphinate, Bu₃SnO₂PPh₂, are intermolecularly associated through the O=P=O group both in solution and in the solid state. In contrast, dithiophosphorus acid derivatives show a higher tendency to function as chelating rather than bridging ligands.

The triorganotin phosphinates Me₃SnO₂PMe₂ (147a), Me₃SnO₂PCl₂ (147b) and Bu₃SnO₂PPh₂ (147c) self-assemble in the solid state to give polymeric helical chain structures with pentacoordinated tin and tetracoordinated phosphorus atoms. The Sn–O distances in 147a, 147b and 147c amount to 2.20(1), 2.265(5) and 2.220(6)/2.224(6) Å, respectively, and the P–O distances are in the range of 1.45–1.50 Å.

In contrast to the solid state, the molecular weight determination of tributyltin diphenylphosphinate, Bu₃SnO₂PPh₂, in benzene indicated a dimeric structure in solution at low concentration. Other triorganotin phosphinates, such as Me₃SnO₂PPh₂ (148) and Ph₃SnO₂P(OPh)₂, crystallise as cyclic tetramers and hexamers, respectively.

Some diorganotin derivatives of phosphinic acids were reported to self-assemble in the solid state to give polymeric arrays. In [Et₂ClSnO₂PMe₂]ₙ, the O₂PMe₂ groups act as bidentate bridging ligands between the Et₂ClSn units leading to a polymeric chain structure. The tin atoms exhibit a distorted trigonal–bipyramidal geometry with the oxygen atoms in the axial positions. A peculiarity of the structure is the formation of –P–O–Sn–O– double chains running in relatively close distance to...
each other in the direction of the $c$-axis of the unit cell. The two strands are held together by weak Sn−O interactions [Sn−O 3.162(4) Å], thereby causing a [5+2]-coordination geometry at tin.

In the polymeric diorganotin phosphinates $[\text{Et}_2\text{Sn}(\text{O}_2\text{PPh}_2)_2]_n$ (150a)$^{322}$ and $[\text{Ph}_2\text{Sn}(\text{O}_2\text{PMe}_2)_2]_n$ (150b)$^{323}$, the phosphinate groups function as double bridges between the octahedrally coordinated tin atoms to give centrosymmetric $(\text{SnOP})_2$ eight-membered rings. The Sn−O distances show values of 2.141(4)–2.182(4) Å (150a) and

(150a) $R^1=\text{Et}, R^2=\text{Ph}$

(150b) $R^1=\text{Ph}, R^2=\text{Me}$
2.210(4)–2.229(3) Å (150b). The organic groups are mutually trans and thus linear arrays of the (SnOPO)₂ rings are observed. The diorganotin phosphinate [Et₂Sn(O₂PMe₂)₂]ₙ (151) shows a similar coordination geometry at tin and bidentate bridging O₂PMe₂ groups were found. Somewhat unexpectedly, the diethyltin phosphinate crystallises in a layer structure containing 16-membered (SnOPO)₄ rings.

Among the organotin thiophosphinate derivatives known so far, polymeric chain structures were reported for [Ph₃Sn(OSSH₂)]ₙ, [Me₃Sn(OSPMe₂)]ₙ and [Me₂Sn(OSPPh₂)]ₙ.

Diphosphoryl ligands are able to function either as chelating or as bridging ligands in organotin halide complexes. Infinite chain structures were reported for complexes of diorganotin dichloride with 1,2-bis(diphenylphosphinyl)ethane [dppoe, Ph₂P(O)CH₂CH₂P(O)Ph₂], such as [Bu₂SnCl₂(dppoe)]ₙ and [PhBuSnCl₂(dppoe)]ₙ, as well as for the related complex of dimethyltin dichloride with meso-1,2-bis(α-diethoxyphosphorylbenzylamino)ethane, {Me₂SnCl₂[(EtO)₂P(O)CH₂CH₂CHMeP(O)-(OEt)₂]}ₙ (152) and the diphenyltin dichloride complex {Ph₂SnCl₂[(EtO)₂P(O)CH₂CH₂CHMeP(O)-(OEt)₂]}ₙ. In all complexes the tin atoms are hexacoordinated, but only in the latter are
the phosphoryl oxygens cis. The tin–oxygen distances are in the range of 2.24–2.64 Å, depending on both the steric and electronic properties of the ligands attached to phosphorus and tin.

An infinite chain polymer was also reported for \([\text{[Me}_2\text{Sn}((\text{MeSO}_2)_2\text{N})(\text{OH})]_2\text{dppoe}}]_n\) \((153)\), in which the tin atoms are heptacoordinated as a result of inter- and intramolecular Sn–O interactions.

![Diagram of (153)](image)

Several triorganotin carboxylates crystallise as chain polymers of type \(124c\) in which the carboxylate serves as a bridging ligand. In the one-dimensional polymer structures of triphenyltin diethylphosphonoacetate \((154a)\) \((154b)\), the carboxylates are monodentate and the linear polymeric arrays result from intermolecular phosphoryl oxygen–tin interactions with Sn–O bond lengths of 2.420(3) Å and 2.397(3) Å, respectively. As a result of the slightly different chain length of the CH \(_2\) spacers, the polymeric chains in the acetate \((154a)\) propagates by translation along the \(b\)-axis to give a linear arrangement, whereas in the propionate \((154b)\) the chain propagates along the \(c\)-axis to give a zigzag conformation.

\(3. \text{Intermolecular organotin–nitrogen coordination}\)

Trimethyltin cyanide, \(\text{Me}_3\text{SnCN}\), was among the first coordination polymers investigated with intermolecular tin–nitrogen interactions. The tin atoms are in a trigonal–bipyramidal environment with three equatorial methyl groups and equally distant cyanide groups in the axial positions giving rise to formation of a linear polymeric array of the type \(155a\). It was suggested that the structure ‘is best described as an arrangement
of $\text{Me}_3\text{Sn}^+$ and $\text{CN}^-$ ions with the cyanides ordered in the direction along an axis, but disordered in orientation along this axis, with perhaps a small amount of covalent character to account for the orientation of the CN groups. Triethyltin cyanide, $\text{Et}_3\text{SnCN}$, was reported to have a similar structure whereas trimethylcyanogermane, $\text{Me}_3\text{GeCN}$, does not associate in the solid state. Dimethylditin dicyanide, $\text{Me}_2\text{Sn}($CN$)_2$, forms infinite polymeric sheets as a result of intermolecular tin–nitrogen interactions of 2.641(11) Å. In $\text{Me}_2\text{Sn}($CN$)_2$, the tin atom has a strongly distorted octahedral environment as is illustrated by the C–Sn–C trans angles of 148.7(35)° for the $\text{Me}_2\text{Sn}$ moiety and the NC–Sn–CN cis angles of 85.3(37)° for the Sn($\text{CN})_2$ moiety. The coordination environment of the analogous germanium compound $\text{Me}_2\text{Ge}($CN$)_2$ is close to tetrahedral with C–Ge–C angles of 120.9(8)°, 109.5(5)° and 100.9(7)° for the $\text{Me}_2\text{Ge}$, Ge($\text{CN})_2$ and $\text{MeGeCN}$ moieties, respectively. However, intermolecular Ge–N distances of 3.28(2) Å indicate weak association.

Trimethyltin azide, $\text{Me}_3\text{SnN}_3$, is a one-dimensional zigzag polymer of the type $\text{155b}$ in which tin is trigonal–bipyramidally coordinated with the methyl groups in equatorial and the nitrogens in axial positions. The Sn–N distances are equal and amount to 2.386(3) Å, which is longer than the Sn–N distances in the monomeric t-$\text{Bu}_3\text{SnN}_3$ [Sn–N 2.101(4) Å] and t-$\text{Bu}_2\text{SnN}_3$ [Sn–N 2.156(3), 2.141(2) Å].

Bis(trimethyltin)carbodiimide, $\text{Me}_3\text{SnNCNSnMe}_3$, forms an infinite helical network similar to $\text{Me}_3\text{SnN}_3$, in which trigonal–bipyramidally coordinated tin atoms are linked via $\mu$-nitrogens of the NCN dianion. Both nitrogens of a NCN$^2$ ligand are part of different N–Sn–N–Sn chains, which results in the infinite network with tetradentate NCN$^2$ ligands (155c). $N$-Trimethylstannyl-$N'$-nitrocarbodiimide, $\text{Me}_3\text{Sn}[\text{NCN(NO}_2\text{)}]$341, is an example for a bidentate NCN-group which bridges two tin centers via the 1- and 3-position to give a polymeric chain structure of type 155d.

The crystal structure analysis of trimethyltin dicyanamide, $\text{Me}_3\text{Sn}[\text{N(CN)}_2]$, exhibits a similar structure as that reported for trimethyltin cyanide (155a) containing bipyramidal coordinated tin atoms which are connected by the ligand to give an infinite zigzag chain of the type 155e. The average Sn–N distance is 2.335(9) Å. In the diorganotin compound $\text{Me}_2\text{Sn}[\text{N(CN)}_2]_2$, the tin centres are octahedrally coordinated with the methyl groups mutually trans. Thus, a two-dimensional layer structure composed of fused 16-membered rings (156) is formed. The Sn–N distances of 2.289(6) Å are comparable with the corresponding distances reported for the trimethyltin analogue, $\text{Me}_3\text{Sn}[\text{N(CN)}_2]$.
4,4′-Bipyridine and pyrazine are potentially cross-linking \( N, N′ \)-bidentate ligands which are capable of metal coordination to give one-dimensional polymers. In organotin coordination chemistry, some structural investigations of such coordination polymers were reported\(^{343-346} \). Among these is the acetonitrile solvate of poly[(\( \mu \)-4,4′-bipyridine)trimethyltin]dimesylamide, \( \{ \text{Me}_3\text{Sn}[\text{N(SO}_2\text{Me})_2]\}_{n} \cdot 4,4′\text{-bipy} \) \(^{(157)} \), which forms infinite chains of \( \text{Me}_3\text{Sn}^+ \) cations bridged by 4,4′-bipyridine ligands\(^{345} \). The tin atoms are pentacoordinated and the anions (MeSO\(_2\))\(_2\)N\(^-\) as well as the CH\(_3\)CN molecules are non-coordinating. The Sn–N distances amount to 2.420(2) and 2.411(2) Å and the N–Sn–N angle is 176.8(1)°. In contrast to the coordination polymer \(^{(157)} \), organotin halides form neutral complexes with pyrazine without dissociation of the tin–halide bond.

The one-dimensional coordination polymer \(^{(158)} \) with hexacoordinated tin atoms resulted from the reaction of diphenyltin dibromide with bis(1,2,4-triazol-1-yl)methane\(^{347} \). The bis(triazol-1-yl)methane coordinates to the tin atom in a bidentate bridging fashion through the nitrogen atoms at the 4-position of the triazole rings with intermolecular Sn–N distances of 2.454(7) Å.
Various types of triorganotin compounds bound to nitrogen-containing heterocycles such as imidazole, triazole and tetrazole derivatives were also investigated. In particular, tetrazole derivatives may coordinate to tin in a variety of different bridging modes. One example for a structurally characterised coordination polymer is 2,2-diphenyl-1,7,8,9-tetraaza-2-stannabicyclo[4.3.0]nona-6,8-diene. The tin atom in this compound is pentacoordinated with the nitrogens in axial positions of a trigonal bipyramid. The intramolecular and intermolecular Sn–N bond lengths amount to 2.34(1) Å and 2.39(1) Å, respectively, and the N–Sn–N angle is 173.8(5)°.

A series of bis(triorganostannyl)tetrazoles of the type \((R_3SnN_4C)_2X\) \((X = (CH_2)_n, n = 1, 2, 4–6; 1,2-C_6H_4; 1,3-C_6H_4; 1,4-C_6H_4; R = Me, Et, i-Pr, n-Bu)\) and trifunctional triorganotin tetrazoles of the type \((R_3SnN_4CCH_2CH_2)\)3C(NO2) and \(1,3,5-(R_3SnN_4C)\)3C6H3 \((R = Me, Et, n-Bu)\) were synthesised and characterised by \(^1H\), \(^13C\), \(^{119}Sn\) NMR, \(^{119}Sn\) Mössbauer spectroscopy and single crystal X-ray structure analyses. The single crystal X-ray structure analyses of the coordination polymers revealed that (i) usually a trans-N2SnC3 environment at tin is observed, (ii) each tetrazole moiety acts as a bidentate bridging ligand and (iii) the intramolecular and intermolecular Sn–N distances are in the range of 2.24 to 2.56 Å. Depending on the identity of the tetrazole ligand and the organic groups attached to tin, different two- and three-dimensional structures were observed. It is noteworthy that \([(Et_3SnN_4C)\)2(1,2-C6H4)] \((160a)\) forms a two-dimensional coordination polymer, whereas the closely related \([(n-Bu_3SnN_4C)\)2(1,2-C6H4)] \((160b)\) forms a three-dimensional network.

Triorganotin cyanometallates. A fascinating class of mainly three-dimensional coordination polymers based on Sn–N interactions is accessible via the connection of cyanometallate ions and trialkyl or triaryl tin cations. The general formula of this class of compounds is \([R_3Sn)_M(CN)\]n \((R = alkyl, aryl; M = transition metal)\). These cyanometallates were described to adopt a variety of networks with different topologies. In general, all compounds contain the sequence \(M–C≡N–SnR_3–N≡C–M\), in which the tin atom is pentacoordinated with the nitrogens in the axial and the alkyl or aryl groups in the equatorial positions of a trigonal bipyramid. Some of these compounds have large cavities and, despite their usually low thermal stability with decomposition temperatures in the range from 250–350 °C, these compounds were suggested to be promising candidates for applications such as ion exchange, molecular sieves and heterogenous catalysis. The first structurally characterised example, namely \([(Me_3Sn)_3Co(CN)_6]\)n, has a framework
\[(\text{Sn})\text{N} - \text{N} - \text{N} - \text{N}\text{SnR}_3 \quad (\text{Sn})\text{N} - \text{N} - \text{N} - \text{N}\text{Bu}_3\text{Sn} \quad (\text{Sn})\text{N} - \text{N} - \text{N} - \text{N}\text{SnBu}_3\]

\[(\text{Sn})\text{N} - \text{N} - \text{N} - \text{N}\text{NO}_2 \quad \text{N} - \text{N} - \text{N} - \text{N}\text{SnBu}_3 \]

\[(\text{Sn})\text{N} - \text{N} - \text{N} - \text{N}\text{SnBu}_3 \quad \text{N} - \text{N} - \text{N} - \text{N}\text{SnBu}_3 \quad \text{N} - \text{N} - \text{N} - \text{N}\text{SnBu}_3 \]

\[(\text{SN})\text{N} - \text{N} - \text{N} - \text{N}\text{SnBu}_3 \quad \text{N} - \text{N} - \text{N} - \text{N}\text{SnBu}_3 \]

(160a) \(R = \text{Et}\) two-dimensional sheet
(160b) \(R = \text{Bu}\) three-dimensional array
(160c) bilayer
(160d) mono-layer
(160e) mono-layer
containing large channels\(^{362,363}\). The latter compound was prepared quantitatively by the reaction of Me\(_3\)SnCl with K\(_3\)[Co(CN)\(_6\)] in aqueous solution. The resulting cyanometallate [(Me\(_3\)Sn)\(_3\)]Co(CN)\(_6\)]\(_n\) is not isostructural with [(n-Bu\(_3\)Sn)\(_3\)]Co(CN)\(_6\)]\(_n\) (162)\(^{364}\), which demonstrates that slight modifications of the basic structural building units may result in different three-dimensional architectures. In compound 162 each Co(CN)\(_6\) octahedron is corner shared through Sn atoms with six neighbours and each Co atom is a vertex of three 18- and five 30-membered rings (−C≡N−Sn−N≡C−sequences). The 18-membered ring consists of three Co(CN)\(_6\) octahedra and three Bu\(_3\)Sn moieties.

Much work has been devoted to the preparation and characterization of hexacyanoferrate compounds of the type [(R\(_3\)Sn)\(_x\)]Fe(CN)\(_6\)]\(_n\) (x = 3, 4; R = alkyl, aryl)\(^{364−378}\). An interesting example in this series is [(Ph\(_3\)Sn)\(_3\)]Fe(CN)\(_6\)·H\(_2\)O·2CH\(_3\)CN]\(_n\) (163), in which one nitrogen of the Fe(CN)\(_6\)\(^{3−}\) unit is not coordinated to a triphenyltin moiety. This nitrogen atom is linked to a water molecule via hydrogen bonding [O−N 2.82(2) Å] and the water molecule is coordinated to a Ph\(_3\)Sn\(^+\) cation [Sn−O 2.34(1) Å]. The insertion of water into the framework structure is suggested to result from the steric requirements of the triphenyltin moiety. The average Sn−N distance in 163 is 2.33(1) Å, which is comparable to other values reported for this class of compounds. Channels which are occupied by phenyl groups and acetonitrile molecules were formed along the b axis in the crystal lattice of 163 as shown below.
22. Organometallic polymers of germanium, tin and lead

(163)-coordination environment

(163)-framework
A number of other transition metals including Ru and Os\textsuperscript{369,372,379}, Cu\textsuperscript{380–383}, Zn\textsuperscript{380}, Au, Pd and Pt\textsuperscript{384}, Ni\textsuperscript{385,386}, Mo and W\textsuperscript{387,388} were also used to prepare supramolecular self-assembled triorganotin cyanometallates. A detailed description of all these compounds is beyond the scope of this article and only the structures of two representatives are discussed in more detail. The copper-containing derivative \([\text{CuCN-Me}_3\text{SnCN-0.5 bipy}]_n\) (bipy = 4, 4′-bipyridine) \((164)\) forms planar sheets held together by almost perpendicular bipyridine pillars\textsuperscript{382}. The sheets consist of \([\text{Cu}_2(\mu-\text{CN})_2(\text{CN})_2]\) fragments which are connected via \(\text{CN-SnMe}_3-\text{NC}\) sequences with the nitrogens in the axial positions of a trigonal–bipyramidal configurated tin to give 24-membered rings. The bipyridine ligands, which connect the layers by bridging the copper atoms of different layers, are omitted for clarity. The crystal lattice consists of two equivalent, ideally interpenetrating frameworks in which each bipyridine pillar of one framework passes the centre of the 24-membered ring of the second framework. The second example of the above mentioned series is \([\text{(Me}_3\text{Sn})_4\text{Mo(CN)}_8]_n\). Each of the Mo\textit{(CN)}\textsubscript{8} groups is linked to eight adjacent Mo\textit{(CN)}\textsubscript{8} groups via bridging Me\textsubscript{3}Sn moieties. These eight Mo\textit{(CN)}\textsubscript{8} groups constitute the corners of a tetragonal unit cell\textsuperscript{388}. The Mo atoms itself are in the centre of a square planar antiprism with the cyanide groups occupying the corners. The tin atoms are again pentacoordinated. The heavier analogue \([\text{(Me}_3\text{Sn})_4\text{W(CN)}_8]_n\) is isostructural with the molybdenum compound\textsuperscript{388}.\n
![Diagram 164](image-url)
The organotin cyanometallates show a distinct host–guest chemistry based on a facile ion exchange, e.g. the $\text{Me}_3\text{Sn}^+$ cations were replaced by numerous organic and organometallic guest cations $G_n^{3+}$, such as $\text{NH}_4^+$, $\text{Bu}_4\text{N}^+$, $[\text{methylviologen}]^{2+}$, $[\text{Cp}_2\text{Co}]^+$ or $[\text{Cp}_2\text{Fe}]^+$. Typical examples for this type of reaction are given in equations 3 and 4.

$$[(\text{Me}_3\text{Sn})_4\text{M(CN)}_6]_n \xrightarrow{\text{Et}_4\text{NCl}} [(\text{Et}_4\text{N})(\text{Me}_3\text{Sn})_3\text{M(CN)}_6]_n \quad (3)$$

$$[(\text{Me}_3\text{Sn})_4\text{M(CN)}_6]_n \xrightarrow{[\text{Cp}_2\text{Co}][\text{ClO}_4]} [(\text{Cp}_2\text{Co})(\text{Me}_3\text{Sn})_3\text{Fe(CN)}_6]_n \quad (4)$$

The organotin cyanometallates were also used to intercalate a range of organic compounds such as thiazole and benzothiazole derivatives, polyaniline or polypyrrole.

Diorganotin cyanometallates have received less attention. The syntheses of $\{(\text{Bu}_2\text{Sn})_3[\text{Fe(CN)}_6]_2 \cdot 4\text{H}_2\text{O}\}_n$ and $\{(\text{R}_2\text{Sn})_3[\text{Co(CN)}_6]_2\}_n$ ($\text{R} = \text{vinyl}, \text{n-butyl}, \text{n-propyl}$) were reported, but only the cobalt-containing metallates were characterised by single crystal X-ray diffraction. The size of the organic groups at tin has little effect on the topology of the three-dimensional frameworks made up by bridging $\text{R}_2\text{Sn}$ moieties and distorted octahedral $\text{Co(CN)}_6$ units. Each tin atom is octahedrally coordinated by two carbon atoms of the organic substituents and four nitrogens of the $\text{Co(CN)}_6$ units. In the crystal lattice, channels are formed along the $c$-axis and are occupied by disordered alkyl groups. These channels have bottlenecks which, in the case of $\text{R} = \text{vinyl}$ (see structure below), prevent facile release of solvent molecules.

Similarly to the cyanometallates, rhodium anions $[\text{Rh(SCN)}_6]^{3-}$ and $\text{Me}_3\text{Sn}^+$ cations self-assemble to give the polymeric $[(\text{Me}_3\text{Sn})_3\text{Rh(SCN)}_6]_n$ in the solid state. In the three-dimensional framework, the rhodium atoms are linked via non-linear $\text{SCN}^−−\text{SnMe}_3−\text{NCS}$ spacers. It was suggested that a host–guest chemistry similar to the ion exchange reactions reported for cyanometallates might be possible.

4. Miscellaneous coordination polymers of organotin compounds

Inorganic acid derivatives. Organotin derivatives of polyfunctional inorganic acids usually self-assemble in the solid state to give chain polymers, layered compounds or three-dimensional networks. The carbonates, $(\text{R}_3\text{Sn})_2\text{CO}_3$ ($\text{R} = \text{Me}, \text{n-Bu}$), are illustrative examples of one-dimensional polymers containing helical chains and pentacoordinated tin atoms. In both compounds there are dangling $−\text{OSnR}_3$ side groups pointing away from the polymer backbone. Dimethylin bis(fluorosulphate), $\text{Me}_2\text{Sn(SO}_3\text{F})_2$ ($\text{R} = \text{Me}$, $\text{Et}$), and dimethylin thiosulphate, $\text{Me}_2\text{SnS}_2\text{O}_3$, are typical examples of layered compounds. Three-dimensional supramolecular structures were reported for compounds such as tris(trimethyltin) chromate hydroxide, $(\text{Me}_3\text{Sn})_3\text{CrO}_4(\text{OH})$, and dimethylin molybdate, $\text{Me}_2\text{SnMoO}_4$.

