Tin Chemistry
Fundamentals, Frontiers, and Applications

Edited by

ALWYN G. DAVIES

University College London, UK

MARCEL GIELEN

Free University of Brussels VUB, Belgium

KEITH H. PANNELL

University of Texas at El Paso, USA

EDWARD R. T. TIEKINK

University of Texas at San Antonio, USA

Tin Chemistry

Tin Chemistry

Fundamentals, Frontiers, and Applications

Edited by

ALWYN G. DAVIES

University College London, UK

MARCEL GIELEN

Free University of Brussels VUB, Belgium

KEITH H. PANNELL

University of Texas at El Paso, USA

EDWARD R. T. TIEKINK

University of Texas at San Antonio, USA

WILEY

A John Wiley and Sons, Ltd, Publication

Dedicated to the memory of Des Cunningham, 1942–2006

Contents

Preface

The chemistry of tin has now grown to the stage where a dedicated monograph can do little more than trace the structure of the subject and provide a guide to the literature. We felt that authoritative, in-depth, reviews were now needed of those branches, both pure and applied, where developments have been most pronounced, and the present volume is the result. Each chapter, by specialists in the field, deals with one important aspect of tin chemistry, and gives a detailed account of its present standing.

Both inorganic and organic aspects are covered, though progress has been most extensive in organotin chemistry which is living up to its reputation of being studied by more techniques, and finding more applications, than the organic derivatives of any other metal.

Advances in techniques include sophisticated NMR methods, both in solution and the solid-state, and computational methods, and these, coupled with X-ray diffraction and other established methods, have been applied to the study of a wide variety of structures. Topics covered in the book include Sn(II) clusters, tin Zintl ions, Sn(II) heterobimetallic compounds, R_3Sn^+ cations, stannylenes (R_2Sn:), stannenes ($R_2Sn{=}SnR_2$ and $R_2Sn{=}CR_2$), stannynes ($RSn{\equiv}SnR$), organotin oxide, carboxylate and sulfonate clusters, dendrimers and macrocycles, organotin polymers, Sn-π interactions, unusual bondings and structures, and compounds with non-linear optical properties.

Non-metallurgical uses of tin reflect the biological activity of organotin compounds, and the non-toxicity of inorganic tin. Inorganic tin compounds are used in flame-retardants and smoke suppressants, and SnO_2 for coating glass (though usually deposited from organotin compounds). The principal use for organotin compounds is still as a stabiliser for PVC, and a small but important application is as ionophores in sensors, and as precursors for hybrid organic-inorganic nanometric materials. The use as marine anti-foulants is being phased out because of its effect on other marine life, but organotin compounds are showing promise as larvicides, insecticides, and fungicides, and, particularly, in cancer therapy.

Organotin compounds find wide applications in organic synthesis, and their dominance in some homolytic mechanisms has been referred to as the tyranny of tin. In particular, tin hydrides still hold the field in ring-closing cyclisations. The established use of organotin compounds as reactants has been developed in carbon-carbon crosslinking catalysed by transition metals, in carbohydrate synthesis, in the conjugative electrophilic substitution of allylstannanes, and in the of the reaction of allyltin compounds and organotin phenoxides catalysed by lithium perchlorate. They are used as catalysts in a number of reactions,

particularly esterification and transesterification. Relatively new applications are in carbostannylation of multiple bonds, and in the anionic capture of the intermediates from palladium-catalysed ring-closing reactions.

At the same time, there can be concerns about the disposal of organotin residues, and of traces of toxic organotin residues remaining in the products, and fluorous, polymer-bound, and solid-supported organotin compounds are being increasingly used to avoid the problem.

We hope that the chapters of this book will enable readers to keep abreast of these rapidly developing fields.

A. G. Davies, M. Gielen, K. H. Pannell, E. R. T. Tiekink

List of Contributors

Esen Arkis   Izmir Department Institute of Technology, Chemical Engineering Department, Turkey

Hiram I. Beltrán   Departamento de Ciencias Naturales, División de Ciencias Naturales e Ingeniería, Universidad Autónoma Metropolitana – Cuajimalpa, Mexico

Heloisa Beraldo   Inorganic Medicinal Chemistry Laboratory, Departamento de Química – Universidade Federal de Minas Gerais, Brazil

Monique Biesemans   High Resolution NMR Centre (HNMR), Vrije Universiteit Brussels, Belgium