Coordination polymers with coordinative tin–sulphur bonding. Supramolecular self-assembly via coordinative tin–sulphur interactions to give polymeric organotin compounds is less distinctive than in coordination compounds with intermolecular tin–oxygen interactions. Intermolecular $\text{Sn–S}$ bonds were reported for the cyclic tin compounds $\text{R}_2\text{Sn(SCH}_2\text{CH}_2)_2$ ($\text{R} = \text{Me}, \text{Et}, \text{n-Bu}$) and $\text{Me}_2\text{Sn(SCH}_2\text{CH}_2)_2\text{S}$.
R = vinyl, n-Bu, Pr

coordination environment

framework (substituents at tin are omitted for clarity)
which self-assemble to give one-dimensional arrays of five-membered and eight-membered rings, respectively. In 167 an additional intramolecular Sn–S interaction was observed, which results in heptacoordinated tin atoms.

Diisothiocyanate derivatives of tri- and diorganotin compounds are self-assembled in the solid state. Trimethyl- and triphenyltin isothiocyanate, $\text{Me}_3\text{SnNCS}$ and $\text{Ph}_3\text{SnNCS}$, form infinite $\text{S}–\text{Sn}–\text{N}–\text{C}–\text{S}–\text{Sn}$ zigzag chains which are bent at sulphur. Dimethyltin diisothiocyanate, $\text{Me}_2\text{Sn(NCS)}_2$, consists of infinite chains formed along the c-axis. The coordination geometry at tin is best described as that of a strongly distorted octahedron with C–Sn–C angles of approximately 149°. The Sn–N bond distances in the tri- and diorganotin derivatives are in the range of 2.10–2.26 Å and the coordinative Sn–S bonds are in the range of 2.90–3.20 Å.

A more recent example of a one-dimensional polymer formed via S–Sn coordination is trimethyltin dithiotetraphenylimidodiphosphinate, $\text{Me}_3\text{Sn(}\text{SPPh}_2\text{NPPh}_2\text{S)}$ (168). The tin atoms are trigonal–bipiramidally coordinated with the two sulphur atoms occupying the axial positions. The Sn–S distances are quite different and amount to 2.517 and 3.627 Å. The dithioimidophosphinato ligand usually chelates a metal centre, but in 168 it bridges two tin atoms to give a helical chain polymer.
iii. Coordination polymers with coordinative tin–phosphorus bonding. Coordination polymers with coordinative tin–phosphorus bonds are rare. An intermolecular P–Sn coordination was previously suggested to occur in Me₂ClSnCH₂CH₂PPh₂ (169)\(^{409,410}\) which was based on NMR and \(^{119}\)Sn Mössbauer spectroscopic data. Recently, X-ray crystal structure analyses confirmed the previous assumption and showed a linear polymer with pentacoordinated tin atoms\(^{238}\). The phosphorus and the chlorine atoms are located in axial positions. The Sn–P distance in 169 amounts to 3.065(1) Å, which is comparable to the Sn–P distance of 3.078(2) Å in the monomeric, intramolecularly coordinated Me₂ClSnCH₂CH₂CH₂PPhBu-\(^{411}\). The bromo-substituted analogue of 169, Me₂BrSnCH₂CH₂PPh₂, was also suggested to adopt a polymeric chain structure similar to that established for 169\(^{238}\).

B. Organolead Polymers

Despite the strong tendency of lead compounds bearing electron-withdrawing substituents to self-assemble in the solid state, the coordination chemistry of supramolecular organolead compounds was much less investigated than the coordination chemistry of supramolecular organotin compounds. One reason might be the high toxicity of organolead compounds and another one the often very poor solubility of polymeric lead compounds. The large atomic size of lead should give coordination polymers with high coordination number environments at Pb and consequently such polymers might be rather different from those of the tin analogues. Some recent investigations were directed towards the coordination chemistry of inorganic lead salts with organic ligands to give polymeric inorganic–organic hybrid materials. These investigations include examples of coordination polymers of lead(II) halides, nitrate and thiocyanate with aliphatic
and aromatic nitrogen bases. In addition, poly(ethylene glycol) complexes of lead(II) nitrate and bromide were reported. Furthermore, supramolecular self-assembly was also reported to occur in compounds such as lead(II) alkoxydes, lead(II) phosphonates, lead(II) phosphinates, and lead(II) carboxylates. A fascinating example is the bimetallic compound $[\text{Pb}_2\text{Co}_3\text{CCO}_2]_n$ (170), which forms a chain-like array as a result of bridging carboxylate ligands (The carbonyl ligands of the tricobalt clusters are omitted). Pyrolysis of this compound gave a bimetallic material, which is a stable heterogeneous catalyst for the hydrogenation of 1,3-butadiene.

Furthermore, supramolecular polymeric arrays resulting from intermolecular lead–sulphur interactions were reported for some inorganic lead compounds, e.g. bis($O$-methylidithiocarbonato)lead(II), $[\text{Pb(S}_2\text{COMe})]_n$, bis(diethylidithiophosphinato)lead(II), $[\text{Pb(S}_2\text{PEt}_2)_2]_n$, bis(diphenyldithiophosphinato)lead(II), $[\text{Pb(S}_2\text{PPh}_2)_2]_n$, and bis(dimethyldithiophosphinato)lead(II), $[\text{Pb(S}_2\text{PMe}_2)_2]_n$. In the latter compound, dimeric units consisting of eight-membered Pb$_2$S$_4$P$_2$ rings are linked to give a one-dimensional polymer. A two-dimensional polymeric array was reported for the cyclic lead(II) dithiolate $[\text{Pb(DMIT)(DMF)})]_n$ (DMIT = 2-thioxo-1,3-dithiole-4,5-dithiolato).

1. Intermolecular organolead–halide coordination

Triorganolead halides are usually associated in the solid state, which was suggested first on the basis of infrared and Raman studies and later confirmed by X-ray crystallography. Usually, the lead atom is pentacoordinated with the halogen atoms located in the axial positions of a trigonal bipyramid and infinite $-\text{Pb}--\text{X}--\text{chains with unsymmetrical X--Pb--X links are formed. The two lead--halide distances in a given compound differ significantly. Thus in Me$_3\text{PbI}$ the lead--iodine distances amount to 3.038(2}$
and 3.360(2) Å, whereas the lead–bromine distances are 2.852(1) and 3.106(1) Å in Ph₃PbBr, and 2.885(2) and 2.985(2) Å in BzPb₂Br. All structures reported show zigzag chain conformations as a result of bent Pb–X–Pb fragments (171). The Pb–X–Pb angle depends strongly on the nature of the organic groups and the halide bound to Pb, e.g. in Me₃PbI, Ph₃PbBr and Ph₃PbCl the Pb–X–Pb angles amount to 108.10(5)°, 129.5(5)° and 134.0(5)°, respectively.

Diphenyllead dichloride, Ph₂PbCl₂, was reported to form a one-dimensional chain with the chlorine atoms symmetrically bridging adjacent lead atoms. The lead atoms are octahedrally coordinated with the phenyl rings mutually trans and the octahedra linked via opposite edges, giving a one-dimensional coordination polymer. The Pb–Cl distances amount to 2.795(6) Å and symmetrical Pb₂Cl₂ squares are formed (172). Vibrational studies on Ph₂PbX₂ (X = Cl, Br, I) were indicative for hexacoordinated lead atoms in Ph₂PbCl₂ and Ph₂PbBr₂, but pentacoordinated lead atoms in Ph₂Pbl₂.

The arene complex (η⁶-C₆H₆)Pb[AlCl₄]₂·C₆H₆ self-assembles in the solid state to give a chain structure which consists of AlCl₄ tetrahedra bridged by (η⁶-C₆H₆)Pb(II) moieties, and further AlCl₄ tetrahedra chelating the (η⁶-C₆H₆)Pb(II) moieties.

2. Intermolecular organolead–oxygen coordination

Only few examples of self-organised organolead compounds with oxygen-based donors have been reported to date. Triphenyllead hydroxide, Ph₃PbOH (173), is isostructural with its tin analogue and forms zigzag chains in which planar Ph₃Pb fragments are linked by hydroxide groups. In the unsymmetrical O–Pb–O fragment the lead–oxygen bond lengths amount to 2.37(2) and 2.44(2) Å. Triphenyllead 2-fluoro-4-nitrosophenolate is among the few structurally characterised organolead alkoxides. The latter forms a one-dimensional polymer via intermolecular Pb–O interactions of the p-nitroso substituent. One-dimensional zigzag chain structures with pentacoordinated lead atoms are also adopted by trimethyllead carboxylates (174). The intramolecular and the intermolecular Pb–O distances in trimethyllead acetate, Me₃Pb(OOCCH₃) (174a), amount to 2.327(24) and 2.555(25) Å, respectively, and in trimethyllead 2-furoate, Me₃Pb(OOCC₄H₃O) (174b), to 2.553(9) and 2.534(9) Å, respectively.
The crystal structure analyses of water-free diphenyllead diacetate revealed essentially different coordination modes of the carboxylate ligands when compared with the hydrated diphenyllead diacetate. The monohydrate, \([\text{Ph}_2\text{Pb(OAc)}_2]_2 \cdot \text{H}_2\text{O}\) (175), is a dimer in which the lead atoms are heptacoordinated with phenyl groups occupying the axial positions of two pentagonal bipyramids (pbp). The equatorial positions in the first pbp are occupied by four oxygens of two chelating acetate groups and a water molecule. The equatorial positions of the second pbp are occupied by three oxygens of two chelating acetate groups and a weak O–Pb interaction [Pb–O 2.71(2) Å] of an adjacent acetate group chelating the first lead atom. In addition, the coordinated water molecule forms a hydrogen bond to an adjacent acetate group.

In contrast, the water-free \(\text{Ph}_2\text{Pb(OAc)}_2\) (176) is a one-dimensional polymer containing octahedrally configurated lead atoms. One acetate group bridges [Pb–O 2.348(8), 2.547(8) Å] the molecular units to give infinite chains and the other OAc group is symmetrically chelating [Pb–O 2.364(9), 2.354(8) Å]. In contrast, di-o-tolyllead diacetate, \((\text{o-Tol})_2\text{Pb(OAc)}_2\), and phenyllead triacetate, \(\text{PhPb(OAc)}_3\), are monomeric in the solid state with hexacoordinated and heptacoordinated lead atoms, respectively, and unsymmetrically chelating acetate groups.
The crystal structure analyses of two polymeric triorganolead sulphonyl amides were reported. The trimethyllead derivatives $\text{Me}_3\text{PbN(SO}_2\text{Me)}_2$\textsuperscript{460} and $\text{Me}_3\text{PbN(SO}_2\text{F)}_2$\textsuperscript{461} both form similar, chain-like polymeric arrays in which the lead atoms are pentacoordinated with one oxygen and one nitrogen atom occupying the axial positions of a trigonal bipyramid. In $\text{Me}_3\text{PbN(SO}_2\text{F)}_2$, the Pb–N and Pb–O distances are similar and amount to 2.603(6) and 2.615(6) Å, respectively, whereas in $\text{Me}_3\text{PbN(SO}_2\text{Me)}_2$ essentially different bond lengths were observed [Pb–N 2.484(6), Pb–O 2.653(6) Å]. Interestingly, the tin analogue $\text{Me}_3\text{SnN(SO}_2\text{Me)}_2$ is also a chain-like polymer, but the pentacoordinated tin atoms are linked via two oxygens of the dimesylamide ligand, $[\text{N(SO}_2\text{Me)}_2]^–$\textsuperscript{462}. In contrast to the polymeric tin and lead compounds, the germanium analogue $\text{Me}_3\text{GeN(SO}_2\text{Me)}_2$\textsuperscript{460} is monomeric in the solid state.

3. Intermolecular organolead–sulphur coordination

Examples of supramolecular association as a result of intermolecular organolead–sulphur interactions are rare and compounds such as $\text{Me}_3\text{PbSMe}$ and $\text{Ph}_3\text{PbSPh}$ are monomeric in the solid state\textsuperscript{463}. In contrast, triphenylethyl pyridine-4-thiolate, 4-$\text{Ph}_3\text{PbSC}_5\text{H}_4$\textsuperscript{464}, is a chain polymer as a result of intermolecular N–Pb interactions. The cyclic dithiolate 2,2-diphenyl-1,3,2-dithiaplumbolane \textsuperscript{177}\textsuperscript{465} self-assembles in the solid state via intermolecular tin–sulphur interactions into a one-dimensional polymeric array. The intramolecular Pb–S bond lengths amount to 2.52(2) and 2.49(1) Å and the intermolecular Pb–S distances are 3.55(2) Å.

Supramolecular self-assembly was also observed in triphenylethyl dimethyltendiophosphinate, [Ph$_3$PbS$_2$PMe$_2$]$_n$(178)\textsuperscript{466}. The ditiophosphinate ligand unsymmetrically bridges two lead atoms of adjacent molecules to give a polymeric chain with pentacoordinated lead centres. The coordination environment at lead is best described as that of a distorted trigonal bipyramid with the phenyl groups in the equatorial and the sulphur atoms in the axial positions. The Pb–S distances amount to 2.708(4) Å and 3.028(4) Å.
4. Intermolecular organolead–nitrogen coordination

Early examples of structurally characterised organolead coordination polymers with Pb–N interactions are trimethyllead cyanide, $\text{Me}_3\text{PbCN}$, dimethyllead dicyanide, $\text{Me}_2\text{Pb}(\text{CN})_2$, and trimethyllead azide, $\text{Me}_3\text{PbN}_3$ (179). The latter compound forms a linear chain polymer with a $\mu_2$-N atom symmetrically bridging the pentacoordinated lead centres [Pb–N 2.54(1) Å]. The N–Pb–N angle [178.6(5)°] deviates only slightly from the ideal value of 180°.

\[
\begin{array}{c}
\text{Me} & \text{Pb} & \text{Me} \\
\text{N} & & \text{N} \\
& \text{Me} & \text{Me} \\
& \text{Pb} & \text{Me} \\
\end{array}
\]

(179)

In analogy to the organotin cyanometallates, some organolead homologues of the type $[(\text{Me}_3\text{Pb})_3\text{M(CN)}_6]_n$ (M = Fe, Co) and $[(\text{Me}_3\text{Pb})_4\text{M(CN)}_6]_n$ (M = Fe, Ru) were prepared by simply adding a saturated aqueous solution of Me$_3$PbCl to concentrated solutions of $\text{K}_3[\text{M(CN)}_6]$ or $\text{K}_4[\text{M(CN)}_6]$. Structural data for these compounds based on X-ray crystallography are rare and mainly vibrational and solid state NMR spectroscopy were used to characterise the organolead cyanometallates.

A fully characterised compound is $[(\text{Me}_3\text{Pb})_3\text{Co(CN)}_6]_n$. The supramolecular organolead cyanometallate consists of a three-dimensional polymeric network with the sequence $-\text{Co}--\text{C}≡\text{N}--\text{Pb}--\text{N}≡\text{C}$. The network involves Me$_3$Pb$^+$ cations and wide parallel channels whose walls are internally coated by the methyl groups of the Me$_3$Pb$^+$ moieties. A second structurally characterised example of an organolead cyanometallate is $[(\text{Me}_3\text{Pb})_4\text{Fe(CN)}_6·2\text{H}_2\text{O}]_n$, which consists of infinite puckered layers. The sequences $-\text{Fe}--\text{C}≡\text{N}--\text{Pb}--\text{OH}_2$ within each layer form hydrogen bridges between adjacent layers. The anhydrous analogues were obtained after prolonged drying in vacuo at 60–80°C, but their exact structure is not known so far. The lead compounds $[(\text{Me}_3\text{Pb})_4\text{Fe(CN)}_6]_n$ do not display the unique ion-exchange properties of their tin analogues. For example, stirring a suspension of $[(\text{Me}_3\text{Pb})_4\text{Fe(CN)}_6]_n$ with an aqueous solution of Et$_4\text{NCl}$ did not give $[(\text{Et}_4\text{N})(\text{Me}_3\text{Pb})_3\text{Fe(CN)}_6]$ and Me$_3$PbCl. In contrast, $[(\text{Me}_3\text{Sn})_4\text{Fe(CN)}_6]_n$ is almost quantitatively transformed into $[(\text{Et}_4\text{N})(\text{Me}_3\text{Sn})_3\text{Fe(CN)}_6]$ by the release of Me$_3$Sn$^+$. However, it is possible to prepare by cocrystallisation of the appropriate cations and anions host–guest systems of the type $[(\text{G})(\text{Me}_3\text{Pb})_3\text{Fe(CN)}_6]_n$ with G = Et$_4$N$^+$ or Cp$_2$Co$^+$. In addition, the intercalation of heterocyclic organic guest molecules in the host system $[(\text{Me}_3\text{Pb})_4\text{Fe(CN)}_6]_n$ was investigated and compounds of the general type $[(\text{D})(\text{Me}_3\text{Pb})_3\text{Fe}^{II}_x\text{Fe}^{III}_1-x\text{Fe}(\text{CN})_6]_n$ (0 ≤ x ≤ 1; D = oxidised cationic organic guest donor) were synthesised.
V. REFERENCES

22. Organometallic polymers of germanium, tin and lead


22. Organometallic polymers of germanium, tin and lead


22. Organometallic polymers of germanium, tin and lead


1646  Klaus Jurkschat and Michael Mehring


22. Organometallic polymers of germanium, tin and lead

22. Organometallic polymers of germanium, tin and lead


CHAPTER 23

Biological activity of organogermanium compounds

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I. INTRODUCTION

Germanium is the middle element of Periodic Group IVA. The other elements in the Group have extensive and important biochemistries. Little attention has been paid to germanium chemically or biologically until it was found as a decay product of some nuclear disintegrations. Later, when its semiconductor property was found, interest grew. In 1962 van der Kerk and coworkers1 demonstrated that triorganylgermanium acetates had antifungal activities. Then in 1968 carboxyethylgermanium sesquioxide (GeCH₂CH₂COOH)₂O₃ (Ge-132) was synthesized by Asai².³ His goal of synthesizing water-soluble organoger- manium compounds originated from his conception that germanium should have some important significance for life, since this element is distributed universally in coal and is particularly present in valued Chinese herbs and healthy vegetables such as ginseng, garlic, oats or soya beans²,⁴ and is very well absorbed after ingestion (>90%). In the 1970s, dietary germanium supplements became very popular due to the alleged therapeutic value of germanium (stimulation of iron consumption and haemoglobin production). In 1994 the first organogermanium pharmaceutical propagermanium was launched in Japan under the trade name Serocion® (Sanwa Kagaku Kenkyusho Co., Ltd.). Its biological activity
spectrum includes protection against viruses, immunostimulation and hepatoprotection. Propagermanium — belonging to germsesquioxanes — has low toxicity.

This achievement has stimulated further investigations of the biological activity, not only of germsesquioxanes but also of other classes of low toxic organogermanium compounds.

Today, numerous organogermanium compounds possessing antitumor, immunomodulating, interferon-inducing, radioprotective, hypotensive and neurotropic properties have been synthesized\(^4\),\(^5\). The most intensively investigated organogermanium compounds are germsesquioxanes \([(\text{GeCHR}^1\text{CHR}^2\text{COOH})_2\text{O}_3]\), (1, \(\text{R}^1 = \text{R}^2 = \text{H}\), 2-carboxyethylgermanium sesquioxide, Ge-132, repargermanium, rexagermanium, proxigermanium, propagermanium, Serocion\(^\circledR\); \(\text{R}^1, \text{R}^2 = \text{alkyl, aryl, hetaryl}\), 2-(3-dimethylaminopropyl)-8,8-diethyl-2-aza-8-germaspiro[4,5]decane (2, spirogermanium), germatranes (3), germyporphyrines (4) and many germyl-substituted heterocycles (mainly derivatives of furan, thiophene, isoxazoline, uracil). Since biological investigations have become more important, some reviews on the biological properties of organogermanium compounds have appeared\(^2\)–\(^15\).

II. TOXICITY

Toxicological studies have demonstrated that most organogermanium compounds tested were less toxic than the corresponding organosilicon and organotin analogues\(^4\),\(^5\). On the other hand, in some cases nephrotoxicity caused by long-term administration of germanium-containing organic preparations in large doses was documented\(^12\),\(^14\)–\(^24\).
The acute toxicity of organogermanium compounds depends on the type of organogermanium compound, the substituent at the germanium atom and the coordination number of the latter ranging from nontoxic compounds (tetraalkylgermanes, germanols, germoxanes, adamantyl derivatives of germanium) with LD$_{50}$ more than 3000–5000 mg kg$^{-1}$ to highly toxic derivatives having LD$_{50}$ about 11–20 mg kg$^{-1}$ (trifluoroacetylfurylgermanes, thiénylgermatranes).

A group of low toxic germatranes is presented in Table 1. Their mean lethal dose (LD$_{50}$) at intraperitoneal (i.p.) administration varies from 10,000 to 3000 mg kg$^{-1}$. This group of compounds includes the derivatives of pyrrolidone ($\beta$-pyrrolidonyethyl being less toxic than $\alpha$-isomer), adamantane, phthalimide and $N,N'$-dialkylaniline. 1-Hydroxygermatrane (LD$_{50}$ 8400 mg kg$^{-1}$) is a low toxic compound, but the trimethylsilylation of its hydroxyl group increases the toxicity 2.4 times. (2-Methoxycarbonylpropyl)germatrane (LD$_{50}$ 6820 mg kg$^{-1}$), vinylgermatrane (LD$_{50}$ 5600 mg kg$^{-1}$) and $p$-fluorobenzoylaminomethylgermatrane (its chloro derivative being more toxic) also belong to this group of low toxic compounds.

The group of compounds with moderate toxicity (Table 2) includes chloromethylgermatrane (LD$_{50}$ 2960 mg kg$^{-1}$; its bromomethyl derivative appears considerably more toxic with LD$_{50}$ 355 mg kg$^{-1}$), 2- and 4-pyridylethylgermatranes (LD$_{50}$ 2820 and 2580 mg kg$^{-1}$), tris(2-thienyl)siloxy-, methyl(2-thienyl)siloxy-, dimethyl(2-thienyl)siloxy-, diphenylsiloxy- and triphenylsiloxygermatranes (LD$_{50}$ ca 2500, 1000, >2500, 2240, >1000 mg kg$^{-1}$), 2- and 3-furyl-, 2-furfuryl-, methyl(2-furyl)siloxy-, 4-bromo-3-thienyl- and $\beta$-styrylgermatrane (2050, 1630, 2960, 1030, 2240, 1410 mg kg$^{-1}$, respectively). Triphenylgermoxy-, diphenylmethylsiloxy-, $\alpha$-naphtylphenylsiloxygermatrane and all benzylgermatranes also possessed moderate toxicity (LD$_{50}$ >1000 mg kg$^{-1}$).

RCH$_2$-substituted germatranes (Tables 2 and 3), where R = diethylamino-, bromo-, 2-thienyl, form a group of more toxic compounds (LD$_{50}$ 325–350 mg kg$^{-1}$). 1-Hydrogermatrane reveals a similar toxicity (LD$_{50}$ 320 mg kg$^{-1}$).

### TABLE 1. Acute toxicity of germatranes \((\text{RGe(OCH}_{2}\text{CH}_{2})_{3}\text{N (i.p. administration to white mice})\) \(\text{LD}_{50}\) (mg kg$^{-1}$)

<table>
<thead>
<tr>
<th>R</th>
<th>LD$_{50}$ (mg kg$^{-1}$)</th>
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<th>LD$_{50}$ (mg kg$^{-1}$)</th>
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<td>(1\text{-Ad} )</td>
<td>&gt;5000</td>
<td>(\text{Me}<em>{3}\text{SiC=}\text{CH}</em>{2} )</td>
<td>3460</td>
</tr>
<tr>
<td>(\text{F} )</td>
<td>&gt;5000</td>
<td>(\text{Et}_{2}\text{N} )</td>
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TABLE 2. Acute toxicity of germatranes \( \text{RGe(OCH}_2\text{CH}_2)_3\text{N} \)

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TABLE 3. Acute toxicity of thienylgermatranes

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<td>2240</td>
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<tr>
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<td>&gt;1000</td>
<td><img src="image14" alt="Image" /></td>
<td>89</td>
</tr>
<tr>
<td><img src="image15" alt="Image" /></td>
<td>&gt;1500</td>
<td><img src="image16" alt="Image" /></td>
<td>325</td>
</tr>
</tbody>
</table>

All furylgermatranes are less toxic than corresponding thienyl derivatives$^{10}$. 2-Thienyl-, 5-methyl-2-thienyl-, 5-bromo-2-thienyl- and 2-methyl-3-thienylgermatranes are highly toxic compounds with LD$_{50}$ values within the 16.5–20.5 mg kg$^{-1}$ range (Table 3). The position of bromine atom and the germatranyl group in the thiophene ring...
dramatically influences the toxicity of a compound: it varies from the very toxic 5-bromo-2-thienylgermatrane to nontoxic 3-bromo-4-thienylgermatrane (Table 3). 2-substituted isomers belonging to the thiophene series appear to be the most toxic, while in the furan series the 2-derivatives are less toxic than the 3-isomers. Phenylgermatrane is two times less toxic than 2-thienylgermatrane (16.5 mg kg$^{-1}$) but still exhibits high toxicity (LD$_{50}$ 35.5 mg kg$^{-1}$). Introduction of a methyl group in the para-position of a phenyl ring decreases the toxicity 2 times (LD$_{50}$ 70 mg kg$^{-1}$).

The high toxicity of phenyl- and thienylgermatranes cannot be explained either by the presence of the tricyclic germatrane ring with the pentacoordinated germanium atom or by the presence of the $\pi$-electron system in the substituent. Alkylgermatranes containing the same germatrane system and vinylgermatrane (possessing a $\pi$-bond) are nontoxic compounds (Table 1). Hydrolysis of the Ge–O bond decreases the toxicity by more than 500 times. Both products of Ge–O bond hydrolysis—germanic acid (LD$_{50}$ ca 2000 mg kg$^{-1}$) and triethanolamine (LD$_{50}$ 1450 mg kg$^{-1}$)—are also less toxic than the starting 2-thienylgermatrane. As the mechanism of arylgermatrane biological activity is not yet known, one can speculate that both parts of the molecule—the germatrane system (for binding to the receptor?) and the aryl group bound directly to the germanium atom (for toxic bioarylation; 2-thienylmethyl- and benzylgermatranes are less toxic, LD$_{50}$ 325 and >1000 mg kg$^{-1}$)—are important for the exhibition of high toxicity.

Most of the organylgermsesquioxanes (RGeO$_{1.5}$)$_n$ and organylgermsesquithianes (RGeS$_{1.5}$)$_n$ tested are low toxic compounds.

The toxicity of various germesquioxanes (proxigermanium, propagermanium, Ge-132, 2-carboxyethylgermsesquioxane) has been investigated.

2-Carboxyethylgermsesquioxane exhibits acute toxicity for mice and rats with a mean LD$_{50}$ value of 6000–10000 mg kg$^{-1}$ (p.o., i.p.) and 4500–5700 mg kg$^{-1}$ (i.v.) Sub-chronic oral toxicity of [(HOOCCH$_2$CH$_2$Ge)$_2$O$_3$]$_n$ (in rats of 1 g kg$^{-1}$ day$^{-1}$ during six months) has been reported. Daily oral administration of Ge-132 (120 mg kg$^{-1}$) for 24 weeks exhibited no toxic effects in mice.

Oral administration of proxigermanium for a year at 750 mg kg$^{-1}$ day$^{-1}$ induced diarrhea in rats. However, it has been found that a dose of 83 mg kg$^{-1}$ is not toxic. Proxigermanium administered in a dose of 15–240 mg/body has not affected physiological function in healthy volunteers.

The compound is not embriotoxic, teratogenic, mutagenic, carcinogenic or anti-genic. Oral administration of proxigermanium does not affect fertility at 350, 700 and 1400 mg kg$^{-1}$ day$^{-1}$ during 60 days before and at mating in male rats and during 14 days before, and at and during 7 days after mating in female rats.

The histological investigation revealed no significant renal toxic effects of propagermanium when administered at a high dose for 8 weeks. Propagermanium administration was not associated with any alteration in the changes induced by Adriamycin or mercuric chloride. This confirms that propagermanium may be a safe compound for use in individuals with compromised kidneys. On the other hand, case reports on the nephro-toxicity of organogermanium preparations (high doses, long-term administration) have been published. One-month oral subacute toxicity of propagermanium has been studied.

Hydroxamic acid (O$_{1.5}$GeCH$_2$CH$_2$CONHOH)$_n$, its sodium salt and 1-(2-pyrrolidonyl)ethylgermsesquioxane appear to be low toxic compounds as well, their LD$_{50}$ values exceeding 5000 mg kg$^{-1}$. 3,5-Dimethylpyrazolylmethylgermsesquioxane (n = 6) exhibits acute toxicity with a mean LD$_{50}$ value of 708 mg kg$^{-1}$.40.
Cyclic and acyclic organogermanium derivatives of cysteamine and methylcysteamine exhibit toxicity within the 150–1500 mg kg$^{-1}$. Introduction of the germatranyl group into aminothiol molecules decreases the toxicity of the compounds. Germadithioacetals showed moderate toxicity (100–800 mg kg$^{-1}$). Diisoamyldithiagermocane, germylated sulfides and di-$n$-hexylpyridinoxathiagermolane are low toxic compounds (800 to >1500 mg kg$^{-1}$). Subacute toxicity of tetra(2-carboxy-2-aminoethylmercapto)germanium has been studied.

The acute toxicity of a new class of germilisoxazolin-2-yl derivatives (5) has been investigated. These compounds have medium toxicity (mean LD$_{50}$ values within 355–708 mg kg$^{-1}$). The introduction of a methylene group between the triethylgermyl group and the isoxazoline ring, as in the case of germatranes (Table 2), decreases the toxicity 2.2-fold.

![Chemical structure](image)

(5) R = 2-, 3-, 4-pyridyl, n = 0; 2-, 3-pyridyl, n = 1

Trifluoroacetyl derivatives of furan possess a wide range of toxicity (Table 4). In this type of compounds germanium derivatives are more toxic than the corresponding silicon derivatives. The triethylgermyl derivative is a highly toxic compound, LD$_{50}$ 11.2 mg kg$^{-1}$. It is interesting to note that trimethyl derivatives of Ge and Si analogues have comparable toxicity, but substitution of the methyl group by ethyl dramatically changes the toxicity. The germanium derivative becomes 200 times more toxic than the silicon analogue (see Table 4).

The experimental evaluation of acute toxicity of germil(silyl)-substituted furfurylidene Meldrum acid (Table 5) has demonstrated that the introduction of the trimethylgermyl group lowers the toxicity of the compound by ca 4 times. On the other hand, the introduction of the trimethysilyl group does not change significantly the toxicity of the unsubstituted derivative. The carbon analogue is the most toxic derivative in this series of compounds.

Preclinical toxicological evaluation of spiogermanium (2-(3-dimethylaminopropyl)-8,8-diethyl-2-aza-8-germaspiro[4,5]decane) (2) in white mice and beagle dogs confirmed a lack of bone-marrow toxicity and pointed to a dose-limiting toxic effect of the spiogermanium compound on the central nervous system, manifested in dogs by piloerection, nystagmus,

### Table 4. Acute toxicity of R COCF$_3$ (i.p. white mice)

<table>
<thead>
<tr>
<th>R</th>
<th>LD$_{50}$ (mg kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me$_3$C</td>
<td>22</td>
</tr>
<tr>
<td>Me$_3$Si</td>
<td>122</td>
</tr>
<tr>
<td>Et$_3$Si</td>
<td>2240</td>
</tr>
<tr>
<td>Me$_3$Ge</td>
<td>71</td>
</tr>
<tr>
<td>Et$_3$Ge</td>
<td>11.2</td>
</tr>
</tbody>
</table>
TABLE 5. Acute toxicity of \( \text{R} \rightarrow \text{C} \equiv \text{O} \) (i.p. white mice)

<table>
<thead>
<tr>
<th>R</th>
<th>LD(_{50}) (mg kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>515</td>
</tr>
<tr>
<td>Me(_3)C</td>
<td>178</td>
</tr>
<tr>
<td>Me(_3)Si</td>
<td>447</td>
</tr>
<tr>
<td>Et(_3)Si</td>
<td>224</td>
</tr>
<tr>
<td>Me(_3)Ge</td>
<td>2050</td>
</tr>
</tbody>
</table>

tremor and lethal dose generalized seizures\(^{11,47,48}\). A neurotoxicity of the spirogermanium at doses of 32–60 mg m\(^{-2}\) has been observed in clinical trials as well\(^4\). A dose-limiting toxicity has been observed in patients\(^{49}\). Spirogermanium is rapidly removed from the plasma and appears not to be accumulated in tissues\(^{14}\).

III. NEUROTROPIC ACTIVITY

The neurotropic activity of gematranaes, germesquioxanes, germyl-substituted amines, imines, hydroxamic acids, isoxazolines and organogermanium derivatives of furan and adamantane has been studied\(^4,5,10,40,44,50–54\).

The influence of siloxy- and germoxygematranaes \( \text{R}_n \text{MOGe(OCH}_2\text{CH}_2)_3\text{N} \) (M=Si, Ge) on locomotor activity and muscle tone parameters was low. Trimethylsiloxy-, triphenyl siloxy- and triphenylgermylsiloxygematranaes in doses up to 500 mg kg\(^{-1}\) do not affect the parameters mentioned. In rotating-rod, tube and traction tests di(2-thienyl)methyl-, tri(2-thienyl)- and \( \alpha \)-naphtylphenylsiloxygematranaes have ED\(_{50}\) within the 178–410 mg kg\(^{-1}\) range, and (2-thienyl)dimethylsiloxygematrane between 70 and 250 mg kg\(^{-1}\). 1-Hydroxygematrane (ED\(_{50}\) 0.0015 mg kg\(^{-1}\)) exhibits the highest depressant activity on the central nervous system (CNS)\(^{10}\).

1-Hydroxygematrane prevents the hypoxia-caused death in experimental animals. The prolongation of life-span for a mouse under hypoxic hypoxia (i.p. administration, 50 mg kg\(^{-1}\)) is more than doubled under the influence of gematrano. Silylation and gemylation of its hydroxy group significantly decrease the antihypoxic properties as measured by the activity in percentage vs. control (100%) (Table 6). Introduction of alkyl substituents in position 5 of the thiophene ring does not significantly change the antihypoxic activity.

In most cases the hetarylgematranaes [\( \text{R(CH}_2\text{)}_n \text{Ge(OCH}_2\text{CH}_2)_3\text{N} \)] with gematranyl group connected directly to the carbon atom (\( n = 0 \)) possess higher toxicity and higher CNS activity\(^{10}\).

Some regularities have been observed in the series of 5-membered nitrogen heterocycles (Table 7). The 1-isomer of pyrrolidonylethylgematrane is more active than the 2-isomer. Introduction of a second carbonyl group in the ring (R = succinimidomethyl) increases the antihypoxic effect of the compound. Introduction of a double bond (R = maleinimidomethyl) leads to the further increase in the activity (145.5%). The condensation of the latter with the benzene ring (R = phthalimidomethyl) reduces the activity while the substitution of one carbonyl group for the SO\(_2\) group increases the protecting properties.

4-(Dimethylamino)phenylgematrane, belonging to the series of nitrogen-containing phenylgematranaes, shows reliable antihypoxic activity, prolonging the life by 55.4%.
### TABLE 6. Protection against hypoxia by $\text{RGe(OCH}_2\text{CH}_2)_3\text{N}$

<table>
<thead>
<tr>
<th>R</th>
<th>% vs. control</th>
<th>R</th>
<th>% vs. control</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO</td>
<td>186.5</td>
<td>SiMeO</td>
<td>118.0</td>
</tr>
<tr>
<td>Me$_3$SiO</td>
<td>148.1</td>
<td>SiMeO</td>
<td>114.8</td>
</tr>
<tr>
<td>(S$_3$)SiO</td>
<td>136.2</td>
<td>SiMe$_2$O</td>
<td>111.1</td>
</tr>
<tr>
<td>(S$_3$)GeO</td>
<td>116.4</td>
<td>SiMe$_2$O</td>
<td>116.7</td>
</tr>
</tbody>
</table>

### TABLE 7. Protection against hypoxia by $\text{RGe(OCH}_2\text{CH}_2)_3\text{N}$

<table>
<thead>
<tr>
<th>R</th>
<th>% of control</th>
<th>R</th>
<th>% of control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et$_2$NCH$_2$</td>
<td>156.6</td>
<td>CONHCH$_2$</td>
<td>130.7</td>
</tr>
<tr>
<td>NCH$_2$CH$_2$</td>
<td>116.6</td>
<td>NCH$_2$</td>
<td>145.5</td>
</tr>
<tr>
<td>NCHCH$_3$</td>
<td>122.8</td>
<td>NCH$_2$</td>
<td>114.1</td>
</tr>
<tr>
<td>NCH$_2$</td>
<td>136.0</td>
<td>SO$_2$NCH$_2$</td>
<td>139.7</td>
</tr>
<tr>
<td>Me$_2$N</td>
<td>162.3</td>
<td>Me$_2$N</td>
<td>155.4</td>
</tr>
</tbody>
</table>
TABLE 8. Protection against hypoxia by RGe(OCH₂CH₂)₃N

<table>
<thead>
<tr>
<th>R</th>
<th>% of control</th>
<th>R</th>
<th>% of control</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>184.8</td>
<td>CH₂</td>
<td>117.6</td>
</tr>
<tr>
<td>S</td>
<td>150.5</td>
<td>CH₂</td>
<td>132.8</td>
</tr>
<tr>
<td>O</td>
<td>169.5</td>
<td>SMe</td>
<td>132.8</td>
</tr>
<tr>
<td>O</td>
<td>131.8</td>
<td>SMe</td>
<td>126</td>
</tr>
<tr>
<td>S</td>
<td>141.3</td>
<td>SMe</td>
<td>133.4</td>
</tr>
<tr>
<td>SBr</td>
<td>111.3</td>
<td>SBr</td>
<td>146</td>
</tr>
<tr>
<td>CH₂</td>
<td>171</td>
<td>Me</td>
<td>118</td>
</tr>
<tr>
<td>CH₂</td>
<td>127</td>
<td>Me</td>
<td>128</td>
</tr>
<tr>
<td>CH₂</td>
<td>255</td>
<td>Br</td>
<td>150</td>
</tr>
<tr>
<td>CH₂</td>
<td>158</td>
<td>Br</td>
<td>116</td>
</tr>
</tbody>
</table>

5-(1-Cyclohexenyl)-1-germatranyl methyl-5-methylbarbituric acid has the highest antihypoxic activity among the nitrogen-containing compounds (Table 7).

Furyl- and phenylgermatranes are more active against hypoxia than thienylgermatranes and compounds with a nitrogen-containing substituent (Table 8). The protecting potency of 2-furylgermatrane is higher than that of the 3-isomer. Insertion of the CH₂ group between the aromatic or heteroaromatic ring and the germatrane group reduces the activity in all cases (Table 8). Introduction of a methyl group in position 5 of the thiophene ring increases
the antihypoxic activity by 2.6 times. In bromobenzylgermatranes, the antihypoxic activity strongly depends on the position of bromine atom: \( \alpha \)- and \( \beta \)-derivatives are 3 times more active than \( m \)-bromobenzylgermatrane. The \( \beta \)-styrylgermatrane exhibits the highest antihypoxic activity.

Furylgermatranes exhibit stimulating activity in an ethanol anaesthesia test (Table 9). In the thiophene series 2-isomer is a stimulant as well, while the 3-isomer acts as CNS depressant. Introduction of a methyl group increases the stimulating activity of the 2-isomer and the depriming properties of the 3-isomer. Introduction of an ethyl group in position 5 changes the action mode of the 2-isomer from stimulation of CNS to its depression. Some regularities have been observed in aromatic derivatives. All substituted arylogermatranes exhibit a stimulating activity in the ethanol anaesthesia test. \( p \)-Tolylgermatrane has the highest antidepressant activity (68%). Unsubstituted arylogermatranes possess depriming properties. Most tested aryl- and hetarylgermatranes prolong the duration of hexobarbital anaesthesia. High activity is observed for \( p \)-bromobenzyl- (195%) and 5-ethyl-2-thienyl derivatives (205%). The 2-furfuryl derivative is even more active (236.6%). It is interesting to note that in some cases the mode of anaesthetic activity depends on the anaesthetic agent. For example, all furylgermatranes prolong the duration of hexobarbital anaesthesia but shorten the ethanol anaesthetic properties (Table 9).

1-Hydroxygermatrane shortens the duration of ethanol anaesthesia (Table 10). Triphenylgermylation of its hydroxyl group increases the stimulating activity while the silylation in most cases prolongs the ethanol anaesthesia. Methyl(2-furyl)siloxygermatrane and diphenylsiloxygermatrane were the most active compounds in prolongation of hexobarbital anaesthesia.

1-Hydroxygermatrane (p.o.) has been shown to lack any protective activity in corazol-, maximal electric shock- and strychnine-induced convulsions. Hydroxygermatrane hydrate does not prevent tremor caused by the N- and M-ergic substances nicotine and arecoline. However, when thiostemicarbazide was used as a convulsion-inducing agent, germatranol in doses of 100 and 250 mg kg\(^{-1}\) noticeably increased the latent period of the beginning of the first tremor attack. This fact provides indirect evidence for the participation of GABA in the neurotropic mechanism of the compound. With the same dose, germatranol hydrate displays serotonin-blocking activity.

Arylogermatranes were more active than hetaryl derivatives in memory improvement tests (Table 11). Phenylgermatrane, \( p \)-tolylgermatrane, \( p \)-fluorophenylethynylgermatrane, benzylgermatrane and \( \alpha \)- and \( p \)-bromobenzylgermatranes completely prevented animals from retrogradal amnesia caused by electric shock.

Germinol generally undergo dehydration to form the corresponding germonoxanes. Tricyclohexylgermatrane is the sole example which was successfully isolated and studied. This compound in doses of 35–100 mg kg\(^{-1}\) showed some sedative activity, i.e., reduced the duration of phenamine stereotype behavior, and in a dose of 35 mg kg\(^{-1}\) lowered the body temperature by 3°C (or even more) in 50% of the experimental animals. On changing from germatranes to germesquioxanes with the same substituent at the germanium atom, the effect of the latter on locomotor activity, muscle tone and body temperature is increased to some extent. It has been noted that 3,5-dimethylpyrazolymethylgermesquioxanes within their neurotropic activity spectrum have the ability of activating action, in that they strengthen the phenamine stimulation by 55.3 and 34.6%, respectively, and reduce reserpine-depressant activity (ptosis and hypothermia) (Table 12).
TABLE 9. Neurotropic activity of germatranes $\text{RGe(OCH}_2\text{CH}_2)_3\text{N}$

<table>
<thead>
<tr>
<th>R</th>
<th>% of control</th>
<th>% of control</th>
<th>R</th>
<th>% of control</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ethanol</td>
<td>hexobarbital</td>
<td></td>
<td>ethanol</td>
</tr>
<tr>
<td>Cl</td>
<td>166.7</td>
<td>101</td>
<td>Me</td>
<td>32</td>
</tr>
<tr>
<td>CH$_2$</td>
<td>116</td>
<td>162</td>
<td>Br$_2$</td>
<td>80</td>
</tr>
<tr>
<td>CH$_2$=CH</td>
<td>132</td>
<td>150</td>
<td>Br$_2$CH$_2$</td>
<td>60</td>
</tr>
<tr>
<td>Br</td>
<td>163</td>
<td>100</td>
<td>Br$_2$CH$_2$</td>
<td>91</td>
</tr>
</tbody>
</table>
### TABLE 10. Neurotropic activity of germatranes ROGe(OCH₂CH₂)₃N

<table>
<thead>
<tr>
<th>R</th>
<th>% of control anaesthesia</th>
<th>R</th>
<th>% of control anaesthesia</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ethanol</td>
<td>hexobarbital</td>
<td>ethanol</td>
</tr>
<tr>
<td>H</td>
<td>89.4</td>
<td>132.2</td>
<td>140.9</td>
</tr>
<tr>
<td>Me₃Si</td>
<td>151</td>
<td>95.5</td>
<td>110</td>
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<td><img src="image1" alt="Structure" /></td>
<td>87.4</td>
<td>129.4</td>
<td>168.5</td>
</tr>
<tr>
<td><img src="image2" alt="Structure" /></td>
<td>46.2</td>
<td>133.3</td>
<td>156.6</td>
</tr>
<tr>
<td><img src="image3" alt="Structure" /></td>
<td>124.6</td>
<td>201.7</td>
<td>94.5</td>
</tr>
</tbody>
</table>

### TABLE 11. Neurotropic activity of germatranes RGe(OCH₂CH₂)₃N

<table>
<thead>
<tr>
<th>R</th>
<th>Retrogradal amnesia (%)</th>
<th>R</th>
<th>Retrogradal amnesia (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image4" alt="Structure" /></td>
<td>100</td>
<td><img src="image5" alt="Structure" /></td>
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<tr>
<td>Br</td>
<td>83</td>
<td><img src="image6" alt="Structure" /></td>
<td>100</td>
</tr>
<tr>
<td>Me</td>
<td>100</td>
<td><img src="image7" alt="Structure" /></td>
<td>60</td>
</tr>
<tr>
<td><img src="image8" alt="Structure" /></td>
<td>66</td>
<td><img src="image9" alt="Structure" /></td>
<td>100</td>
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<tr>
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<td>33</td>
<td><img src="image11" alt="Structure" /></td>
<td>50</td>
</tr>
</tbody>
</table>
TABLE 12. Neurotropic activity of germesquioxanes

<table>
<thead>
<tr>
<th>Compound</th>
<th>LD$_{50}$ (mg kg$^{-1}$)</th>
<th>Phenamine stereotype behavior (% of control)</th>
<th>Hypothermia (% of control)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$CH$<em>2$GeO$</em>{1.5}$Me$_5$</td>
<td>&gt;5000</td>
<td>155.3</td>
<td>71</td>
</tr>
<tr>
<td>N$_2$CH$<em>2$GeO$</em>{1.5}$Me$_6$</td>
<td>708</td>
<td>134.6</td>
<td>282</td>
</tr>
<tr>
<td>N$_2$CH$_2$Ge(OCH$_2$CH$_2$)$_3$NMe</td>
<td>3600</td>
<td>136.8</td>
<td>870</td>
</tr>
</tbody>
</table>

TABLE 13. Neurotropic activity of germyl-substituted amines and imines

<table>
<thead>
<tr>
<th>R</th>
<th>LD$_{50}$ (mg kg$^{-1}$)</th>
<th>ED$_{50}$ (mg kg$^{-1}$)</th>
<th>Hypothermia (% of control)</th>
<th>Hypoxia (% of control)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Rotating rod test</td>
<td>Tube test</td>
<td>Traction test</td>
</tr>
<tr>
<td>CH$_2$=NNHC(O)NH$_2$</td>
<td>—</td>
<td>51.5</td>
<td>65</td>
<td>51.5</td>
</tr>
<tr>
<td>CH$_2$=NNHC(S)NH$_2$</td>
<td>205</td>
<td>&gt;20</td>
<td>&gt;20</td>
<td>&gt;20</td>
</tr>
<tr>
<td>CH$_2$=NNH</td>
<td>224</td>
<td>18.7</td>
<td>22.4</td>
<td>28.2</td>
</tr>
<tr>
<td></td>
<td>CH$_2$NM$_3$I</td>
<td>81.5</td>
<td>23.5</td>
<td>28.2</td>
</tr>
<tr>
<td></td>
<td>CH$_2$NEt$_2$MeI</td>
<td>81.5</td>
<td>4.1</td>
<td>2.6</td>
</tr>
</tbody>
</table>

as therapeutic agents for brain aging. Germanium-132 can antagonize the damage of neural behavior caused by lead.