Werner J. Blank   89 Spectacle Lane, Wilton, CT, USA

Russell J. Boyd   Department of Chemistry, Dalhousie University, Halifax, Canada

Raymundo Cea-Olivares   Instituto de Química, Universidad Nacional Autónoma de Mexico, Mexico

Vadapalli Chandrasekhar   Department of Chemistry, Indian Institute of Technology Kanpur, India

Nikos Chaniotakis   Laboratory of Analytical Chemistry, Department of Chemistry, University of Crete, Iraklion, Greece

Tristram Chivers   Department of Chemistry, University of Calgary, Canada

Jean-Mathieu Chrétien   Laboratoire de Synthèse Organique (LSO), UFR des Sciences et des Techniques, Université de Nantes, France

Paul A. Cusack   Tin Technology, St. Albans, UK

Alwyn G Davies   Chemistry Department, University College London, UK

Geraldo M. de Lima   Tin Chemistry Laboratory, Departamento de Química – Universidade Federal de Minas Gerais, Minas Gerais, Brazil

Antonio M. Echavarren   Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain

Dana J. Eisler   Department of Chemistry, University of Calgary, Canada

George Eng   Department of Chemistry and Physics, University of the District of Columbia, Washington, DC, USA

Pablo Espinet   IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, Spain

Norberto Farfán   Departamento de Química, Facultad de Química, Universidad Nacional Autónoma de Mexico, Mexico

Miroslav Genov   IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, Spain

Kandasamy Gopal   Department of Chemistry, Indian Institute of Technology Kanpur, India

Ron Grigg   Molecular Innovation, Diversity and Automated Synthesis (MIDAS) Centre, School of Chemistry, Leeds University, UK

T. Bruce Grindley   Department of Chemistry, Dalhousie University, Halifax, Canada

Imtiaz-ud-Din   Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan

F. Ekkehardt Hahn   Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Germany

Ionel Haiduc   Department of Chemistry, Babes-Bolyai University, Cluj-Napoca, Romania

Edward T. Hessell   King Industries Inc. Norwalk, CT, USA

Herbert Höpfl   Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Mexico

Vojtech Jancik   Instituto de Química, Universidad Nacional Autónoma de Mexico, Mexico

Bernard Jousseaume   Groupe Matériaux, Université Bordeaux 1, Talence, France

Klaus Jurkschat   Lehrstuhl für Anorganische Chemie der Universität, Dortmund, Germany

Jeremy D. Kilburn   School of Chemistry, University of Southampton, UK

Cezary M. Kinart   Department of Chemistry, University of Łodz, Poland

Wojciech J. Kinart   Department of Organic Chemistry, University of Łodz, Poland

Pascal G. Lacroix   Laboratoire de Chimie de Coordination du CNRS, Toulouse, France

Joseph B. Lambert   Department of Chemistry, Northwestern University, IL, USA

Erwan Le Grognec   Laboratoire de Synthèse Organique (LSO), UFR des Sciences et des Techniques, Université de Nantes, France

Fabio Marchetti   Dipartimento di Scienze Chimiche, University of Camerino, Italy

M. Mazhar   Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan

Yoshiyuki Mizuhata   Institute for Chemical Research, Kyoto University, Japan

Mónica Moya-Cabrera   Instituto de Química, Universidad Nacional Autónoma de Mexico, Mexico

Partha P. Nag   Department of Chemistry, Indiana University, Bloomington, IN, USA

Mala Nath   Department of Chemistry, Indian Institute of Technology Roorkee, India

Junzo Otera   Department of Applied Chemistry, Okayama University of Science, Japan

Keith H. Pannell   Department of Chemistry, University of Texas at El Paso, TX, USA

Sergio Pascual   Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain

Claudio Pettinari   Dipartimento di Scienze Chimiche, University of Camerino, Italy

Vanja Pinoie   High Resolution NMR Centre (HNMR), Vrije Universiteit Brussels, Belgium

Kevin Poelmans   High Resolution NMR Centre (HNMR), Vrije Universiteit Brussels, Belgium

Jean-Paul Quintard   Laboratoire de Synthèse Organique (LSO), UFR des Sciences et des Techniques, Université de Nantes, France

François RiBOT   Chimie de la Matière Condensée de Paris, Université Pierre et Marie Curie, Paris

Rosa Santillan   Departamento de Química, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Mexico.