Furan-containing germyl-substituted amines have moderate toxicity (LD$_{50}$ 205–234 mg kg$^{-1}$). Their methylammonium derivatives have been found to possess the highest toxicity (LD$_{50}$ 81.5 mg kg$^{-1}$) in this group of compounds. The methyldiethylammonium compound shows the highest depressant activity in rotating-rod, tube, traction and hypothermia tests. Substitution of the ethyl groups for methyl groups in the ammonium derivatives evokes a considerable decrease in depressant activity component (Table 13).
It has been found that the neurotropic activity of 2-trialkylgermyl-5-trifluoroacetylfurans depends on the alkyl substituent at the germanium atom: the 2-triethylgermyl derivative exhibits the highest activity in the hexobarbital anaesthesia test and prolongs its duration by 137%. The 2-trimethylgermyl derivative exhibits a stimulating activity in the ethanol anaesthesia test and completely prevents animals from retrogradal amnesia (Table 14). All germyl-substituted compounds possess anti-Corazol potency; however, the trimethylsilyl and tert-butyl derivatives were more active. The pharmacological effects of phenamine are depressed by all the trifluoroacetyl derivatives. It has been found that the neurotropic activity of 2-trialkylgermyl-5-trifluoroacetylfurans depends on the alkyl substituent at the germanium atom: the 2-triethylgermyl derivative exhibits the highest activity in the hexobarbital anaesthesia test and prolongs its duration by 137%. The 2-trimethylgermyl derivative exhibits a stimulating activity in the ethanol anaesthesia test and completely prevents animals from retrogradal amnesia (Table 14). All germyl-substituted compounds possess anti-Corazol potency; however, the trimethylsilyl and tert-butyl derivatives were more active. The pharmacological effects of phenamine are depressed by all the trifluoroacetyl derivatives.

TABLE 14. Neurotropic activity of $\text{R} = \text{Me}_3\text{C}, \text{Me}_3\text{Si}, \text{Me}_3\text{Ge}, \text{Et}_3\text{Si}, \text{Et}_3\text{Ge}$.

<table>
<thead>
<tr>
<th>R</th>
<th>Anaesthesia</th>
<th>% vs. control</th>
<th>Corazol-induced spasms</th>
<th>Phenamine stereotype</th>
<th>RA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ethanol</td>
<td>hexobarbital</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Me$_3$C</td>
<td>320</td>
<td>133</td>
<td>175</td>
<td>61</td>
<td>60</td>
</tr>
<tr>
<td>Me$_3$Si</td>
<td>240</td>
<td>86</td>
<td>224</td>
<td>44</td>
<td>16.7</td>
</tr>
<tr>
<td>Me$_3$Ge</td>
<td>51</td>
<td>96</td>
<td>149</td>
<td>58</td>
<td>100</td>
</tr>
<tr>
<td>Et$_3$Si</td>
<td>74</td>
<td>89</td>
<td>94</td>
<td>90</td>
<td>50</td>
</tr>
<tr>
<td>Et$_3$Ge</td>
<td>71</td>
<td>237</td>
<td>129</td>
<td>84</td>
<td>80</td>
</tr>
</tbody>
</table>

TABLE 15. Neurotropic activity of $\text{R} = \text{Et}_3\text{Ge(CH}_2\text{)}_{n}\text{HCl}$.

<table>
<thead>
<tr>
<th>R</th>
<th>$n$</th>
<th>Anaesthesia</th>
<th>% vs. control</th>
<th>Corazol-induced spasms</th>
<th>Phenamine stereotype</th>
<th>Hypoxia</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ethanol</td>
<td>thiopeutal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-pyridyl</td>
<td>0</td>
<td>99</td>
<td>209</td>
<td>156</td>
<td>113</td>
<td>125.5</td>
</tr>
<tr>
<td>3-pyridyl</td>
<td>0</td>
<td>336.7</td>
<td>74.1</td>
<td>174</td>
<td>28.5</td>
<td>136</td>
</tr>
<tr>
<td>4-pyridyl</td>
<td>0</td>
<td>216.7</td>
<td>138.8</td>
<td>114</td>
<td>117.8</td>
<td>102</td>
</tr>
<tr>
<td>2-pyridyl</td>
<td>1</td>
<td>72</td>
<td>133</td>
<td>140</td>
<td>91</td>
<td>134</td>
</tr>
<tr>
<td>3-pyridyl</td>
<td>1</td>
<td>32</td>
<td>119</td>
<td>120.7</td>
<td>94.1</td>
<td>113.7</td>
</tr>
</tbody>
</table>

All germyl-isoxazolin-2-yl pyridine derivatives exhibit low activity in rotating-rod, tube and traction tests. The 2-pyridyl-substituted germylisoxazoline ($n = 0$) was the most active in increasing the duration of thiopental anaesthesia by 109%, while the 3-pyridine-substituted analogue decreased it by 25.9% (Table 15). The introduction of the methylene group between the triethylgermyl group and the isoxazoline ring caused an opposite effect, i.e. shortening the anaesthesia time by 28% and by 70%44. Germyl-isoxazolin-2-yl derivatives possess low antihypoxic activity. The stimulating effects of phenamine strengthened under the influence of 4-(5′-triethylgermyl-3′-isoxazoliny)pyridine hydrochloride by 55.3%. (3-Ethyl-4-triphenylgermylisoxazolinyl-2)-5-carboxylic acid ethyl ester exhibits...
TABLE 16. Neurotropic activity of $R\begin{array}{c}O \\ \end{array}CH=\begin{array}{c}O \\ \end{array}$

<table>
<thead>
<tr>
<th>R</th>
<th>Anaesthesia</th>
<th>% vs. control</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ethanol</td>
<td>thiopental</td>
</tr>
<tr>
<td>H</td>
<td>108.4</td>
<td>130</td>
</tr>
<tr>
<td>Me$_3$C</td>
<td>64</td>
<td>84</td>
</tr>
<tr>
<td>Me$_3$Si</td>
<td>117.2</td>
<td>160</td>
</tr>
<tr>
<td>Me$_3$Ge</td>
<td>85.3</td>
<td>79</td>
</tr>
</tbody>
</table>

the highest effect (by 104%)$^{44}$. 2-(5'-Triethylgermylmethyl-3'-isoxazolinyl)pyridine hydrochloride and 3-(5'-triethylgermylmethyl-3'-isoxazolinyl)pyridine hydrobromide in comparatively small doses (50 mg kg$^{-1}$) completely prevented retrogradal amnesia caused by electric shock.

The germanium derivative of Meldrum’s acid (Table 16) exhibits the highest anti-Corazol activity (262%) and depressed pharmacological effects of phenamine by 55.5% $^{46}$.

Neurotropic activity of propiohydroxamic acids and isobutyrohydroxamic acids $^6$ has been studied$^5$.$^{10}$. When $\beta$-trimethylgermylpropiohydroxamic acid is administered p.o. in doses of 20 and 250 mg kg$^{-1}$ it prolonged the life of animals under hypoxic hypoxia by 70–149.2%. In very low doses (5 mg kg$^{-1}$) it favorably affects the elaboration of passive conditional responses. At higher doses the depressant activity appears. This is confirmed by the hexenal anaesthesia test. Thus, $\beta$-trimethylgermylpropiohydroxamic acid in doses of 5 and 50 mg kg$^{-1}$ reduces the duration of hexenal anaesthesia by 34.5 and 20.1%, respectively, whereas a large dose (250 mg kg$^{-1}$) prolongs this parameter by 282.1%. The pronounced protective action of $\beta$-trimethylgermylpropiohydroxamic acid on strychnine-induced convulsions is the evidence for its influence on the spinal cord. Obviously, the mechanism of $\beta$-trimethylgermylpropiohydroxamic acid action implies an influence on the central serotoninergic processes. During its application in large doses (100 and 250 mg kg$^{-1}$) GABA-ergic processes are involved as well$^{10}$.

$R_3$GeCH$_2$CHR$'CONHOH$

(6)

RR$'Ge(CH_2)_nN$

(8)

CH$_2$OH

(7)

All the organogermainium derivatives of 1-adamantane $^7$ studied are low toxic substances; their mean lethal doses exceed 1000 mg kg$^{-1}$ (Table 17)$^{40}$. However, some patterns
TABLE 17. Neurotropic activity of organogermanium derivatives of adamantane

<table>
<thead>
<tr>
<th>R</th>
<th>LD&lt;sub&gt;50&lt;/sub&gt; mg kg&lt;sup&gt;−1&lt;/sup&gt;</th>
<th>% of control</th>
<th>Hypoxia</th>
<th>Hexenal anaesthesia</th>
<th>Hypothermia</th>
<th>Corazol convulsion</th>
</tr>
</thead>
<tbody>
<tr>
<td>AdGe(OCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;N</td>
<td>&gt;5000</td>
<td>173.8</td>
<td>139.5</td>
<td>&gt;500</td>
<td>155.4</td>
<td></td>
</tr>
<tr>
<td>AdGe(NOCOCH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3250</td>
<td>165.5</td>
<td>160.6</td>
<td>447</td>
<td>148.7</td>
<td></td>
</tr>
<tr>
<td>Ad(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;GeMe&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1480</td>
<td>96.5</td>
<td>62.5</td>
<td>&gt;1000</td>
<td>90.7</td>
<td></td>
</tr>
<tr>
<td>Ad(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;GeMe&lt;sub&gt;3&lt;/sub&gt;</td>
<td>&gt;5000</td>
<td>174.0</td>
<td>84.0</td>
<td>47.7</td>
<td>185.2</td>
<td></td>
</tr>
<tr>
<td>AdNHCO(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;GeMe&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3600</td>
<td>124.7</td>
<td>113.6</td>
<td>23.2</td>
<td>143.3</td>
<td></td>
</tr>
<tr>
<td>AdMe&lt;sub&gt;2&lt;/sub&gt;GeCH(CH&lt;sub&gt;3&lt;/sub&gt;)COOH</td>
<td>5150</td>
<td>132.0</td>
<td>167.9</td>
<td>410</td>
<td>96.6</td>
<td></td>
</tr>
<tr>
<td>AdMe&lt;sub&gt;2&lt;/sub&gt;Ge(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CONH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2820</td>
<td>145.0</td>
<td>144.8</td>
<td>103</td>
<td>131.3</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Ad = 1-adamantyl.

governing the toxic properties and neurotropic activity of these compounds have been revealed. Thus, comparison of 1-adamantylgermatrane with 1-adamantyl germatrandione has shown that the introduction of two carbonyl groups into the germatrane ring increases to some extent the toxicity and decreases the anticonvulsant activity of the compound. At the same time, the latter has the highest depressant activity among adamantylgermatranes. The 1-adamantyl derivative with two methylene groups between the germanium atom and the adamantyl group is more toxic than the corresponding substance containing three methylene groups. On changing from 2-(1-adamantyldimethylgermyl)propionic acid to β-(1-adamantyldimethylgermyl)propiohydroxamic acid, the toxicity of the compound increased 1.8-fold. It has been found that some 1-germyladamantanes increase the Corazol dose, causing tonic convulsions with lethal outcome. Duration of hexenal anaesthesia is statistically increased by 2-(1-adamantyldimethylgermyl)propionic acid and 1-adamantylgermatranedione, while under the influence of 1-adamantylethylgermane it is decreased. All the organogermanium derivatives of adamantane studied at a dose of √50 mg kg<sup>−1</sup> exhibit antihypoxic activity, mostly expressed in 1-adamantylgermatrane, germatrandione and 1-(γ-trimethylgermyl)propyladamantane. The 1-adamantylamide of trimethylgermylpropionic acid decreased hypothermia in a dose of 50 mg kg<sup>−1</sup> by 3 °C and reserpine-induced ptosis by 25%.

1-Adamantylgermatrane has been studied more thoroughly during its administration to the stomach in doses from 5 to 250 mg kg<sup>−1</sup>. Administer p.o., it also reveals pronounced antihypoxic activity which increases with dose. 1-Adamantylgermatrane in doses of 50–250 mg kg<sup>−1</sup> reveals antihypoxic potency also at haemic hypoxia.<sup>10</sup>

A reproducible effect of 1-adamantylgermatrane on the pharmacological activity of phenamine, 5-oxytryptophan and strychnine has been observed. In the mechanism of action of 1-adamantylgermatrane, a considerable role is played by its M-cholinemimetic influence (i.e. it strengthens the adrenaline tremor) and GABA-ergic structure.

The antimuscarnic activity of (hydroxymethyl)diorgano(2-piperidinoalkyl)germanes has been studied.<sup>58–60</sup>

The (R)- and (S)-enantiomers of (hydroxymethyl)diorgano(2-piperidinoethy1)germanes [Ph(−Hex)Ge(CH<sub>2</sub>OH)CH<sub>2</sub>CH<sub>2</sub>NR<sub>2</sub>, Ph(−Hex)Ge(CH<sub>2</sub>OH)CH<sub>2</sub>CH<sub>2</sub>NR<sub>2</sub> · CH<sub>3</sub>I] and their
achiral derivatives \([\text{Ph}_2\text{Ge(CH}_2\text{OH})\text{CH}_2\text{CH}_2\text{NR}_2, \text{Ph}_2\text{Ge(CH}_2\text{OH})\text{CH}_2\text{CH}_2\text{NR}_2 \cdot \text{CH}_3\text{I, (c-Hex)}_2\text{Ge(CH}_2\text{OH})\text{CH}_2\text{CH}_2\text{NR}_2, (c-Hex)_2\text{Ge(CH}_2\text{OH})\text{CH}_2\text{CH}_2\text{NR}_2 \cdot \text{CH}_3\text{I, NR}_2 = \text{piperidino}]\) exhibited their affinities for muscarinic M1, M2, M3 and M4 receptors by functional pharmacological experiments (M1, rabbit vas deferens; M2, guinea-pig atria; M3, guinea-pig ileum) and radioligand binding experiments (M1, human NB-OK 1 cells; M2, rat heart; M3, rat pancreas; M4, rat striatum). According to these studies\(^{59,60}\) all the germanes and the related silicon analogues behaved as simple competitive antagonists at muscarinic M1–M4 receptors. The \((R)-\text{enantiomers of the Ge/Si pair Ph(c-Hex)Ge(CH}_2\text{OH})\text{CH}_2\text{CH}_2\text{NR}_2\) and \(\text{Ph(c-Hex)Ge(CH}_2\text{OH})\text{CH}_2\text{CH}_2\text{NR}_2 \cdot \text{CH}_3\text{I}\) exhibited higher affinities (up to 26-fold) for M1–M4 receptors than their corresponding \((S)-\text{antipodes, the stereoselectivity ratios being higher at M1, M3 and M4 than at M2 receptors.}\)

4,4-Dimethyl-4-germa-\(\gamma\)-butyrolactone strongly inhibits dipeptidylcarboxypeptidase degradation of enkephalins\(^61\). This result suggests that the compound may be effective in the physiological pain-regulation system \textit{in vivo}.\)

\textbf{IV. CARDIOVASCULAR ACTIVITY}

Cardiovascular activity of 2-carboxyethylgermanium sesquioxane (Ge-132) has been studied in rats anaesthetized with urethane \((i.p.)\). It produced a dose-related reduction in either the mean arterial pressure or the heart rate. The data indicate that Ge-132 induces both hypotension and bradycardia by promoting an activation of the parasympathetic efferent mechanisms and an inhibition of the sympathetic efferent mechanisms. On the other hand, following \(i.p\). injection of Ge-132, increased grooming and head swaying were provoked. Thus, it appears that Ge-132 acts through the catecholaminergic mechanisms in the brain to induce locomotor stimulation in rats\(^62\).\)

The germyl- and silyl-substituted adrenaline derivative \(3,4\)-bis(trimethylsiloxy)-4-\(\alpha\)-(trimethylsiloxy)-\(\beta\)-(methyl)(triethylgermylamino)ethylbenzene \((0.1 \text{ mg kg}^{-1}, i.v.)\) increased the blood pressure twice as effectively than the same dose of adrenaline. This compound is 7 times less toxic than adrenaline\(^63\).\)

4-(5-Trimethylgermyl-2-furyl) substituted 1,4-dihydropyridine administered \(i.v\). in a 0.05 \(\text{mg kg}^{-1}\) dose increased the blood flow in the common carotid of cats by 31\%, and in a 0.1 \(\text{mg kg}^{-1}\) dose it dilates the coronary vessels by 11\% and decreased the arterial pressure by 12\%\(^5\).\)

The vasodilating, anticoagulant and cardioprotective activities of 5-germanium substituted isoxazolines-2 have been studied \textit{in vitro} and \textit{in vivo}\(^64\). 2-(5'-Triethylgermyl-3'-isoxazolinyl)pyridine hydrochloride and 3-(5'-triethylgermyl-3'-isoxazolinyl)pyridine hydrochloride induced significant vasodilatation, the latter being the most active. It has been found that silicon analogues were less active. Insertion of the methylene group between the germanium and the isoxazoline ring reduced the vasodilating activity. All the investigated germylisoxazolinyl substituted pyridines prolonged the coagulation time. 3-(5'-Triethylgermyl-3'-isoxazolinyl)pyridine hydrochloride was the most active anticoagulant among the studied compounds. In the experiments on anaesthetized rats, 2-(5'-triethylgermyl-3'-isoxazolinyl)pyridine hydrochloride and 3-(5'-triethylgermyl-3'-isoxazolino)pyridine hydrochloride protected animals from ischaemia; the 3-isomer also protected the heart from ventricular fibrillation.\)

\textbf{V. ANTITUMOR, ANTIVIRAL AND IMMUNOMODULATING ACTIVITY}

2-(3-Dimethylaminopropyl)-8,8-diethyl-2-aza-8-germaspiro[4,5]decane (spirogermanium) was the first organogermanium compound tested clinically as an antitumor
agent\textsuperscript{4,5,11,48,65–76}. The described mode of action is inhibition of protein synthesis with secondary suppression of RNA and DNA synthesis. It has been reported that spirogermanium has also antiarthritic and suppressor cell-inducing activity\textsuperscript{77}. Phase I clinical study\textsuperscript{49,78,79} showed good drug tolerance. Further evaluation in Phase II revealed consistent neurotoxicity, ranging from dizziness to disorientation, as well as mild hematological and hepatic toxicity. Modest activity was demonstrated in ovarian cancer. No responses were seen in patients with refractory colorectal carcinoma or non-small cell lung cancer\textsuperscript{75,80–82}. Low response and relatively high toxicity have been found also in Phase II treatment of gastric carcinoma\textsuperscript{83}.

The antitumor activity of 2-carboxyethylgermsesquioxane (Ge-132) and its derivatives has been studied. 2-Carboxyethylgermsesquioxane has been revealed to possess antitumor\textsuperscript{2–4,11,84}, interferon-inducing\textsuperscript{4,11,85–87}, immunomodulating\textsuperscript{4,88–94} and antiviral\textsuperscript{4,95} properties. Japanese scientists first discovered antitumor activity of (O\textsubscript{1.5}GeCH\textsubscript{2}CH\textsubscript{2}COOH)\textsubscript{n} and (O\textsubscript{1.5}GeCH\textsubscript{2}CH\textsubscript{2}CONH\textsubscript{2})\textsubscript{2}.\textsuperscript{3} Mouse with Ehrlich ascite tumor received 20 µg ml\textsuperscript{-1} (O\textsubscript{1.5}GeCH\textsubscript{2}CH\textsubscript{2}COOH)\textsubscript{n} and 20 and 40 µg ml\textsuperscript{-1} (O\textsubscript{1.5}GeCH\textsubscript{2}CH\textsubscript{2}CONH\textsubscript{2})\textsubscript{n} during 7 days. The inhibition of the tumor cells growth was higher than in control by 25.9, 46.85 and 31.45%, respectively. 2-Carboxyethylgermsesquioxane exhibited some antitumor activity in adenocarcinoma LA-795, in the Lewis lung carcinoma 3LL\textsuperscript{96–99}, melanoma B16\textsuperscript{100} and leukaemia L-1210\textsuperscript{101} and had a limited antimetastatic effect in mice\textsuperscript{97}. Complete remission of pulmonary spindle cell carcinoma has been observed after oral administration of germanium sesquioxide\textsuperscript{102}. In some cases 2-carboxyethylgermsesquioxane reinforces the effect of bleomycine and 5-fluourouacil (5-FU)\textsuperscript{103}. It has been shown that (O\textsubscript{1.5}GeCH\textsubscript{2}CH\textsubscript{2}COOH)\textsubscript{n}\textsuperscript{104,105}, (O\textsubscript{1.5}GeCH\textsubscript{2}CH\textsubscript{2}COONa)\textsubscript{n}\textsuperscript{96} and (O\textsubscript{1.5}GeCH\textsubscript{2}CH\textsubscript{2}CONH\textsubscript{2})\textsubscript{n}\textsuperscript{106} prolong the life of a mouse with implanted ascitic hepatomas AH-44 and AH-66 and also of rats with syngenic bladder carcinoma BC47\textsuperscript{107}.

2-Carboxyethylgermsesquioxane was not cytotoxic to carcinoma cells growing in vitro\textsuperscript{97} and had its antitumor effect via the stimulation of host-mediated, immunopotentiating mechanisms\textsuperscript{9,97,108}, leading to augmentation of natural killer cell activity and activation of macrophages in mice\textsuperscript{97}. Carboxyethylgermaniumsesquioxane (Ge-132, 600 mg kg\textsuperscript{-1}) has some preventive effect on the precancerous lesion in rat glandular stomach induced by N-methyl-N’-nitrosoguanidine\textsuperscript{109}. A histopathological study has demonstrated that propagermanium had no biochemical influence on the renal function of renal injured (by adriamycin or mercuric chloride) rats. This confirms that propagermanium is a safe compound for use in individuals with compromised kidneys\textsuperscript{38}. The Ge-132 administered p.o. activated mouse murine macrophage-mediated tumor cytotoxicity. When Ge-132 activated macrophages have been treated with ganglioside in vitro, synergistic activity appeared\textsuperscript{110}. 2-Carboxyethylgermsesquioxane, 2-carbamoyethylgermsesquioxane and α,β-dicarboxyethylgermsesquioxane significantly stimulated mouse peritoneal macrophages and human monocytoïd cells by oral administration of a single dose of 100 mg kg\textsuperscript{-1}\textsuperscript{111}.

Antitumor activity of various organogermanium sesquioxanes [(O\textsubscript{1.5}GeCH\textsubscript{2}CHRCOX)\textsubscript{n}, R=H, Me; X=OH, NH\textsubscript{2}]\textsuperscript{100} and sesquisulfides\textsuperscript{112} has been studied. The most active was a methacrylic acid derivative (80% life prolongation in melanoma B16 and 72% life prolongation in mice with Lewis lung carcinoma).