Slavi C. Sevov   Department of Chemistry and Biochemistry, University of Notre Dame, IN, USA

Hemant K. Sharma   Department of Chemistry, University of Texas at El Paso, TX, USA

Eiji Shirakawa   Department of Chemistry, Graduate School of Science, Kyoto University, Japan

Puja Singh   Department of Chemistry, Indian Institute of Technology Kanpur, India

Xueqing Song   Department of Chemistry and Physics, University of the District of Columbia, Washington, DC, USA

V. Sridrahan   Molecular Innovation, Diversity and Automated Synthesis (MIDAS) Centre, School of Chemistry, Leeds University, UK

Edward R.T. Tiekink   Department of Chemistry, The University of Texas at San Antonio, TX, USA

Norihiro Tokitoh   Institute for Chemical Research, Kyoto University, Japan

Thierry Toupance   Institut des Sciences Moléculaires, Groupe Matériaux, University of Bordeaux 1, Institut des Sciences Moléculaires, France

Margaret M. Whalen   Department of Chemistry, Tennessee State University, Nashville, TN, USA

Sarah R. Whittleton   Department of Chemistry, Dalhousie University, Halifax, Canada

Rudolph Willem   High Resolution NMR Centre (HNMR), Vrije Universiteit Brussels, Belgium

David R. Williams   Department of Chemistry, Indiana University, Bloomington, IN, USA

Bernd Wrackmeyer   Anorganische Chemie II, Universität Bayreuth, Germany

David Young   Eskitis Institute of Cell and Molecular Therapies, Griffith University, Queensland, Australia

Alexander V. Zabula   Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Germany

Françoise Zammattio   Laboratoire de Synthèse Organique (LSO), UFR des Sciences et des Techniques, Université de Nantes, France

Julio Zukerman-Schpector   Department of Chemistry, Universidade Federal de Sáo Carlos, Brazil

1

Introduction and Overview

1.1 Introduction

Alwyn G. Davies
Chemistry Department, University College London, UK

1.1.1 History, Occurrence, Production, and Applications

Tin has been known as a metal since time immemorial, and the discovery, in about 3500 BC, that it formed a strong, hard alloy with copper, started the Bronze Age, which lasted until about 1200 BC.

The abundance of tin in the Earth's surface is about 2 ppm, significantly less than that of zinc (94 ppm), copper (63 ppm), or lead (12 ppm). The most important ore is cassiterite, SnO_2, which occurs as placer (alluvial) deposits. The breakdown of the current production of tin by area is shown in Figure 1.1.1. About 75% of the world's production comes from China and South East Asia, and about 18% from South America, but the annual figures are sensitive to political, social, and economic factors.[1]

The cassiterite ore is obtained by dredging, open-cast mining, or gravel-washing, in which the ore is washed out of the deposit with high-pressure jets of water. The cassiterite has a density 2.5 times that of sand, and the ore is concentrated by gravity. It is roasted to remove arsenic and sulfur, and to convert metal sulfides into oxides, then it is reduced by smelting with coal or fuel oil in a reverberatory, rotary, or electric furnace (Equation 1.1.1).

$$SnO_2 + 2CO \longrightarrow Sn + 2CO_2 \qquad (1.1.1)$$

An increasing amount of tin is also being recovered, by melting, from food and drink cans and industrial scrap.

In 2005 and 2006, the total annual production of refined tin was about 350 000 tonnes. At the time of writing (April, 2008), demand exceeds supply, and the price of high-grade tin has just hit a record high of US$22 150/tonne.

The applications of tin are shown in the pie chart in Figure 1.1.2.

About half the production of tin is used in solders, and this is increasing with the increasing production of telecommunication and electronic equipment, and the need to eliminate lead, because of its toxicity.

China	37.2%
Indonesia	23.2%
Malaysia	6.5%
Thailand	7.9%
Bolivia	4.0%
Brazil	2.5%
Peru	11.7%
Belgium	2.3%
Russia	1.1%
Other	3.7%
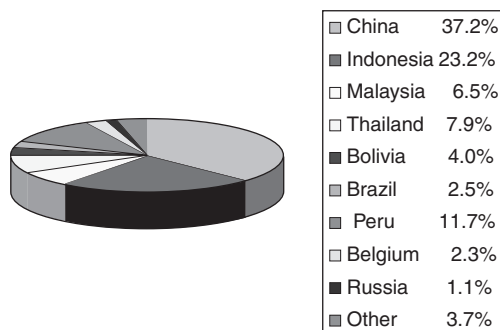
Figure 1.1.1   *World production of tin*

Conventional tin/lead solders have the approximate composition Sn63/Pb37 by weight, corresponding to the eutectic mixture, which is close to Sn_3Pb, with a melting point of 183 °C. Lead-free solders are often composed of tin with 3–4% silver and 0.5–1% copper, and have a melting point of 215–220 °C.

Some 20% of the production of tin goes into tinplate, which is produced by hot-dipping or electroplating; its use in canning has reduced because of the increasing competition from aluminium cans, and protective polymer layers for steel cans.

As an alloy with lead, tin has been used also in pewters, for making organ pipes, and, alloyed with copper, for making bronze. Babbitt metal, used in bearings, commonly contains about 90% of tin, together with a small amount of harder metals such as copper or antimony.

About 14% of the production of tin goes into tin chemicals; a further breakdown is not possible because of the commercial sensitivity of the information. Tin tetrachloride and butyltin trichloride are used for coating glass with SnO_2 (see Chapter 3.1), and float glass is produced on a molten pool of tin.

The first organotin compound, diethyltin dichloride, was prepared by Frankland in 1849 by heating ethyl chloride with metallic tin, and this is often taken to mark the beginning of organometallic chemistry. The first application of organotin compounds came in about 1943, when they were used first for the stabilization of PVC against heat during processing, and a variety of industrial and biological applications were subsequently developed, although, in recent years these have been somewhat curtailed by concerns about toxicity.

Solders	49.7%
Tinplate	18.3%
Chemicals	14.1%
Brass and bronze	5.6%
Glass	1.8%
Other	10.4%
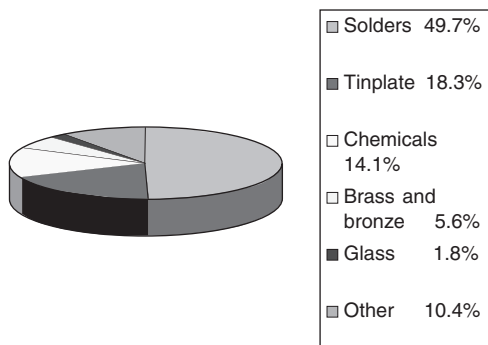
Figure 1.1.2   *Applications of tin*

Table 1.1.1   *Properties of tin*

Property	Value	Property	Value
Atomic number	50	Electronegativity	1.96 (Pauling)
Atomic mass	118.710	Atomic radius	1.45 pm
Melting point	232 °C	Covalent radius	1.41 pm
Boiling point	2625 °C	van der Waals radius	2.17 pm
Density (white tin)	5.769 g cm^{-3}		
Density (grey tin)	7.280 g cm^{-3}		

In the last half century, there has been much more research activity in the organometallic chemistry of tin than in its inorganic chemistry, and this is reflected in the contents of this book.

1.1.2   The Element

Selected properties of the element are shown in Table 1.1.1. It is in Group 14 of the Periodic Table, with the electronic configuration [Kr] $4d^{10} 5s^2 5p^2$; its principal valence state is Sn(IV), though Sn(II) inorganic compounds are common, and many stannous organic compounds, with specially designed structures, have been prepared in recent years. Tin has 10 stable isotopes (Table 1.1.2), which is the largest number for any element, and results in very characteristic mass spectra. The ^{117}Sn and ^{119}Sn isotopes, each with spin $^1/_2$, are used in NMR spectroscopy. The γ-active ^{119m}Sn isotope, which is prepared by the neutron-irradiation of enriched ^{118}Sn, is used in Mössbauer spectroscopy.

Metallic tin exists in two allotropes. White tin, or β-tin, is a silvery-white, electrically conducting, metal, with a distorted cubic structure. Below about 10 °C, it slowly coverts into grey tin, or α-tin, with a 26% increase in volume, which creates excrescences on the surface, called tin pest or plague. α-Tin is a semiconductor with a diamond structure, with $\Delta H_f = 2.51$ kJ mol^{-1} compared with metallic tin.[2]

Table 1.1.2   *Tin isotopes*

Isotope	Mass	Abundance (%)	Spin
112	111.90494	0.95	0
114	113.90296	0.65	0
115	114.90353	0.34	1/2
116	115.90211	14.24	0
117	116.90306	7.57	1/2
118	117.90179	24.01	0
119	118.90339	8.58	1/2
120	119.90213	32.97	0
122	121.90341	4.17	0
124	123.90524	5.98	0