The sesquioxanes (O\textsubscript{1.5}GeCH\textsubscript{2}CHRCOX)\textsubscript{n}\textsuperscript{113,114} and (4-RC\textsubscript{6}H\textsubscript{4}GeO\textsubscript{1.5})\textsubscript{n} (R=Hal, CN)\textsubscript{115–117} exhibited antitumor activity and prolonged the life of animals with Ehrlich ascite tumor.

Organogermanium sesquioxanes containing uracil or 5-fluourouracil (5-FU) moieties possess antitumor activity against IMC carcinoma in mice\textsuperscript{118,119}. 1-[p-[Bis(β-chloroethylamino)phenyl]-2-amino-2-carboxyethylgermanium sesquioxane (LD\textsubscript{50} 1765 mg kg\textsuperscript{-1})
inhibited the growth of sarcoma S-180 by 78% (in mice, i.p.), whereas a 65% inhibition was achieved with 5-FU under the same experimental conditions. Some germanyl heterocyclic (indolyl or furyl) amino acid derivatives, such as 1-(3′-indolyl)-2-amino-2-carboxyethylgermaniumsesquioxane and the corresponding sesquisulfide, have antitumor activity comparable with 5-FU in sarcoma S-180.

The results of bioassay showed that the organogermanium sesquioxanes containing the α-aminophosphonate group $O_1^5 GeCHR'(CHR)C(O)NHCH(R)P(O)(OPh)_2$ exhibit anticancer activity in vitro.

Preliminary pharmacological investigations of 2-(2-germaoxa-3H-benzofuran-3-yl)-2-acetylaminoglycine and 1-(2-hydroxyphenyl)-2-amino-2-carboxyethylgermanium sesquioxane showed that the sesquioxane derivative has low toxicity ($LD_{50} > 10 \text{ g/kg}$ for mice) and inhibited the growth of S-180 in mice by 51.6% (orally). The activity of this compound was slightly higher than that of 5-fluorouracil under the same experimental conditions.

Glucopyranosyl derivatives of carboxyethylgermanium sesquioxane, such as 2,4-di($O$-acetyl)-1,3,6-tri-$O$-(carboxyethyl)germanyl-$β$-D-glucopyranose, showed EEAC growth inhibition in mice (i.p.) by 62%.

Besides spirogermanium and germanium sesquioxanes, numerous other organogermanium compounds have shown antitumor activity against experimental tumors. They include the octahedral complex dimethyl-5,19,15,20-tetra-bis[3′,5′-bis(1′,1′′-dimethyl-ethylphenyl)]porphynato-germanium(IV) and some decaphenylgermanocene derivatives. 1,1-Bis(1,3-dithian-2-yl)-1-germa-3-cyclopentene has been reported to be more potent against IMC carcinoma in mice than 2-carboxyethylgermanium sesquioxane.

5-Trimethylgermyluracil and 1-(2-tetrahydrofurfuryl)-5-trimethylgermyluracil display similar cytotoxicity to melanoma B16 cells ($EC_{50}$ 32 $\mu$ g ml$^{-1}$). Preliminary biological investigations of 1-(2-tetrahydrofurfuryl)-5-fluoro-6-trimethyl(ethyl)-germyluracils have demonstrated that both derivatives inhibit the DNA and RNA biosynthesis in Frhk cells by 1.5–2 times more than Fltorafur, the well-known antitumor agent.

1-(5-Nitrofurylacryloyl)-5-trimethylgermyluracil suppresses the growth of melanoma B16 ($EC_{50}$ 10 $\mu$ g ml$^{-1}$). This compound is three times more active than its silicon analogue.

5-Trimethylgermyl derivatives of 2′-deoxyuridine exhibit antimetabolic properties: the $β$-anomer possesses weak biological action, the $α$-anomers inhibits the replication of herpes simplex virus HSV-1 and fails to display antitumor action in vivo. The $α$-anomer of 5-Trimethylgermyl-2′-deoxyuridine suppresses the incorporation of 2′-deoxyuridine and thymidine into the DNA of hepatoma 22A cells in vitro more effectively (by 88 and 27%) than the $β$-anomer (50 and 0%, respectively).

Carbofunctional organogermanium derivatives of $sym$-triazine exhibit immunodepressant properties. 1,3-Bis[γ-(triethylgermyl)propyl]-5-β-cyanoethyl-2,4,6-trioxo-1,3,5-triazine decreases the number of tumocytes 1.6-fold and significantly inhibits the growth of Sarcoma 45 in white mice.

Germanium and silicon derivatives of N-methyl-N-nitrosourea [RCH$_2$N(NO)CONH$_2$, R = Me$_2$Ge, Me$_2$PhGe, Me$_3$Si, Me$_2$PhSi, Me$_3$C] exhibit considerably higher cytotoxicity to leukaemia L1210 cells than the carbon analogue. One can suppose that it is determined by their greater lipophilicity. Dimethylphenyl derivatives are significantly more cytotoxic due either to their increased lipophilicity or to the splitting of the phenyl group.
Some trimethylgermyl and trimethylsilyl derivatives of retinobenzoic acids show high retinoidal activity in human promyelocytic leukaemia cells HL-60\(^\text{135}\).

Antitumor activity of germyl derivatives of hetaryldiketones have been tested on HT-1080 and MG-22A tumor cell cultures\(^\text{46,136}\). 2,2-Dimethyl-5-(5′-trimethylgermyl-2′-furfurylidene)-1,3-dioxane-4,6-dione and 2,2-dimethyl-5-(5′-trimethylgermyl-2′-thienylidene)-1,3-dioxane-4,6-dione (IC\(_{50}\) ca 100 µg ml\(^{-1}\)) have low influence on the HT-1080 cell line but the cytotoxicity considerably increases in MG-22A cells (IC\(_{50}\) 1–10 µg ml\(^{-1}\)).

1-Triphenylgermyl-4-propiono-substituted semicarbazides, thiosemicarbazides \(\text{Ph}_3\text{GeCH}_2\text{CONHCH}(\text{X})\text{NHR}^{\text{R′}}\) (\(\text{R′} = \text{H, Ph; R″} = \text{Ph, p-tolyl; X} = \text{O, S}\)) and their heterocyclic derivatives have been found to possess inhibitory effects on gastric carcinoma MGC-803 \textit{in vitro}\(^\text{137}\).

Germanium and silicon derivatives of furfural semicarbazone and thiosemicarbazone exhibited similar antitumor activity to melanoma B16 in mice (40–48% inhibition of the growth)\(^\text{138}\).

The germanium derivative of furfural oxime had significant activity on HT-1080, MG-22A and B16 cells, but not on Neuro 2A. The activity of carbon and silicon analogues was lower in all cell lines (Table 18)\(^\text{139}\).

\(t\)-Butyl \(\alpha\)-cyano-(5-trimethylgermyl-2-furyl)acrylate possesses significant cytotoxicity on four (HT-1080, MG-22A, B16, Neuro 2A) tumor cell lines and it is a strong NO-inducer\(^\text{46}\). However, the silicon analogue was more active in 3 cell lines (Table 19).

2-(5′-Triethylgermyl-3′-oxazolinyl)pyridine hydrochloride, 2-(5′-triethylgermylmethyl-3′-oxazolinyl)pyridine hydrochloride, (3-methyl-4-triphenylgermylisoaxazolinyl-2)-5-carboxylic acid ethyl ester and (3-ethyl-4-triphenylgermylisoaxazolinyl-2)-5-carboxylic acid ethyl ester had medium activity on HT-1080 and MG-22A tumor cell cultures, and low activity on B16. The most active antitumor substance was (3-ethyl-4-triphenylgermylisoaxazolinyl-2)-5-carboxylic acid ethyl ester. Germlyisoaxazolin-2-yl derivatives are stronger tumor growth inhibitors and NO-inducers than their silyl analogues\(^\text{44}\). Cytotoxic activity of germyl-substituted 4,4-dioxo-3a,6a-dihydrothieno[2,3-d]isoaxazolines-2 has been studied\(^\text{140}\). Germanium-containing compounds had a cytotoxic effect on Neuro 2A and B16 cell lines. 4,4-Dioxo-3-phenyl-5-trimethylgermyl-3a,6a-dihydrothieno[2,3-d]isoaxazoline-2 showed the highest tumor growth inhibiting activity.

### TABLE 18. Cytotoxicity of \(R\) \(\text{O} \quad \text{CH} = \text{NOH}\)

<table>
<thead>
<tr>
<th>R</th>
<th>(\text{HT-1080})</th>
<th>(\text{MG-22A})</th>
<th>(\text{B16})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CV</td>
<td>MTT</td>
<td>NO (%)</td>
</tr>
<tr>
<td>H</td>
<td>c</td>
<td>c</td>
<td>2</td>
</tr>
<tr>
<td>Me3C</td>
<td>57</td>
<td>56</td>
<td>57</td>
</tr>
<tr>
<td>Me3Si</td>
<td>c</td>
<td>c</td>
<td>9</td>
</tr>
<tr>
<td>Me3Ge</td>
<td>42</td>
<td>7</td>
<td>250</td>
</tr>
</tbody>
</table>

\(^a\)CV = Crystal Violet.

\(^b\)MTT = 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide.

\(^c\)Not active.
The antitumor activity of two types of gematrane, RGe(OCH₂CH₂)₃N and R₃MOGe(OCH₂CH₂)₃N (R = alkyl, aryl, furyl, thienyl, phenyl; M = Si, Ge), has been studied. The gematrane R₃MOGe(OCH₂CH₂)₃N possess higher activity on HT-1080, MG-22A, B16 and Neuro 2A tumor cells (IC₅₀ 0.9–6.1 µg ml⁻¹) than RGe(OCH₂CH₂)₃N (IC₅₀ ca 100 µg ml⁻¹). Hydroxygermatrane had the highest cytotoxic activity on HT-1080 tumor cells. 1-Trimethylgermoxygermatrane (EC₅₀ 3.2 µg ml⁻¹) suppressed the growth of melanoma B16 cells three times more effectively than 1-trimethylsiloxygermatrane (EC₅₀ 10 µg ml⁻¹). 1-Trimethylsiloxy- and 1-trimethylgermoxy gematrane inhibited the growth of Sarcoma 37 in mice more effectively than the parent 1-hydroxygermatrane (by 75, 60 and 40% respectively). Administration of 3-(1-germatranyl)propionic acid to mice afflicted with Ehrlich ascites tumor caused a 78% increase in survival time. Germatrane-N(CH₂CH₂O)₃Ge(CHR)₂CONH₂ (R = H, Ph) showed activity against IMC carcinoma in mice.

Some alkyldigermanes possess antitumor activity against leukaemia L-1210 in vitro. Further investigations in vivo have demonstrated that these compounds possess low activity and exhibit antitumor activity only against leukaemia P-388.

Water-soluble derivatives of n-Bu₂Sn(O₂CCHR₁CHR₂GeR₃)₂·H₂O [type I: R¹ = H; R² = H, CH₃, C₆H₅, 4-ClC₆H₄, 2-CIC₆H₄, 4-CH₃C₆H₄, 2-CH₃C₆H₄, 2,4-Cl₂C₆H₃, 4-CH₃OC₆H₄; R³ = (OCH₂CH₂)₃N; type II: R¹ = H; R² = CH₃, C₆H₅, 4-ClC₆H₄, 4-CH₃C₆H₄, 4-CH₃OC₆H₄; R³ = Ph₃] were screened in vitro for their antitumor activity against KB cells, HCT-8 cells and Bel7402. All compounds showed some activity. The gematrane-substituted derivatives were more active than the GePh₃-substituted derivatives.

The effects of propagermanium on various virus-infected mice were investigated. Oral administration of propagermanium in mice infected with herpes simplex virus type I (HSV-1) significantly prolonged the mean survival time. In vaccinia virus-infected mice (oral doses 0.2–10 mg kg⁻¹) it suppressed the number of pocks on the tail which were induced by the virus. Propagermanium (0.5–10 mg kg⁻¹), given orally to HSV-1-infected mice, induced cytotoxic T lymphocytes against HSV-1 antigen. In addition, propagermanium (1–10 mg kg⁻¹) enhanced interferon-γ (IFN-γ) induction in mice treated with Mycobacterium bovis. In mice spleen cell cultured with Concanavalin A, 0.1–10 mg ml⁻¹ of propagermanium stimulated interleukin 2 production. It seems likely that the antiviral activity of propagermanium was exerted via enhancement of host immune resistance against viral infection. Propagermanium improves hepatitis.
through mechanisms including the reduced production of tumor necrosis factor without modification of Th-1 and Th-2 cell function\textsuperscript{147}.

Investigations of new biological applications of Ge-132 are presently proceeding in Japan. For example, a biologically active composition for treatment of acquired immune deficiency syndrome and cancer has been prepared by extraction maitake (mushroom) with solvents and mixing the extract containing D fraction and glucan with organogermainium sesquioxane [(GeCH\(_2\)CH\(_2\)COOH)\(_2\)O\(_3\)]\textsuperscript{148}. A composition of Ge-132 (>10%) and mushroom extracts (>70%) have been claimed to increase therapeutic efficacy and decrease toxicity and side effects of antiviral agent (e.g. HIV reverse transcriptase inhibition) against the AIDS virus\textsuperscript{149}. Foods containing fucoidan, polysaccharides and (GeCH\(_2\)CH\(_2\)COOH)\(_2\)O\(_3\) showed synergistic anticancer activity\textsuperscript{150}. Activated water containing ferrous ferric salts and Ge-132 showed natural killer activity enhancement of volunteers\textsuperscript{151,152}.

The effects of the synthetic germanium antioxidant (Ge-132) have been studied on liver oxidative damage induced by pararquat in senescence-accelerated mice. Pararquat administered intravenously to SAM-P/8 (susceptible) or SAM-R/1 (resistant) mice increased liver DNA strand breakage and malondialdehyde levels, which are indicators of oxidant damage. Ge-132 effectively blocked pararquat-induced effects on liver DNA strand breaks and malondialdehyde levels. In addition, Ge-132 significantly elevated the activities of hepatic superoxide dismutase and catalase following pararquat pretreatment. Histopathologically, Ge-132 inhibited pararquat-induced hepatic mitochondrial injury in both strains, but more effectively in the susceptible strain. The data suggest that Ge-132 may be useful as an antioxidant in view of its ability to prevent pararquat-induced hepatic oxidant injury\textsuperscript{153}. Ge-132 has a cell membrane stabilizing effect\textsuperscript{154}.

Some plants have been cultivated by germanium penetration into the plant from its roots and organogermainium pharmaceuticals have been prepared\textsuperscript{155}. Cultivation of Saccharomyces cerevisiae or Ganoderma lucidum in carboxyethylgermanium sesquioxane medium gave a product with antitumor and interferon-inducing activity\textsuperscript{156}.

\section*{VI. RADIOPROTective ACTIVITY}

The radioprotective activity of several classes of organogermainium derivatives (germatiazolines, germadithioacets, germaranes and germylated sulfides) has been studied\textsuperscript{41,43,157–159}.

The radiation (\textsuperscript{60}Co \(\gamma\)-ray source) protection was obtained in mice after \textit{i.p.} administration of germainiazolines. Generally, these organogermainium compounds have a lower toxicity and a radioprotective activity equal to or greater than that of the starting organic derivatives (Table 20). It is necessary to underline that in some cases this increased radioprotective activity was obtained with organogermainylated or organosilylated derivatives injected in lower doses than those used for the parent organic compounds\textsuperscript{42,43,159}.

Germadithioacetals R\(^1\)R\(^2\)Ge[SCH(R\(^3\))CH\(_2\)R\(^4\)]\(_2\) have an important radioprotective activity (DRF 1.5–1.7)\textsuperscript{42,43,159–162}.

Four aminoalkylthio germaranes YNHCH\(_2\)CH(R)S-Ge[(OCH\(_2\)CH\(_2\))]\(_3\)N; R = H, Me, Y = H · HCl, H\(_2\)N(CH\(_2\))\(_3\), 2HCl · H\(_2\)N(CH\(_2\))\(_3\) have been tested as radioprotective agents\textsuperscript{157}. They demonstrated low toxicity (LD\(_{50}\) 300–1500 mg kg\(^{-1}\)) and medium radioprotective activity (DRF 1.4–1.5). Similar radioprotective potency has been found for derivatives of cysteamine, with its sulfur atom being bound with silatrane or germatrane groups, as well as for their thia analogues H\(_2\)N(CH\(_2\))\(_2\)SM(XCH\(_2\)CH\(_2\))\(_3\)N (M = Si, Ge; X = O, S)\textsuperscript{158}.

Germylated sulfides [(HCl · H\(_2\)NCH\(_2\)CH\(_2\)S\(_2\))GeS\(_3\)]\(_3\)\textsuperscript{157} and [(HCl · H\(_2\)NCHMeCH\(_2\)S\(_2\)GeS\(_3\)]\(_3\)\textsuperscript{159} have significant radioprotective activity (DRF >1.5, LD\(_{50}\) 800 mg kg\(^{-1}\) and DRF 1.6, LD\(_{50}\) 1000 mg kg\(^{-1}\), respectively).
TABLE 20. Radioprotective activity of \( \text{Ge} \)

<table>
<thead>
<tr>
<th>( R^1 )</th>
<th>( R^2 )</th>
<th>( R^3 )</th>
<th>( R^4 )</th>
<th>( LD_{50} ) (mg kg(^{-1}))</th>
<th>DRF(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>Ph</td>
<td>H</td>
<td>H</td>
<td>600</td>
<td>1.6</td>
</tr>
<tr>
<td>Me</td>
<td>Ph</td>
<td>Me</td>
<td>H</td>
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<td>Me</td>
<td>( p-\text{MeOC}_6\text{H}_4 )</td>
<td>H</td>
<td>H</td>
<td>700</td>
<td>1.45</td>
</tr>
<tr>
<td>Me</td>
<td>( p-\text{MeOC}_6\text{H}_4 )</td>
<td>Me</td>
<td>H</td>
<td>600</td>
<td>1.45</td>
</tr>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>H</td>
<td>H</td>
<td>400</td>
<td>1.4</td>
</tr>
<tr>
<td>( n-\text{Bu} )</td>
<td>( n-\text{Bu} )</td>
<td>H</td>
<td>H</td>
<td>700</td>
<td>1.45</td>
</tr>
<tr>
<td>( n-\text{Bu} )</td>
<td>( n-\text{Bu} )</td>
<td>Me</td>
<td>H</td>
<td>300</td>
<td>1.4</td>
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<td>( n-\text{Am} )</td>
<td>H</td>
<td>H</td>
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<td>1.4</td>
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<td>700</td>
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<tr>
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<td>Me</td>
<td>H</td>
<td>800</td>
<td>1.45</td>
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<tr>
<td>Me</td>
<td>Ph</td>
<td>Me</td>
<td>MeCO</td>
<td>900</td>
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<tr>
<td>( i-\text{Am} )</td>
<td>( i-\text{Am} )</td>
<td>Me</td>
<td>MeCO</td>
<td>1000</td>
<td>1.35</td>
</tr>
<tr>
<td>( i-\text{Am} )</td>
<td>( i-\text{Am} )</td>
<td>H</td>
<td>(^b)</td>
<td>800</td>
<td>1.3</td>
</tr>
<tr>
<td>( n-\text{Hex} )</td>
<td>( n-\text{Hex} )</td>
<td>H</td>
<td>(^b)</td>
<td>1500</td>
<td>1.5</td>
</tr>
<tr>
<td>Me</td>
<td>( p-\text{MeC}_6\text{H}_4 )</td>
<td>H</td>
<td>((\text{CH}_2)_2\text{CONH}_2)</td>
<td>&gt;1500</td>
<td>1.4</td>
</tr>
<tr>
<td>( i-\text{Am} )</td>
<td>( i-\text{Am} )</td>
<td>H</td>
<td>(^c)</td>
<td>80</td>
<td>1.33</td>
</tr>
<tr>
<td>( n-\text{Hex} )</td>
<td>( n-\text{Hex} )</td>
<td>Me</td>
<td>(^c)</td>
<td>1500</td>
<td>1.5</td>
</tr>
<tr>
<td>( i-\text{Am} )</td>
<td>( i-\text{Am} )</td>
<td>Me</td>
<td>(^c)</td>
<td>150</td>
<td>1.3</td>
</tr>
<tr>
<td>( n-\text{Hex} )</td>
<td>( n-\text{Hex} )</td>
<td>Me</td>
<td>(^c)</td>
<td>200</td>
<td>1.3</td>
</tr>
</tbody>
</table>

\(^a\)Dose reduction factor = \([LD_{50} \text{ (30 days) treated}]/LD_{50} \text{ (30 days) untreated}]\).

\(^b\)\( R^4 = \begin{array}{c}
\text{O} \\
\text{N(CH}_2\text{)}_3
\end{array} \)

\(^c\)\( R^4 = \begin{array}{c}
\text{N} \\
\text{N}
\end{array} \)

VII. MISCELLANEOUS ACTIVITIES

The germanium analogue of the leading agricultural fungicide flusilazole has been synthesized\(^{163}\). The fungicidal properties of flusilazole and of bis(4-fluorophenyl)methyl(1\(H\)-1, 2,4-triazol-1-yl methyl)germane have been compared and found to be similar. Dose-
TABLE 21. Growth inhibition (%) of \textit{Gaecemannomyces graminis} in vitro by

<table>
<thead>
<tr>
<th>M</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Si</td>
<td>92</td>
</tr>
<tr>
<td>Ge</td>
<td>100</td>
</tr>
<tr>
<td>Sn</td>
<td>100</td>
</tr>
</tbody>
</table>

dependent fungicidal activity has been demonstrated for the germanium derivative of \textit{o-chlorobenzamide} (Table 21)\textsuperscript{164}.

Antimutagenic activity of bis(D,L-lactato)-, bis(L-lactato)-, bis(thiolactato)- and bis (thioglycolato)germanium(IV) has been tested in \textit{Salmonella typhimurium} strains TA98 and TA100. They showed moderate activity against the mutagenic effect of nitroaromatic compounds\textsuperscript{165}.

Spirogermanium has antimalarial activity\textsuperscript{9}, but had no effect on \textit{Babesia microti} infection in the hamster model\textsuperscript{166}.

2-Carboxyethylgermsesquioxane can inhibit bone resorption by osteoclasts in a concentration-dependent manner\textsuperscript{167}. The therapeutic effect of 2-carboxyethylgermanium sesquioxide (Ge-132) for experimental osteoporosis has been studied using ovariectomized rats maintained on a low calcium containing diet. The Ge-132 decreased the bone strength, and affected the femur cortical bone index and bone mineral mass caused by osteoporosis\textsuperscript{168}.

The non-enzymic glycosylation (Maillard reaction) of amino acids with glucose has been markedly suppressed in the presence of Ge-132 in the range of 1–10 mmol l\textsuperscript{-1}. These results demonstrated antidiabetic properties of Ge-132\textsuperscript{169}. Some derivatives of carboxyethylgermsesquioxane also inhibited the Maillard reaction\textsuperscript{170,171}. As protein modification, such as glycation, may play a role in initiating changes that lead to cataract development, the effect of Ge-132 on galactose-induced cataractogenesis has been studied. It has been found that Ge-132 acted as antiglycation agent and delayed cataract formation. This compound was effective in maintaining Na(+)-K(+) -ATPase\textsuperscript{172,173}.

The interaction of carbonic anhydrase (CA) isozymes I and II with a series of organogermanium derivatives such as Mes\textsubscript{3}GeOH, Mes\textsubscript{3}GeNH\textsubscript{2}\textsuperscript{174} and aryl-substituted sulfonamides RR'RR''GeNSO\textsubscript{2}GeC\textsubscript{6}H\textsubscript{4}X-p (R = R' = Mes (mesityl), R'' = Cl, X = Me; R = R' = R'' = Ph, X = Me, NH\textsubscript{2}; R = R' = R'' = Et, X = Me), Mes\textsubscript{2}Ge=NSO\textsubscript{2}C\textsubscript{6}H\textsubscript{4}Me-p, Mes\textsubscript{2}Ge(NHSO\textsubscript{2}C\textsubscript{6}H\textsubscript{4}Me-p)\textsubscript{2} has been studied\textsuperscript{175}. The germanols and germylamine demonstrated selective inhibition of CA II. Sulfonamides were active in inhibiting both isozymes, the ethyl derivative being the most active CA II inhibitor in this series of compounds.

The first germanium-containing decapeptide \[\text{Ac-D-Nal}^1-4-\text{Cl-D-Phe}^2-\text{D-Pal}^3-\text{Ser}^4-\text{Me}_{3}\text{GeAla-D-Cit}^6-\text{Leu}^7-\text{Arg}^8-\text{Pro}^9-\text{D-Ala}^{10}-\text{NH}_2; \text{Me}_3\text{GeAla} = \text{Me}_3\text{GeCH}_2\text{CH(\text{NH}_2) COOH}] has been studied \textit{in vitro} in receptor binding and functional assays using recombinant cell lines expressing the human gonadotropin-releasing hormone (GnRH) receptor\textsuperscript{60,176}. This decapeptide like its silicon and carbon analogues behaved as potent GnRH antagonist,
the binding affinities and antagonistic potencies of the three analogues being quite similar. The investigation in vivo in the male rat after s.c. administration demonstrated that they produced both a strong testosterone suppression (single-dose treatment 1.5 mg kg$^{-1}$) and a strong luteinizing hormone (LH) suppression (castrated male rat; single-dose treatment, 0.05 mg kg$^{-1}$). For germanium and silicon-containing decapeptides, the testosterone and LH suppression lasted for a significantly longer period of time compared with the effects of the carbon analogue.

VIII. REFERENCES

23. Biological activity of organogermanium compounds


23. Biological activity of organogermain compounds


139. L. Ignatovich, I. Shestakova and E. Lukevics, unpublished results.


23. Biological activity of organogermanium compounds


Biological activity of organotin and organolead compounds

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Fax: 371-7550338; e-mail: sinta@osi.lv, olga@osi.lv

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I. TIN

A. Introduction

Organotin compounds (OTCs) are extensively used in a variety of industrial processes as catalysts and stabilizers for polyvinyl chloride plastics. The biological interest in this class of compounds for agriculture is due to high fungicidal, bactericidal and insecticidal activity. They were also incorporated into paints applied as antifouling agents on fishing nets and on boat hulls and used as preservatives for wood, textiles, paper, leather and electrical equipment. Recently, different di- and triorganotin carboxylates were investigated for antitumor activity. The increasing environmental pollution by the organotin derivatives has become a serious problem for various ecosystems, including humans. Due to this fact the toxic effects of OTCs have been widely explored and general trends in toxicity and biological activity were reviewed. 

B. Toxicity

Organotin derivatives exhibit genotoxic, neurotoxic, immunotoxic and hepatotoxic effects. It is important to study the genotoxicity of tin compounds, as they have the
potency to induce mutations and cancer. The genotoxicity of various methyl-, butyl- and phenyltins as well as tetrachlorostannane was studied in the SOS chromotest and rec-assay with *Escherichia coli* PQ37 and *Bacillus subtilis*. Organotin chlorides Me₃SnCl, Me₂SnCl₂, Bu₃SnCl, Bu₂SnCl₂ and bis(tributyltin)oxide (Bu₃Sn)₂O were recognized as genotoxic chemicals by the rec-assay, they damaged DNA in *Bacillus subtilis*, were SOS inducers in *Escherichia coli* PQ37 strain⁷ and were mutagens in *Salmonella typhimurium* TA100 and TA98 strains by an induced mutation frequency test⁸. However, when isolated λ-DNA was incubated with MeSnCl₃, Me₂SnCl₂, Me₃SnCl, BuSnCl₃ and Bu₂SnCl₂ in reaction systems both with and without hydrogen peroxide, the DNA breakage was not observed. Bivalent (SnCl₂) and tetravalent (SnCl₄) tin chlorides caused DNA breakage in the presence of hydrogen peroxide. The DNA damage activity for the bivalent compound was much more potent than for the tetravalent one⁹. Submicromolecular concentrations of tributyltin derivatives were found to induce the expression of several stress proteins, most notably HSP89 and HSP70, in IMR-90 human diploid fibroblasts in a time- and dose-dependent manner¹⁰.

Triphenyltin acetate and triphenyltin hydroxide were evaluated to induce micronuclei and sister chromatid exchange *in vitro* using cultured Chinese hamster ovary cells and *in vivo* on BALB/c mouse erythrocytes. This study demonstrated that both compounds are potential chromosome mutagens¹¹. Genotoxicity testing was performed for Et₂SnCl₂·L [L = N-(2-pyridylmethylene)-4-toluidine] complex in mouse bone-marrow cells *in vivo*. This compound induced delay in cell-cycle kinetics and significant sister chromatid changes¹². An increasing effect of different tributyl- and triphenyltins on the frequency of chemically induced breaking-type chromatid aberrations in cultured Chinese hamster ovary cells was observed¹³.

The chromosome abnormalities caused by different chlorostannanes and their complexes and occurring during both mitotic and meiotic processes have been studied *in vitro* on V79 Chinese hamster cells¹⁴ and *in vivo* on mitotic chromosomes of *Rutilus rubilio* (Pisces, Cyprinidae)¹⁵, gill tissue of *Aphanius Fasciatus* (Pisces, Cyprinodontiformes)¹⁶, male gonads of *Truncatella subcyllindrica* (Mollusca, Mesogastropoda)¹⁷ and *Ciona intestinales* fertilized eggs at different stages of development¹⁸.

The frequency of micronuclei induced by mitomycin C in mouse peripheral reticulocytes was enhanced by treatment with bis(tributyltin) oxide and triphenyltin chloride. These compounds did not themselves induce micronucleated reticulocytes (MNRET); however, 50 mg kg⁻¹ of (Bu₃Sn)₂O or 100 mg kg⁻¹ Ph₃SnCl given orally to mice, simultaneously with an intraperitoneal administration of mitomycin C (1 mg kg⁻¹), caused about 55% and 51% increases of MNRET frequency. These data demonstrate that OTCs act as coclastogens in a whole mammalian system¹⁹.

A synergistic effect of 2,3,3′,4,4′-pentachlorobiphenyl with triphenyltin derivatives in induction of the aberrant mitosis was detected. Inactive concentrations of both agents caused abnormal configurations when combined²⁰.

OTCs have severe effects on the immune systems, causing premature atrophy of thymus gland and lymphoid tissues as well as inhibition of spleen cell activity. Inhibition of phagocytosis and cytolyis of polymorphonuclear leukocytes with resultant depression of cell-mediated immune responses have also been demonstrated²¹–³⁷. The influence of the thymus atrophy-inducing dibutyltin dichloride Bu₂SnCl₂ on the differentiation and proliferation of immature rat thymocyte subsets were studied *in vivo* and *in vitro*. The atrophy results from a depletion of small CD4+CD8+ thymocytes which is caused by a diminished production of immature CD4+CD8+ and CD4+CD8+ thymoblasts. Dibutyltin dichloride inhibits the activation, but not the differentiation of immature CD4+CD8+ thymocytes *in vivo* and *in vitro*, suggesting a selective antiproliferative activity of this compound. It also
inhibits the adhesion molecule-mediated binding of thymocytes to thymic epithelial cells and enhances the \( \text{Ca}^{2+} \) release elicited by cross-linking of the T cell receptor complex on thymocytes. It may be concluded that dibutyltin dichloride possibly interferes with the functioning of the cytoskeleton\(^{21–26}\).

As organotin derivatives are the most harmful compounds of coastal pollutants, their immunotoxic effects were studied in aquatic organisms such as channel catfish \( \text{Ictalurus punctatus} \)^{33}, cultivated clam \( \text{Tapes philippinarum} \)^{36}, tunicates \( \text{Botryllus schlosseri} \)^{34,35} and \( \text{Ciona intestinalis} \)^{37}. Single intraperitoneal injections of corn oil with 0, 0.01, 0.1 and 1.0 mg kg\(^{-1} \) of tributyltin chloride were given to channel catfish. Three and seven days later, non-specific cytotoxic cell functions and humoral blood response were evaluated for allometric indices and hematology. Peripheral blood neutrophilia and specific antibody secreting cell numbers were the most sensitive parameters and were affected in all concentration groups. Allometric indices, peripheral blood lymphocyte and monocyte percentages, non-specific cytotoxic cell functions and phagocyte oxidative burst were less sensitive and were affected only at the higher dose of tributyltin chloride\(^{33}\).

Phagocytosis of yeast \textit{cells in vitro} by \( \text{Botryllus schlosseri} \) hemocytes is negatively affected by organotins present in the incubation medium. \( \text{Bu}_3\text{SnCl}, \text{Bu}_2\text{SnCl}_2 \) and \( \text{BuSnCl}_3 \) significantly reduce the phagocytic index, which ranges between 12 and 15 in controls, at a concentration of 10 \( \mu \text{M} \); \( \text{Bu}_3\text{SnCl} \) and \( \text{Bu}_2\text{SnCl}_2 \) significantly inhibit at 1 \( \mu \text{M} \) also, \( \text{Bu}_2\text{SnCl}_2 \) being more effective than \( \text{Bu}_3\text{SnCl} \)^{34}. After 1 h of \( \text{Botryllus schlosseri} \) hemocytes exposure to tributyltin chloride, nuclear changes, i.e. significant collapse and cleavage of chromatin, were observed. Hemocyte mortality increased significantly only after 2 h. All these apoptotic events may be closely related to cytosolic calcium increase resulting in activation of endonucleases\(^{35}\).

The effects of different OTC in human immune tissue were studied in isolated tonsil B cells. Non-stimulated B cells were killed by 100 nM concentration of all tested OTC after 8 h \textit{in vitro} culture. Organotin derivatives also decreased the proliferation of tonsillar B lymphocytes stimulated with \( \text{Staphylococcus aureus} \) Cowan 1 and IL-2, when present at 100 nM and higher concentrations. Increased phosphatidylserine exposure demonstrated that 100 nM concentration of triphenyltin chloride and dibutyltin dichloride induced B cells to die by apoptosis\(^{38}\).

The histopathological examination of the human thymus grafts of SCID-hu mice (SCID mice engrafted with human fetal thymus) exposed to dibutyltin dichloride showed a reduction in the relative size of the thymus cortex, an effect also described in rodents. These results indicate that the human thymus is a target for immunotoxic action of organotins\(^{27}\).

OTCs have toxic effects on the central nervous system. The neurotoxicity of trimethyltin derivatives was investigated widely\(^{39–41}\). Organotin exposure culminates in its accumulations in the CNS and PNS; the clinical picture is dominated by neurological disturbances. Trimethyltin chloride is primarily a CNS neurotoxin affecting neurons within the hippocampal pyramidal band and the fascia dentata. The triethyltin analogue is a neurotoxin that produces a pathological picture dominated by brain and spinal cord edema\(^{39}\). Developmental neurotoxicity may be influenced by effects of OTCs on endocrine function. Thus, trimethyltin hydroxide increases the corticosterone response to stress in developing rat pups (Long-Evans rat pups were injected i.p. with either 6 mg kg\(^{-1} \) \( \text{Me}_3\text{SnOH} \) in 10 \( \mu \text{l} \) \( \text{kg}^{-1} \) BW NaCl or vehicle on postnatal day 5 or 10)^{40}. Tributyltin and triphenyltin acetates produced significant central nervous system and respiratory depressions at single doses of 200 and 300 mg kg\(^{-1} \), respectively (the median lethal doses were 297.54 and 402.38 mg kg\(^{-1} \), p.o.). The histopathological findings showed pulmonary, hepatic and renal congestion, brain hemorrhages and destruction of the intestinal mucosa\(^{32}\).
The gliotoxicity of different organotins was investigated\textsuperscript{43,44}. The exposure of C6 glioma cells\textsuperscript{43} to OTCs at subtoxic concentrations for 24 h increased the amount of reduced glutathione (GSH). Increases of glutathione-S-transferase enzyme activity were also demonstrated after organotin exposure. This suggests that glutathione increases occur in glial cells after toxic insults, possibly acting as a protective mechanism. To test whether GSH plays a role in organotin-induced cell death, the effect of GSH addition in the culture media or via intracellular increase was studied. The GSH addition to the culture media did not protect the cells. However, pre-treatment with (-)-2-oxo-4-thiazolidine carboxylic acid, which increases intracellular GSH level, protected the cells against organotins.

The course of pancreatic fibrosis in rats induced by dibutyltin dichloride was studied 2–36 weeks after single i.v. treatment of rats with dose of 6 or 8 mg kg\textsuperscript{-1}. The pancreatic fibrosis induced by Bu\textsubscript{2}SnCl\textsubscript{2} differs from other experimental models of acute pancreatitis. Extensive infiltration is present in fibrotic areas without pancreatic atrophy or lipomatosis. The presence of chronic inflammatory lesions characterized by the destruction of exocrine parenchyma and fibrosis, and in the later stages the endocrine parenchyma, indicates a chronic pancreatitis\textsuperscript{45}.

Assessment of the relative teratogenic potential of triphenyltin chloride, trimethyltin chloride, triethyltin bromide, bis(tributyltin) oxide, tributyltin chloride and its metabolites, i.e. (3-hydroxybutyl)dibutyltin chloride, dibutyltin dichloride and butyltin trichloride, have been conducted using rat embryo limb bud cell cultures (LBC) to gain some knowledge of OTC’s embryotoxicity and teratogenicity\textsuperscript{46}. Fifty-percent inhibition concentration for cell proliferation (IP\textsubscript{50}) and for cell differentiation (ID\textsubscript{50}) and the ratio of the former to the latter (P/D ratio) were obtained. The ID\textsubscript{50} values increased in the following order of compounds: Ph\textsubscript{3}SnCl, Bu\textsubscript{2}SnCl\textsubscript{2} < Bu\textsubscript{3}SnCl, (Bu\textsubscript{3}Sn)\textsubscript{2}O < MeCH(OH)CH\textsubscript{2}CH\textsubscript{2}SnBu\textsubscript{2}Cl < Et\textsubscript{3}SnBr < Me\textsubscript{3}SnCl ≪ BuSnCl\textsubscript{3}. With the exception of BuSnCl\textsubscript{3}, the organotin compounds tested were very strong inhibitors of cell differentiation (ID\textsubscript{50} = 0.13–1.71 µM) and cell proliferation (IP\textsubscript{50} = 0.12–2.81 µM). P/D ratios for Bu\textsubscript{3}SnCl, MeCH(OH)CH\textsubscript{2}CH\textsubscript{2}SnBu\textsubscript{2}Cl, Bu\textsubscript{2}SnCl\textsubscript{2} and BuSnCl\textsubscript{3} were 1.0, 1.43, 1.32 and 1.08, respectively. The results suggest that tributyltin chloride is rather embryocidal than teratogenic.

The hemolytic effects of different organotin compounds were studied with white rabbit erythrocytes. Tributyltin chloride showed the highest hemolytic activity (EC\textsubscript{50} = 7.48 µM) and the hemolysis by this compound proceeded rapidly. Methyltin derivatives are less toxic (EC\textsubscript{50} = 364 µM). No significant difference in hemolytic activity based on divergences of the anionic functional group X in R\textsubscript{3}SnX (X = F, Cl, Br, OH, OMe, OEt, OAc) was observed\textsuperscript{47}. Various cations (Zn\textsuperscript{2+}, Co\textsuperscript{2+}, Cd\textsuperscript{2+} in a concentration of 50 µM) totally protect the erythrocytes against hemolysis induced by Pr\textsubscript{3}SnCl. The monovalent K\textsuperscript{+} and (C\textsubscript{12}H\textsubscript{25})Me\textsubscript{3}N\textsuperscript{+} ions are less potent inhibitors of hemolysis\textsuperscript{48}.

The stability of trout hemoglobin was examined in the presence of some organotin compounds. Tributyltin and triphenyltin chlorides protect HbI from the oxidation; the same compounds accelerate precipitation process in HbIV to a great extent. Mercury p-hydroxymercuribenzoate, an agent blocking free SH-groups of the protein, abolished the ability of triphenyltin chloride to decrease the oxidation rate of HbI\textsuperscript{49}.

The \textit{in vitro} effects of triphenyltin acetate on cytochrome P450 content and functions were investigated in liver microsomes from untreated and phenobarbital- or β-naphthoflavone pretreated rats. At a concentration of 0.5 mM, Ph\textsubscript{3}SnCl caused a marked loss in the spectrally detectable content of cytochrome P450, up to 27% of its original value, along with an increase in the inactive form cytochrome P420 and acted as an almost specific and powerful \textit{in vitro} inhibitor of cytochrome P450-dependent monoxygenases, apparently through the interaction with sulfhydryl groups of the hemoprotein\textsuperscript{50}. Subchronic
(70 days) oral exposure from moderate to high levels of triphenyltin acetate would affect the microsomal hepatic and renal drug-metabolizing enzymes in rabbits and lambs. In the rabbit livers, Ph$_3$SnCl failed to affect the cytochrome P450 content or the oxidative, hydrolytic or conjugative enzyme activities. In contrast, a striking dose-related increase in both P450 content and carboxylesterase activity (up to 280%) was detected in rabbit’s kidneys.

The interaction of triphenyltin chloride with fish microsomal monooxygenase systems has been studied in vitro and in vivo in the marine fish scup (Stenotomus chrysops). In vitro incubation of fish liver microsomes with Ph$_3$SnCl resulted in the conversion of about 40% of the native total spectral P450 to P420. In addition, a strong concentration-related inhibition of ethoxyresorufin O-deethylase activity was observed, with complete loss at concentration of 1.0 mM. Further in vitro incubation showed that NADPH, but not NADH, cytochrome c reductase was strongly inhibited at 100 µM and higher. To investigate this effect further, fish were injected with single doses of 5, 25 and 50 µM Ph$_3$SnCl (1.9, 9.6 and 19.3 mg kg$^{-1}$), and 24 and 48 h later, hepatic microsomes were analyzed for total P450 content, ethoxyresorufin O-deethylase activity and NAD(P)H cytochrome c reductase. Ethoxyresorufin O-deethylase activity tended to be decreased in Ph$_3$SnCl-treated scup, with the response being stronger after 48 h than after 24 h. No significant conversion of spectrally determined P450 to cytochrome P420 was found. These data combined with previous results indicate a general degenerative effect of organotins on the fish microsomal monooxygenase system.

The biochemical mechanism through which OTCs induce cell damages remains unclear. However, it was suggested that tetracoordinate organotin compounds R$_3$SnCl (R = Bu, Ph) are potent inhibitors of the mitochondrial ATP synthase complex, all acting on the membrane sector F0 of ATP synthase. Tributyltin derivatives induced rapid (maximal by 3 min) and sustained elevation in intracellular calcium levels in Jurkat T cells. This was preceded by mitochondrial hyperpolarization with subsequent loss of membrane potential over the next 15 min. The effect of R$_3$SnCl (R = Ph, Bu, Et, Me) on intracellular Ca$^{2+}$ level and survival in PC12 cells was examined. Treatment with micromolar concentrations of tributyl and triphenyl derivatives caused a rapid increase in the cytosolic free Ca$^{2+}$ concentration. When the Ca$^{2+}$ elevation was maintained for over 30 min, internucleosomal DNA cleavage typical of apoptotic cell death followed. These data suggest that the toxicity of organotins in PC12 cells is linked to their ability to promote intracellular Ca$^{2+}$ overload, which triggers apoptosis.

Tributyltin chloride Bu$_3$SnCl and its in vitro metabolites in rat liver microsomal enzyme systems, (3-hydroxybutyl)dibutyltin chloride, (3-oxobutyl)dibutyltin chloride, Bu$_2$SnCl$_2$ and BuSnCl$_3$, were intraperitoneally administered to male rats in order to investigate sulfur-containing metabolites in the urine. Administration of (3-hydroxybutyl)dibutyltin chloride and (3-oxobutyl)dibutyltin chloride gave higher amounts of mercapturic acid derivatives, such as N-acetyl-S-(3-oxobutyl)-L-cysteine and N-acetyl-S-(3-hydroxybutyl)-L-cysteine, than Bu$_2$SnCl$_2$ and BuSnCl$_3$. On the other hand, dibutyltin dichloride and butyltin trichloride did not yield measurable amounts of N-acetyl-S-(3-oxobutyl)-L-cysteine and/or N-acetyl-S-(3-hydroxybutyl)-L-cysteine. The appearance of organotin metabolites in urine indicates that (3-hydroxybutyl)dibutyltin chloride, (3-oxobutyl)dibutyltin chloride and hypothesized secondary metabolites, such as butyl(3-hydroxybutyl)(3-oxobutyl)tin chloride, butyl(3-hydroxybutyl)(4-hydroxybutyl)tin chloride, etc., are subject to the action of glutathione S-transferase to give mercapturic acid derivatives.

Antidotal effects of 2,3-dimercaptopropane-1-sulfonic (DMPS) and meso-2,3-dimercaptosuccinic (DMSA) acids on the toxicity of dibutyltin dichloride in rats were
studied using different doses and routes of administration (i.p. and p.o.) of both chelators. Several parameters of organotoxicity (thymus weight and cellularity, bile duct diameter, histological lesions of pancreas and liver, activities of amylase, lipase and alkaline phosphatase, bilirubin and hyaluronic acid in serum) were measured from 6 h to 8 weeks. DMPS and DMSA diminished the dibutyltin dichloride induced bile duct, pancreas and liver lesions more strongly than the thymus atrophy. Moreover, the development of a fibrosis of the pancreas and cirrhosis of liver several weeks after single administration of Bu₂SnCl₂ to rats was inhibited by DMPS and DMSA⁵⁹.

Some cases of human intoxication by OTCs were reported. Three patients who developed acute nephropathy after ingestion of triphenyltin acetate Ph₃SnOAc had significant proteinurea, azotemia and polyurea. Mild neurological manifestations in all patients were also noted. Hematuria and pyuria were detected in one severely poisoned patient. Evidence for hepatitis was present in two patients, and for pancreatitis in one. Renal biopsy showed focal fusion of glomerular cell processes and proximal tubular damage with cellular necrosis. Two patients survived with complete recovery of renal functions. One old patient died of aspiration pneumonia⁶⁰. A chemistry student was acutely exposed to vapors of an organotin compound. Seventy-two hours later he exhibited delirium, spatial disorientation, perseveration, inappropriate affect and memory defects. Trimethyltin derivatives were identified in blood and urine samples taken 17 days after the accident; the level of tin in blood was elevated 35 days after exposure. Serial electroencephalograms showed memory defects, cognitive dysfunction and dysphoria four years after⁶¹.

As the elevation of tin concentrations in human blood was detected in Alzheimer’s disease, attempts to detect organotins in a human brain tissue which showed neuropathological evidence of Alzheimer’s disease were undertaken. However, OTCs with low molecular weight were not found. It is possible that tin derivatives form complexes with large organic molecules, which are not volatile for gas chromatography⁶².

C. Antimicrobial Activity

The effects of triorganotin 2-naphthylthiolates 2-C₁₀H₇SSnR₃ (R = Me, c-C₆H₁₁, PhCH₂, Ph) and diorganotin bis(2-naphthyl)thiolates (2-C₁₀H₇S)₂SnR₂ (R = Me, Bn) were tested against 10 bacteria: Salmonella typhi, Shigella boydii, Corynebacterium diphtheria, Staphylococcus pyogenes, Escherichia coli, Corynebacterium hoffmannii, Staphylococcus faecalis, Klebsiella pneumoniae, Proteus vulgaris and Staphylococcus aureus⁶³. The antibacterial activity is maximal for the tributyl compound 2-C₁₀H₇SSnBu₃ (MIC < 100–150 µg ml⁻¹), whereas the tricyclohexyl derivative 2-C₁₀H₇SSn(C₆H₁₁-c)₃ was inactive.

The results of antimicrobial action in vitro of Ph₂SnCl₂, Bu₂SnO and their complexes R₂SnL (L = dianion of alanylatedalanine, phenylalanylleucine, phenyalanylphenylalanine and glycoisoleucine) are presented in Table 1⁶⁴. Dibutyl complexes are found to be more active than Bu₂SnO whereas diphenyltin derivatives with some exceptions are less active than Ph₂SnCl₂. Minimum inhibitory concentration for diphenyltin complexes Ph₂SnL₂ varied in the <12.5–50 µg ml⁻¹ region (Staphylococcus faecalis, Klebsiella pneumoniae, Escherichia coli, Pseudomonas aeruginosa and Staphylococcus aureus)⁶⁵. The organotin derivatives of amino acids having nitrogen-containing heterocyclic rings, i.e. L-histidine and L,D-tryptophan, have been tested in vitro against the same bacteria. Bactericidal activity decreased in the order Ph₃SnL > Bu₂SnL₂ > Me₃SnL (HL = L,D-tryptophan)⁶⁶.
24. Biological activity of organotin and organolead compounds

\[
\begin{align*}
\text{LH} & = \begin{array}{c}
\text{OMe} \\
\end{array} \\
\text{Ar} & = \\
\end{align*}
\]

\[
\begin{align*}
R = \text{H, Me}; \text{Ar} = \\
\end{align*}
\]

**TABLE 1. Antibacterial activity of organotin compounds \( \text{R}_2\text{SnL} \)**

<table>
<thead>
<tr>
<th>R, L</th>
<th>MIC, ( \mu\text{gml}^{-1} )</th>
<th><em>Escherichia coli</em></th>
<th><em>Rhizobium mellioti</em></th>
<th><em>Pseudomonas putida</em></th>
<th><em>Aeromonas putida</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{R} = \text{Bu}, \text{L} = \text{O} )</td>
<td>50</td>
<td>50</td>
<td>12.5</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>( \text{R} = \text{Bu}, \text{L} = \text{NHCHOCH(Bn)CONHCH(Bn)COO} )</td>
<td>25</td>
<td>50</td>
<td>12.5</td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td>( \text{R} = \text{Bu}, \text{L} = \text{NHCHOCH}(\text{i-Bu})\text{COO} )</td>
<td>25</td>
<td>25</td>
<td>6.25</td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td>( \text{R} = \text{Bu}, \text{L} = \text{NHCHOCH}(\text{Bu})\text{COO} )</td>
<td>50</td>
<td>50</td>
<td>12.5</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>( \text{R} = \text{Bu}, \text{L} = \text{NHCHOCH}(\text{s-Bu})\text{COO} )</td>
<td>50</td>
<td>50</td>
<td>6.12</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>( \text{R} = \text{Ph}, \text{L} = \text{Cl}_2 )</td>
<td>12.5</td>
<td>50</td>
<td>12.5</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>( \text{R} = \text{Ph}, \text{L} = \text{NHCHOCH}(\text{Bu})\text{CONHCH}(\text{i-Bu})\text{COO} )</td>
<td>50</td>
<td>50</td>
<td>12.5</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>( \text{R} = \text{Ph}, \text{L} = \text{NHCHOCH}(\text{s-Bu})\text{COO} )</td>
<td>50</td>
<td>50</td>
<td>6.12</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

Organotin complexes of di(2-pyridyl) ketone 2-thenoylhydrazone, 1 and 2, with 6- and 5-coordinated tin atom are less active than the parent organotins\(^{67,68}\). Compound 2 showed good results in tests against *Bacillus subtilis*, *Staphylococcus aureus* and also toward several *Bacilli* with minimum inhibitory concentration ranging from 1.5 to 3 \( \mu\text{gml}^{-1} \).\(^{167}\) At the same time this complex is devoid of DNA-damaging activity in the *Bacillus subtilis* rec-
assay and of mutagenicity in the *Salmonella* test. Organotin complexes \( \text{Ph}_2\text{SnCl}_2\text{L}\cdot2\text{H}_2\text{O} \)\(^{69}\) (\( \text{L} = \text{pyrrole}-2\)-carboxaldehyde 2-hydroxybenzoylhydrazone) and \( \text{Ph}_2\text{Sn}(\text{L-H})\cdot\text{Me}_2\text{SO} \)\(^{70}\) (\( \text{L} = \text{pyrrole}-2,5\)-dicarboxaldehyde bis(2-hydroxybenzoylhydrazone)) have MIC values between 3–6 µg ml\(^{-1}\) against *Bacillus subtilis* and *Staphylococcus aureus* and between 6–25 µg ml\(^{-1}\) against *Escherichia coli*.

Although the ligands of complexes 3 and 4\(^{71}\) are active against *Escherichia coli*, *Pseudomonas syringae*, *Proteus mirabilis* and *Staphylococcus aureus* in the paper disc plate method, their bactericidal effects are smaller as compared with tin derivatives 3 and 4.

The antibacterial activity of heterobimetallic complexes 5\(^{72}\) was determined by the inhibition zone technique (*Escherichia coli*, *Klebsiella aerogenous* and *Pseudomonas*...
cepacica). These complexes are more active than their precursors \((C_5H_7N_3)_2MCl_2\) (\(M = \text{Pd, Pt})\).

### D. Fungicidal Activity

Various organotin derivatives have very high fungicidal activity and, in addition, these compounds show an interesting range of structural variations which allow one to advance some conclusions concerning structure–activity relationships. The fungicidal activity of a series of \(-o, m-\) and \(-p\)-substituted aryltin compounds \((YC_6H_4)_3SnX\)\(^{73,74}\) has been studied by radial growth assays on \(Aspergillus niger\), \(Botrytis cinerea\), \(Mucor hiemalis\), \(Fusarium solani\), and \(Penicillium chrysogenum\). As shown by the ED\(_{50}\) values (Table 2), both \(3\)-\(MeC_6H_4)_3SnOAc and \([3\)-(\(MeOC_6H_4)_3Sn]_2O\) have similar fungicidal effects. They are generally more active than their \(-p\)-tolyl analogues but are still less effective than the parent phenyl biocides already in use, i.e. Brestan (Ph\(_3SnOAc\)) and Du-Ter (Ph\(_3SnOH\)). Two \(-m\)-Me groups, as in \((3,5\)-\(Me_2C_6H_3)\)_3SnOAc, cause an overall decrease in activity — except with \(M. hiemalis\) — and complete loss of activity against \(P. chrysogenum\). In contrast to its \(-p\)-analogue, which is completely ineffective against all the test fungi, \([3\)-(\(MeOC_6H_4)\)_3Sn]_2O is relatively active except with \(P. chrysogenum\). The \(-o\)-tolyl compounds present a less uniform aspect of biological activity. Thus \((2\)-\(MeC_6H_4)\)_3SnOAc is only slightly less effective than \((3\)-\(MeC_6H_4)\)_3SnOAc or \((4\)-\(MeC_6H_4)\)_3SnOAc, but for the oxide the results unexpectedly depend on the fungi being tested. Both trimesityl tin derivatives are ineffective fungicides but they do not promote fungi growth.

The pathogenic fungus \(Ceratocystis ulmi\) (\(C. ulmi\)), responsible for Dutch elm disease, causes a blockade in the vascular tissue that can lead to the eventual death of the

<table>
<thead>
<tr>
<th>Compound</th>
<th>(A. niger)</th>
<th>(B. cinerea)</th>
<th>(M. hiemalis)</th>
<th>(F. solani)</th>
<th>(P. chrysogenum)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph(_3SnOAc)</td>
<td>2.0 (0.1)</td>
<td>5.2 (2.6)</td>
<td>1.9 (0.6)</td>
<td>0.7 (0.2)</td>
<td>5.0 (1.0)</td>
</tr>
<tr>
<td>((4)-(FC_6H_4))_3SnOAc</td>
<td>4.6 (1.3)</td>
<td>7 (6)</td>
<td>1.4 (0.1)</td>
<td>2.4 (1.0)</td>
<td>14 (10)</td>
</tr>
<tr>
<td>((4)-(ClC_6H_4))_3SnOAc</td>
<td>8.2 (2.3)</td>
<td>6 (4)</td>
<td>3.8 (0.3)</td>
<td>3.7 (0.7)</td>
<td>11 (8)</td>
</tr>
<tr>
<td>((4)-(MeC_6H_4))_3SnOAc</td>
<td>8 (8)</td>
<td>5.0 (1.4)</td>
<td>7.6 (4.4)</td>
<td>3.8 (1.5)</td>
<td>11.7 (3.8)</td>
</tr>
<tr>
<td>((3)-(MeC_6H_4))_3SnOAc</td>
<td>2</td>
<td>6</td>
<td>3.6 (0.9)</td>
<td>3.4 (2.3)</td>
<td>9.1 (8.4)</td>
</tr>
<tr>
<td>((2)-(MeC_6H_4))_3SnOAc</td>
<td>9.6 (4.7)</td>
<td>16 (11)</td>
<td>4.2 (1.4)</td>
<td>11</td>
<td>9.6 (2.7)</td>
</tr>
<tr>
<td>((3)-(Me_2C_6H_3))_3SnOAc</td>
<td>22</td>
<td>13 (12)</td>
<td>4</td>
<td>7.5 (6.3)</td>
<td>NE</td>
</tr>
<tr>
<td>((2,4,6)-(Me_3C_6H_2))_3SnOAc</td>
<td>NE</td>
<td>NE</td>
<td>NE</td>
<td>NE</td>
<td>NE</td>
</tr>
<tr>
<td>((4)-(EtC_6H_4))_3SnOAc</td>
<td>2.4 (1.6)</td>
<td>1.7 (1.4)</td>
<td>2.6 (1.1)</td>
<td>4.8 (1.2)</td>
<td>1.3 (1.7)</td>
</tr>
<tr>
<td>((4)-(MeOC_6H_4))_3SnOAc</td>
<td>NE</td>
<td>NE</td>
<td>NE</td>
<td>NE</td>
<td>NE</td>
</tr>
<tr>
<td>Ph(_3SnOH)</td>
<td>0.5 (0.1)</td>
<td>5 (4)</td>
<td>1.5 (0.4)</td>
<td>1.1 (0.2)</td>
<td>3.7 (0.9)</td>
</tr>
<tr>
<td>((4)-(FC_6H_4))_3SnOH</td>
<td>1.4 (0.3)</td>
<td>3.2 (1.7)</td>
<td>2.0 (0.8)</td>
<td>3.1 (0.8)</td>
<td>9.1 (4.4)</td>
</tr>
<tr>
<td>((4)-(ClC_6H_4))_3SnOH</td>
<td>4.5 (1.6)</td>
<td>5.0 (3.3)</td>
<td>2.0 (0.7)</td>
<td>5.3 (2.5)</td>
<td></td>
</tr>
<tr>
<td>((4)-(MeC_6H_4))_3SnOH</td>
<td>4.3 (1.6)</td>
<td>6</td>
<td>7 (7)</td>
<td>3.4 (0.7)</td>
<td>5.5 (2.2)</td>
</tr>
<tr>
<td>([2)-(2,4,6)-(Me_3C_6H_2))_3Sn]_2O</td>
<td>NE</td>
<td>NE</td>
<td>13</td>
<td>NE</td>
<td>NE</td>
</tr>
<tr>
<td>((Ph_3Sn)_2O)</td>
<td>0.7 (0.1)</td>
<td>3 (3)</td>
<td>1.4 (0.2)</td>
<td>0.9 (0.1)</td>
<td>5 (5)</td>
</tr>
<tr>
<td>([2)-(2,4,6)-(Me_3C_6H_2))_3Sn]_2O</td>
<td>NE</td>
<td>19</td>
<td>7</td>
<td>NE</td>
<td>NE</td>
</tr>
<tr>
<td>([3)-(MeC_6H_4))_3Sn]_2O</td>
<td>1.2 (0.5)</td>
<td>5.1 (4.0)</td>
<td>3.0 (2.1)</td>
<td>3.8 (3.6)</td>
<td>8.8 (7.6)</td>
</tr>
<tr>
<td>([4)-(r)-(BuC_6H_4))_3Sn]_2O</td>
<td>NE</td>
<td>NE</td>
<td>NE</td>
<td>NE</td>
<td>NE</td>
</tr>
<tr>
<td>([4)-(MeOC_6H_4))_3Sn]_2O</td>
<td>NE</td>
<td>NE</td>
<td>NE</td>
<td>NE</td>
<td>NE</td>
</tr>
<tr>
<td>([3)-(MeOC_6H_4))_3Sn]_2O</td>
<td>6.6 (1.4)</td>
<td>6.7 (4.8)</td>
<td>3.3 (2.9)</td>
<td>5.3 (3.6)</td>
<td>NE</td>
</tr>
</tbody>
</table>

\(^a\)NE = no effect
elm. It has been established that various organotin compounds such as tetraarylstanannanes, triarylchlorostannanes, triphenyltin carboxylates, triphenyltin sulfides, and complexes of triphenylchloro- and triphenylisothiocyanatostannanes with various nitrogen-containing compounds are highly effective in the inhibition of *C. ulmi* (Table 3). The data indicate that all substituted tetraaryl compounds are less effective in the inhibition of the fungus when compared with the parent tetraphenylin. A comparison of the IC50 values for the tetraarylstanannanes Ar₄Sn with those for the triarylstannyl derivatives Ar₃SnX clearly indicates that the latter are far superior in their inhibition of *C. ulmi*.

Diorganotin carboxylates and chlorides have been tested for antifungal activity against *Aspergillus niger*, *Aspergillus flavus* and *Penicillium citrinum* (Table 4). It is evident that diphenylstanannanes are more effective than their dibutyl analogues. Triphenyltin 2-pyrimidylthioacetate Ph₃Sn(OOCCH₂SC₄H₃N₂-2) tested on *Helminthosporium maydis* has greater activity than the tributyltin derivatives. On the contrary, the effect of tributyltin 2-pyrimidylthioacetate Bu₃Sn(OOCCH₂SC₄H₃N₂-2) against *Helminthosporium oryzae* is higher as compared with the triphenyltin compound. Tributyltin hydantooate Bu₃SnOOCCH₂NHC(O)NH₂ is also more effective against spore germination (*Alternaria alternata*, *Helminthosporium sativum*, *Helminthosporium maydis*, *Piricularia oryzae* and *Oryzae sativa*) than the diphenyl and dicyclohexyl derivatives.

N-phthaloyl-protected amino acids react with triorganotin hydroxides to form the hydrated triorganotin carboxylates, which display a wide spectrum of antifungal activity (Table 5). The ED50 values for the tributyltin derivatives generally fall below the 1 ppm range; the ED50 values for the triphenyltin derivatives range from 0.22 to 10.00 ppm, which demonstrates that these compounds possess a higher degree of selectivity in their fungitoxic action.

The organotin derivatives of amino acids having nitrogen-containing heterocyclic rings, i.e. L-histidine and L,D-tryptophan (HL), have been tested in vitro against *Candida albicans*, *Cryptococcus neoformans*, *Sporotrichum schenckii*, *Trichophyton mentagrophytes* and *Aspergillus fumigatus*. The fungicidal activity under experimental conditions decreased in the order: Ph₃Sn > Bu₂Sn > Me₃Sn. Because of the high antifungal effects, they have been screened in vivo against a multi-infection model in mice. However, at 100 mg kg⁻¹ (p.o) these compounds were very toxic, whereas at a dose of 50 mg kg⁻¹ they showed insignificant activity.

Tin derivatives of 4-acetyl and 4-benzoyl-3-methylpyrazol-5-ones (L) were tested to determine the concentrations causing 50% inhibitions of the lateral micelial growth of the six fungi chosen: *Trichoderma viride*, *Colletotrichum gloeosporioides*, *Verticillium fungicola*, *Piricularia oryzae*, *Sclerotinia fruticola* and *Fusarium culmorum*. The general trend of observed fungitoxicity in the test compounds is summarized as R₂SnL₂ < trans-R₃SnL(H₂O) < cis-R₃SnL. 
### TABLE 3. Inhibitory concentrations of organotin compounds against *C. ulmi*

<table>
<thead>
<tr>
<th>Compound</th>
<th>IC$_{50}$ (mg dm$^{-3}$)</th>
<th>lg IC$_{50}$ (mM)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph$_4$Sn</td>
<td>7.6</td>
<td>-1.75</td>
<td>75</td>
</tr>
<tr>
<td>(3-ClC$_6$H$_4$)$_4$Sn</td>
<td>15.7</td>
<td>-1.54</td>
<td>75</td>
</tr>
<tr>
<td>(3-MeOC$_6$H$_4$)$_4$Sn</td>
<td>19.4</td>
<td>-1.45</td>
<td>75</td>
</tr>
<tr>
<td>(3-MeC$_6$H$_4$)$_4$Sn</td>
<td>11.1</td>
<td>-1.63</td>
<td>75</td>
</tr>
<tr>
<td>(4-ClC$_6$H$_4$)$_4$Sn</td>
<td>21.9</td>
<td>-1.40</td>
<td>75</td>
</tr>
<tr>
<td>(4-MeSC$_6$H$_4$)$_4$Sn</td>
<td>15.4</td>
<td>-1.60</td>
<td>75</td>
</tr>
<tr>
<td>(4-MeC$_6$H$_4$)$_4$Sn</td>
<td>11.5</td>
<td>-1.62</td>
<td>75</td>
</tr>
<tr>
<td>(4-t-BuC$_6$H$_4$)$_4$Sn</td>
<td>10.1</td>
<td>-1.81</td>
<td>75</td>
</tr>
<tr>
<td>Ph$_3$SnCl</td>
<td>2.10</td>
<td>-2.26</td>
<td>75</td>
</tr>
<tr>
<td>(3-ClC$_6$H$_4$)$_3$SnCl</td>
<td>2.10</td>
<td>-2.37</td>
<td>75</td>
</tr>
<tr>
<td>(3-MeOC$_6$H$_4$)$_3$SnCl</td>
<td>1.60</td>
<td>-2.47</td>
<td>75</td>
</tr>
<tr>
<td>(3-MeC$_6$H$_4$)$_3$SnCl</td>
<td>2.30</td>
<td>-2.27</td>
<td>75</td>
</tr>
<tr>
<td>(4-ClC$_6$H$_4$)$_3$SnCl</td>
<td>1.45</td>
<td>-2.53</td>
<td>75</td>
</tr>
<tr>
<td>(4-MeSC$_6$H$_4$)$_3$SnCl</td>
<td>2.50</td>
<td>-2.32</td>
<td>75</td>
</tr>
<tr>
<td>(4-MeC$_6$H$_4$)$_3$SnCl</td>
<td>2.60</td>
<td>-2.22</td>
<td>75</td>
</tr>
<tr>
<td>(4-FC$_6$H$_4$)$_3$SnCl</td>
<td>1.85</td>
<td>-2.48</td>
<td>75</td>
</tr>
<tr>
<td>(4-t-BuC$_6$H$_4$)$_3$SnCl</td>
<td>4.60</td>
<td>-2.08</td>
<td>75</td>
</tr>
<tr>
<td>PhCOOSnPh$_3$</td>
<td>1.0</td>
<td>-1.81</td>
<td>76</td>
</tr>
<tr>
<td>COOSnPh$_3$</td>
<td>2.19</td>
<td>-2.19</td>
<td>76</td>
</tr>
<tr>
<td>COOSnPh$_3$</td>
<td>2.50</td>
<td>-2.50</td>
<td>76</td>
</tr>
<tr>
<td>4-MeOC$_6$H$_4$COOSnPh$_3$</td>
<td>2.66</td>
<td>-2.66</td>
<td>76</td>
</tr>
<tr>
<td>4-MeC$_6$H$_4$COOSnPh$_3$</td>
<td>2.78</td>
<td>-2.78</td>
<td>76</td>
</tr>
<tr>
<td>4-H$_2$NC$_6$H$_4$COOSnPh$_3$</td>
<td>3.08</td>
<td>-3.08</td>
<td>76</td>
</tr>
<tr>
<td>4-O$_2$NC$_6$H$_4$COOSnPh$_3$</td>
<td>2.63</td>
<td>-2.63</td>
<td>76</td>
</tr>
<tr>
<td>3-MeCOOC$_6$H$_4$COOSnPh$_3$</td>
<td>2.42</td>
<td>-2.42</td>
<td>76</td>
</tr>
<tr>
<td>2-(PhN=CH)C$_6$H$_4$COOSnPh$_3$</td>
<td>0.8</td>
<td>0.8</td>
<td>77</td>
</tr>
<tr>
<td>2-(4-MeC$_6$H$_4$N=CH)C$_6$H$_4$COOSnPh$_3$</td>
<td>0.4</td>
<td>0.4</td>
<td>77</td>
</tr>
<tr>
<td>2-(2-MeC$_6$H$_4$N=CH)C$_6$H$_4$COOSnPh$_3$</td>
<td>0.6</td>
<td>0.6</td>
<td>77</td>
</tr>
<tr>
<td>2-(2-HOC$_6$H$_4$N=CH)C$_6$H$_4$COOSnPh$_3$</td>
<td>0.8</td>
<td>0.8</td>
<td>77</td>
</tr>
<tr>
<td>HOCH$_2$CH$_2$SSnPh$_3$</td>
<td>0.50</td>
<td>0.50</td>
<td>78</td>
</tr>
<tr>
<td>4-H$_2$NC$_6$H$_4$SSnPh$_3$</td>
<td>1.35</td>
<td>1.35</td>
<td>78</td>
</tr>
<tr>
<td>Pr$_2$NC(S)SSnPh$_3$</td>
<td>0.45</td>
<td>0.45</td>
<td>78</td>
</tr>
<tr>
<td>PhNHNHC(N=NPh)SSnPh$_3$</td>
<td>0.8</td>
<td>0.8</td>
<td>78</td>
</tr>
<tr>
<td>Ph$_3$SnCl-o-HOC$_6$H$_4$CH$_2$CH$_2$CH=NM</td>
<td>1.2</td>
<td>1.2</td>
<td>78</td>
</tr>
<tr>
<td>Pr$_3$SnCl-o-HOC$_6$H$_4$CH$_2$CH=NM</td>
<td>5.6</td>
<td>5.6</td>
<td>78</td>
</tr>
<tr>
<td>Pr$_3$SnNCS-o-HOC$_6$H$_4$CH$_2$CH=NM</td>
<td>4.7</td>
<td>4.7</td>
<td>78</td>
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<tr>
<td>Pr$_3$SnCl-o-HOC$_6$H$_4$CH=NC$_6$H$_13$-n</td>
<td>3.9</td>
<td>3.9</td>
<td>78</td>
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<tr>
<td>Pr$_3$SnCl-o-HOC$_6$H$_4$CH=NC$_6$H$_11$-c</td>
<td>1.9</td>
<td>1.9</td>
<td>78</td>
</tr>
</tbody>
</table>

(continued overleaf)
TABLE 3. (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>IC₅₀ (mg dm⁻³)</th>
<th>lg IC₅₀ (mM)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph₃SnNCS•O-HOC₆H₄CH=NC₆H₁₁⁻c</td>
<td>5.5</td>
<td>78</td>
<td></td>
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<tr>
<td>Ph₃SnCl•O-HOC₆H₄CH=NCH₂Ph</td>
<td>2.0</td>
<td>78</td>
<td></td>
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<tr>
<td>Ph₃SnNCS•O-HOC₆H₄CH=NCH₂Ph</td>
<td>2.3</td>
<td>78</td>
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<tr>
<td>Ph₃SnCl•O-HOC₆H₄CH=NBU⁻t</td>
<td>2.8</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>Ph₃SnNCS•O-HOC₆H₄CH=NBu⁻t</td>
<td>2.4</td>
<td>78</td>
<td></td>
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<tr>
<td>Ph₃SnCl•O-HOC₆H₄CH=NCH₂CH₂OH</td>
<td>3.4</td>
<td>78</td>
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<tr>
<td>Ph₃SnNCS•O-HOC₆H₄CH=NCH₂CH₂OH</td>
<td>3.6</td>
<td>78</td>
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<tr>
<td>Ph₃SnCl•O-HOC₆H₄CH=NCH₂COOEt</td>
<td>2.8</td>
<td>78</td>
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<tr>
<td>Ph₃SnCl•O-HOC₆H₄CH=NCH(Me)COOMe</td>
<td>3.2</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>Ph₃Sn(OOCCH₂NH₂Me)Cl</td>
<td>2.51</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>Ph₃Sn(OOCCH₂NH₂Me)NCS</td>
<td>2.37</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>Ph₃Sn(OOCCH₂NMe₂)Cl</td>
<td>0.2ᵃ</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>Ph₃Sn(OOCCH₂NMe₂)NCS</td>
<td>0.4ᵃ</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>Ph₃SnCl•Ph[CHN(Ph)C(O)CH₂S]ᵇ</td>
<td>2.73</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>Ph₃SnCl•o-FC₆H₄[CHN(Ph)C(O)CH₂S]ᵇ</td>
<td>2.64</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>Ph₃SnCl•p-FC₆H₄[CHN(Ph)C(O)CH₂S]ᵇ</td>
<td>2.56</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>Ph₃SnCl•p-BrC₆H₄[CHN(Ph)C(O)CH₂S]ᵇ</td>
<td>2.95</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>Ph₃SnCl•m-Cl₃C[CHN(Ph)C(O)CH₂S]ᵇ</td>
<td>2.70</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>Ph₃SnCl•Cl₃C[CHN(Ph)C(O)CH₂S]ᵇ</td>
<td>2.45</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>Ph₃SnCl•[OCN(Ph)(C(O)CH₂S)]ᶜ</td>
<td>2.38</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>Ph₃SnCl•[OCN(Ph)(C(O)(CH₂)₂S)]ᵈ</td>
<td>2.45</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>(OC₆H₄CH=NCMeCOO)SnMe₂</td>
<td>8.5</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>(OC₆H₄CH=NCPhCOO)SnMe₂</td>
<td>9.9</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>[OC₆H₄CH=NC(CHA(O)C(OH)COO)]SnMe₂</td>
<td>4.3</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>[OC₆H₄CH=NC(CHA(O)COO)]SnMe₂</td>
<td>7.1</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>(OC₆H₄CH=NCBH₂COO)SnBu₂</td>
<td>15.5</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>(OC₆H₄CH=NCMeCOO)SnBu₂</td>
<td>5.9</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>(OC₆H₄CH=NCPhCOO)SnBu₂</td>
<td>3.1</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>[OC₆H₄CH=NC(CHA(O)C(OH)COO)]SnBu₂</td>
<td>14.7</td>
<td>78</td>
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</tr>
<tr>
<td>[OC₆H₄CH=NC(CHA(O)COO)]SnBu₂</td>
<td>11.8</td>
<td>78</td>
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</tr>
<tr>
<td>(OC₆H₄CH=NC(i-Pr)COO)SnBu₂</td>
<td>13.9</td>
<td>78</td>
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</tr>
<tr>
<td>(OC₆H₄CH=NC(CH₂COO)SnBu₂</td>
<td>11.9</td>
<td>78</td>
<td></td>
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<tr>
<td>(OC₆H₄ClMe=NC(H₂COO)SnBu₂</td>
<td>18.1</td>
<td>78</td>
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</tr>
</tbody>
</table>

ᵃThe minimal inhibitory concentration in ppm.
24. Biological activity of organotin and organolead compounds

TABLE 4. Minimum inhibition concentrations (MIC, mmol l\(^{-1}\)) of diorganotin chlorides and carboxylates\(^{82}\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>A. flavus</th>
<th>A. niger</th>
<th>P. citrinum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bu(_2)SnCl(_2)</td>
<td>16.45</td>
<td>8.22</td>
<td>16.45</td>
</tr>
<tr>
<td>Ph(_2)SnCl(_2)</td>
<td>0.73</td>
<td>0.72</td>
<td>0.77</td>
</tr>
<tr>
<td>Bu(_2)Sn(OAc)(_2)</td>
<td>7.12</td>
<td>7.53</td>
<td>7.44</td>
</tr>
<tr>
<td>Ph(_2)Sn(OAc)(_2)</td>
<td>0.13</td>
<td>&gt;0.13</td>
<td>&gt;0.13</td>
</tr>
<tr>
<td>Bu(_2)Sn(OOCC(_6)H(_4)OH-2)(_2)</td>
<td>4.93</td>
<td>4.98</td>
<td>5.19</td>
</tr>
<tr>
<td>Bu(_2)Sn(OOCC(_6)H(_4)COOMe-2)(_2)</td>
<td>0.87</td>
<td>0.86</td>
<td>0.84</td>
</tr>
<tr>
<td>1,2-C(_6)H(_4)(COO)(_2)SnBu(_2)</td>
<td>12.59</td>
<td>12.59</td>
<td>12.59</td>
</tr>
<tr>
<td>1,2-C(_6)H(_4)(COO)(_2)SnPh(_2)</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
</tr>
</tbody>
</table>

TABLE 5. ED\(_{50}\) (ppm) values for compounds\(^{685}\)

<table>
<thead>
<tr>
<th>Fungi</th>
<th>R, R'</th>
<th>R = H; R' = Bu</th>
<th>R = Me; R' = Bu</th>
<th>R = H; R' = Ph</th>
<th>R = s-Bu; R' = Ph</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alternaria padwickii</td>
<td>0.69</td>
<td>1.21</td>
<td>0.89</td>
<td>9.00</td>
<td></td>
</tr>
<tr>
<td>Botryodiplodia theobromae 122</td>
<td>0.42</td>
<td>0.69</td>
<td>2.18</td>
<td>2.06</td>
<td></td>
</tr>
<tr>
<td>Colletotrichum musae</td>
<td>0.49</td>
<td>0.68</td>
<td>0.84</td>
<td>1.03</td>
<td></td>
</tr>
<tr>
<td>Colletotrichum musae 246</td>
<td>0.81</td>
<td>1.00</td>
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<td>0.95</td>
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<td>Pyricularia oryzae</td>
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The effects of diorganotin and triorganotin complexes obtained from various Schiff bases have been evaluated on different species of pathogenic fungi\(^{65,87-90}\).

Besides the discussed types of biological properties, OTCs showed different kinds of biocidal activity, e.g. trypasanocida\(^{91,92}\), herbicida\(^{65}\), insecticida\(^{93-97}\) and ovicida\(^{97}\); they have also toxic effects on fresh water and marine algae\(^{98-100}\).

E. Antitumor Activity

The cytotoxic effect and antitumor activity induced by different organotin compounds have been widely studied. These intensive investigations led to the discovery of compounds with excellent \textit{in vitro} cytotoxic activity. The cytotoxicity of organotin carboxylates with the following structures: RCOOSnR\(_1\)^{1}, (RCOO)\(_2\)SnR\(_1\)^{1} and \{[(RCOO)SnBu\(_2\)]^2O\}_2\), has been tested on several human tumor cell lines (MCF-7 and EVSA-T, two breast tumors; WiDr, a colon carcinoma; IGROV, an ovarian cancer; M19 MEL, a melanoma; A498, a renal cancer). The results of the \textit{in vitro} screening expressed as inhibitory doses (ID\(_{50}\) in ng ml\(^{-1}\)) are presented in Tables 6–8. The majority of presented compounds have activities which are comparable or better than those for cisplatin, 5-fluorouracil, methotrexate and doxorubicin.
TABLE 6.  *In vitro* cytotoxic activities (ID<sub>50</sub>, ng ml<sup>-1</sup>) of tributyl- and triphenyltin carboxylates RCOOSnR<sub>1</sub>\(^3\)

<table>
<thead>
<tr>
<th>R</th>
<th>R&lt;sup&gt;1&lt;/sup&gt;</th>
<th>MCF-7</th>
<th>EVSA-T</th>
<th>WiDr</th>
<th>IGROV</th>
<th>M19 MEL</th>
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<tr>
<td>Ph</td>
<td>Ph</td>
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<td></td>
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<td></td>
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<td>13</td>
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<td>101</td>
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<tr>
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<td>Bu</td>
<td>23</td>
<td>&lt;3</td>
<td>45</td>
<td>38</td>
<td>47</td>
<td>63</td>
<td>101</td>
</tr>
<tr>
<td>PhCH=CH</td>
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<td>3</td>
<td>22</td>
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<td>101</td>
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<td>Ph</td>
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<td></td>
<td></td>
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<td>Ph</td>
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<td>C&lt;sub&gt;6&lt;/sub&gt;F&lt;sub&gt;5&lt;/sub&gt;</td>
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Diagram showing structures of chemical compounds with labeled atoms and groups.
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TABLE 8. *In vitro* cytotoxic activities (ID$_{50}$, ng ml$^{-1}$) of carboxylates \([\{(RCOO)SnBu_2\}_2O\}_2\)

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![Chemical structures](image)

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The ID$_{50}$ of 2,6-pyridinedicarboxylatodiorganotin derivatives (16) \((R = R' = Bu, 4-\text{MeOC}_6\text{H}_4, 9-(\text{o-C}_2\text{B}_{10}\text{H}_{11}), 9-(\text{m-C}_2\text{B}_{10}\text{H}_{11}); R = \text{Ph, R'} = \text{Ph, Me, Et, Pr, i-Pr, Bu, i-Bu, Bn})$\textsuperscript{117,118} varied in the wide region from 10 \text{ng ml}^{-1} \text{ for R}=R'=(\text{o-C}_2\text{B}_{10}\text{H}_{11})$ to 4930 ng ml$^{-1}$ \text{ for R}=R'=(\text{4-MeOC}_6\text{H}_4)$ on the MCF-7 cell line.

Anhydrous bis(2,6-pyridinedicarboxylato) dibutylstannane (17)$\textsuperscript{123}$, containing according to X-ray data a 7-coordinated tin atom, was also tested on MCF-7, EVSA-T, WiDr, IGROV, M19 MEL and A498 cell lines and the inhibition doses were found to be 46, 27, 172, 25, 48 and 96 ng ml$^{-1}$, respectively.

The cytotoxic effects of $N$-arylidene [\(\text{OC}_6\text{H}_4\text{C}(R'') = \text{NCHR'}\text{COO}]\text{SnBu}_2$\textsuperscript{124} and ethylene diphosphonate (EtO)$_2$P(O)CH$_2$CH$_2$P(O)(OEt)$_2$•Et$_2$SnCl$_2$\textsuperscript{125} complexes have
been studied against the National Cancer Institute panel of 60 cell lines. These complexes exhibit their highest cytotoxic effect on the NCI-522 (non-small cell lung cancer) cell line. In general, a low to moderate cellular response was observed for all these compounds.

The cyclic derivative of salicylhydroxamide 18 is more active in vitro than cisplatin and 5-fluorouracil against human origin cell lines (MCF-7, EVSA-T, WiDr, IGROV, M19 MEL, A498 and H226), but less active than methotrexate and doxorubicin.

Dibutyl-1,3,2-dioxastannolanes 19–21, including two enantiomeric pairs, were tested in vitro on a variety of human tumor cell lines (HeLa, MM96L, MM418c5, C180-13S). There is no significant difference in cytotoxicity of optical isomers or between compounds 19–22 and dibutyltin dichloride towards HeLa cells (ID$_{50}$ = 0.2–0.5 µM). This lack of difference is consistent with hydrolysis to a common cytotoxic Bu$_2$Sn$^{2+}$ species.

Triphenyltin o-aminophenyl- and 2-pyridylthiolates (2-H$_2$NC$_6$H$_4$SSnPh$_3$ and 2-C$_5$H$_4$NSSnPh$_3$), containing Sn–S bonds, showed high cytotoxicity (ID$_{50}$ = 3–38 ng ml$^{-1}$) on six cell lines (MCF-7, EVSA-T, WiDr, IGROV, M19 MEL and A498) 128.

In the series of [1,2-α]-fused pyrimidin-4-one complexes R$_2$SnCl$_2$$^*$$L^n$ ($R$ = Me, Ph) the most notable activity was demonstrated by the complex with L$^1$ ($R^' = H$, $R'' = CH_2Br$)
against Hep-2, HeLa, RD, BGM cell lines\textsuperscript{129}. The only cell line that was resistant to all complexes was L\textsubscript{20B}. Furthermore, the complex \(\text{Me}_2\text{SnCl}_2\cdot L^3\) (\(R' = \text{MeCOO}\)) showed low cytotoxic activity against the cell lines used (ID\textsubscript{50} > 10 \(\mu\)g ml\textsuperscript{-1}).

In the series of the \(N\)-methyl-2,2\textsuperscript{′}-bisimidazole (MBI) complexes \(R_2\text{SnX}_2\cdot (\text{MBI})\)\textsuperscript{130} (\(R = \text{Me}, \text{Et}, \text{Bu}, \text{Ph}; X = \text{Cl}, \text{Br}\)) the butyl derivatives were the most active against KB (oral epidermoid human carcinoma) cell line. The nature of the halogen bound to the metal atom does not seem to have any influence on activity, except for the butyl complexes, for which the chloride is much more active (ID\textsubscript{50} = 0.023 \(\mu\)g ml\textsuperscript{-1}), than bromide (ID\textsubscript{50} = 0.170 \(\mu\)g ml\textsuperscript{-1}).

The antitumor activity of some organotin carboxylates (7–15) and dibutyltin bisphenylacetate (BnCOO)\textsubscript{2}SnBu\textsubscript{2} (23) was screened on tumor-bearing mice\textsuperscript{101,130,131}. At their maximum tolerated doses, compounds 7–9, 11, 13 and 15 were inactive \textit{in vivo} against colon 26 tumors in Balb/c mice, and carboxylates 10 and 12 showed slight \textit{in vivo} antitumor activity. Compounds 14 and 23 have clear antitumor effect after single dose administration (ratio of the tumor size for the treated mice to that of control mice is 0.51 and 0.42, respectively). The pyridine derivative 16 \([R=R'=9-(m-C_2B_{10}H_{11})]\)\textsuperscript{128} is active \textit{in vivo} against L1210 murine leukemia at doses of 7 and 10 mg kg\textsuperscript{-1}, but toxic at 14 mg kg\textsuperscript{-1}. Noteworthy is that one mouse was cured at a dose of 7 mg kg\textsuperscript{-1}.

The cytotoxic effect and antitumor activity of triethyltin lupinyl sulfide hydrochloride have been investigated\textsuperscript{133}. Different patterns of antiproliferative effects have been observed in a panel of human cell lines \textit{in vitro}. Acute toxicity at doses of 21 and 17.5 mg kg\textsuperscript{-1} in mice was reported and disappeared progressively at lower concentrations. On this base, the doses of 3.5, 7 and 14 mg kg\textsuperscript{-1} were selected to assess the antitumor activity \textit{in vivo} against the P388 leukemic cells xenografted in mice. This compound was able to induce a dose-dependent significant reduction of tumor volume, up to 46\%. 

\begin{align*}
\text{L}^1 &= \begin{array}{c}
\text{N}
\end{array} \text{O} \\
\text{L}^2 &= \begin{array}{c}
\text{N}
\end{array} \text{O} \\
\text{L}^3 &= \begin{array}{c}
\text{N}
\end{array} \text{O}
\end{align*}

\(R' = \text{H, Me}; R'' = \text{CH}_2\text{Br, MeCOO}\)
Data concerning the abundance of lead in nature, its production and industrial application, toxicology of organolead derivatives, their bioaccumulation, health effects and safety of organolead derivatives were summarized and analyzed in an excellent review2.

The mutagenic activity of triethyllead acetate was determined by measuring the induction of chromosomal aberrations in Chinese hamster ovary cells. The results indicate that Et₃PbOAc is very cytotoxic and a potent clastogen. Test concentrations of Et₃PbOAc for chromosomal aberrations were approximately 10 µM in the absence of, and 80 µM in the presence of, metabolic activation. The maximal response was greater with metabolic activation than without; however, a much higher dose was required to elicit a significant response134.

Effects of triethyllead acetate on the cholinergic system in the brain of the rats were investigated in vitro. At concentrations below 0.1 µM it inhibited the depolarized release of acetylcholine (ACh) from slices of cortex and the synthesis of ACh, while the non-depolarized release of ACh was potent in a dose-dependent manner135.

Low levels of ethyllead compounds (0.1 nM–5 µM) interfere with the normal development of cultured E18 rat hippocampal neurons, probably through increases in intracellular free calcium ion concentration135. Survival of neurons was significantly reduced at 5 µM and the overall production of neurites was reduced at concentrations ≥2 µM. The length of axons and the number of axons and dendrites were reduced at ≥1 µM. Neurite branching was inhibited at 10 nM for dendrites and 1000 nM for axons. Increases in intracellular calcium were observed during a 3.75 h exposure of newly plated neurons at a concentration of 5 µM136.

The neuropathologic effects of low level triethyllead acetate exposure (0.05, 0.10, 0.20, 0.50 and 1.00 mg kg⁻¹ for 91 days, 5 days per week by oral) were studied in male Sprague–Dawley weaning rats. Sections of the central, peripheral and autonomic nervous systems were examined and lesions scored. No lesions were noted in the brain, but randomly distributed light microscopic changes of spinal cord Wallerian degradation were noted to increase in a dose responsive manner. Ultrastructural examination of selected sections of the lumbosacral nerves revealed lesions characterized by reduced neurofilaments and neurotubules, and irregular lamellated axoplasmic dense bodies in all animals receiving lead137. Exposure of neonatal Fischer-344 rats to triethylleads causes permanent hippocampal damage138. Male Fischer-344 rats (>42 days old) were exposed to 8 or 16 ppm of trimethyllead derivatives in drinking water for up to 14 days. The hippocampus was the region very sensitive to organoleads. Control rats had the expected brain regional pattern of glial fibrillary acidic protein (GFAP) concentration with the highest in the hippocampus and cerebellum and lowest in the cerebral cortex. There was significant time-response of GFAP concentration in the hippocampus of rats exposed to 8 ppm dose with decrease on day 7 and increase on day 14139. Comparative observations on organic and inorganic Pb²⁺ neurotoxicity showed a preferential involvement of the hippocampus in both cases, and the clinical syndromes of irritability, hyperactivity, aggression and seizures are common features of disturbed hippocampal function140.

The effects of triethyllead acetate or tetraethyllead, as well as an inorganic lead nitrate Pb(NO₃)₂ on human erythrocytic δ-aminolevulinic acid dehydratase activity was investigated. There was no discernible inhibitory effect of tetraethyllead at any concentration, with and without pre-incubation. Lead nitrate is a much more potent inhibitor of δ-aminolevulinic acid dehydratase activity (0.77 µM) than triethyllead acetate (130.37 µM)141.

Ethyllead compounds in concentrations of 1−10 µM inhibit the proliferation of normal human lymphocytes through decreased expression of the p55 polypeptide chain (Tac
molecule) of the interleukin-2 receptor. The effect of organolead derivatives was also associated with a dose-dependent decrease of the Na\(^{+}\)-K\(^{+}\)-ATPase activity of normal lymphocytes\(^{142}\).

Alkyl leads are environmentally prevalent compounds, which have been shown to produce a variety of neurological and behavioral deficits in both laboratory animals and humans. Heavy abuse of leaded gasoline resulted in an encephalopathy, cerebellar and corticospinal symptoms, dementia, mental status alterations and persistent organic psychosis. However, much of this is due to the hydrocarbons of gasoline, while the tetraethyl lead contributes to the altered mental status and is responsible for the persistent psychosis\(^{143}\).

The influence of organolead compounds on human health was evaluated in clinical tests of organolead manufacturing workers\(^{144−152}\). In March 1990, 222 workers and 62 control group members were administered neurobehavioral tests\(^{144,145}\) that included simple visual reaction time. It was measured over 44 trials; interstimulus intervals ranged from 1 to 10 s in a randomly generated sequence that was identical for all persons. Mean reaction times for both lead-exposed and non-exposed subjects were the longest for interstimulus intervals of 1 and 2 seconds. Mean reaction times in response to moderate (4–6 s) and long (7–10 s) interstimulus intervals were mainly associated with lead exposure and a stronger relationship between reaction time and lead exposure was found. The relations between recent and cumulative exposure to organic and inorganic lead and blood lead level were also examined\(^{146}\). Recent exposure to organic and combined (organic and inorganic) lead was significantly and positively related to blood lead levels. Age and cigarette smoking were positively associated with blood lead levels, whereas alcohol use was associated with lower levels.

To evaluate the connections between tibial lead, dimercaptosuccinic acid (DMSA), chelatable lead and neurobehavioral functions, the clinic investigation of 543 former organolead manufacturing workers (mean age 57.6 years) with an average of 17.8 years since last exposure to lead compounds was undertaken\(^{147,148}\). The average tibial lead concentration in bone mineral was 14.4 µg g\(^{-1}\). DMSA chelatable lead ranged from 1.2 to 136 µg g\(^{-1}\) with a mean value of 19.3 µg g\(^{-1}\). In a multiple linear regression model of tibial lead, age, duration of exposure, current and past cigarette smoking, and diabetes were independent positive predictors, whereas height and exercise inducing sweating were both negative predictors\(^{148}\). Peak tibial lead level was a significant negative predictor of performance on the Wechsler Adult Intelligence Scale-Revised vocabulary subtest, serial digit learning test, Rey Auditory-Verbal Learning Test (immediate recall and recognition), Trail Making Test B, finger tapping (dominant hand, non-dominant hand), Purdue pegboard (dominant hand, non-dominant, both hands, and assembly) and Stroop Test. Moreover, with one exception, average neurobehavioral test scores were poorer at higher peak tibial lead levels\(^{147}\).

III. REFERENCES

24. Biological activity of organotin and organolead compounds


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