Mass Spectrum
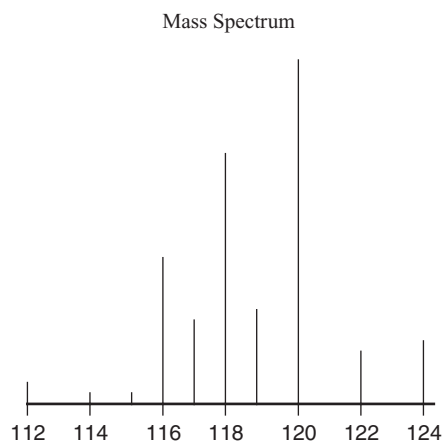
White tin is inert to air at room temperature, but at 200 °C it is oxidized to SnO_2. Samples for microanalysis for C, H, and N, by combustion in oxygen, are usually sealed in tin capsules. The heat of combustion of the tin ($\Delta H_c = -142$ kJ mol^{-1}) raises the temperature from about 1000 °C to 1800 °C, and the SnO_2 which is formed acts as an oxidation catalyst.

Tin shows no reaction with water and dilute acids, but concentrated hydrochloric acid reacts to give $SnCl_2$ and hydrogen, and concentrated sulfuric acid gives $SnSO_4$ and SO_2. In ether, HCl gas reacts to give solvated H_2SnCl_2, which, together with $HSnCl_3$ from HCl and $SnCl_2$, finds some use in organic synthesis. Hot aqueous alkali, MOH, reacts to give $M_2[Sn(OH)_6]$.

If electrons are added into the crystal structure, they lead to the breaking of the Sn–Sn bonds, each atom carrying an unshared electron pair, and ultimately to the formation of isolated anionic clusters with triangular faces (deltahedra), known as Zintl ions (e.g. **1** and **2**; see Chapter 1.6).[3] These compounds are diamagnetic and poor conductors. They can be prepared either by reduction of tin with an alkali metal or electrochemically, and are soluble in polar, basic solvents. For example, $[Na^+]_4 [Sn_9]^{4-}$ can be prepared from the reaction of tin with sodium in ethylenediamine, or in the presence of a crown ether to associate with the sodium cations. The most common structure is a nine-atom cluster **2**.[4]
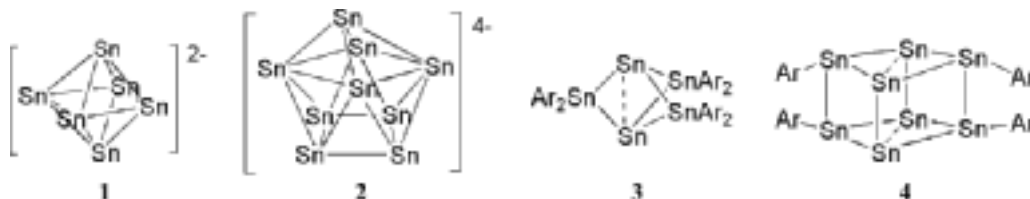
Surprisingly little work appears to have been carried out on the reaction of these cluster anions with organic electrophiles, but electrically neutral organotin clusters can be prepared, usually by the reduction of organotin(II) compounds carrying bulky aryl groups. Examples are Sn_5Ar_6, with a propellane structure (**3**), and Sn_8Ar_4 (**4**) and Sn_8Ar_8, with cubic structures.[5]

1.1.3   Structure and Bonding

Both the Sn(II) and Sn(IV) states are stable. The Sn(II) state uses mainly the 5p orbitals for bonding, leaving the unshared singlet pair in the largely 5s state, with a little p character, and compounds SnX_2 (**5**, the stannylenes) have an XSnX angle of about 90–100°. These compounds are most stable when there are strongly electron-attracting ligands, which make loss of the remaining electron pair more difficult (e.g. $:SnF_2$, $:SnCl_2$), or when the ligands X are very bulky, and sterically protect the tin against further ligation (e.g. $:Sn[N(SiMe_3)_2]_2$). Otherwise, oxidation readily occurs to the Sn(IV) state, where the tin is sp^3 hybridized, and the SnX_4 (**8**, stannane) molecule has tetrahedral symmetry.

However, both the stannylenes and the stannanes have vacant 5d orbitals, which can accept one or more further ligands, The stannylenes readily form the pyramidal sp^3 complexes $:SnX_3$ (**6**), and the trigonal bipyramidal sp^{3}d complexes $:SnX_4$ (**7**), and the stannanes form the trigonal bipyridamidal sp^{3}d complexes SnX_5 (**9**) or octahedral sp^{3}d^2 complexes SnX_6 (**10**). All of these may carry charges corresponding to the charge of the new ligands X. These basic structures are often distorted, and higher coordination states are sometimes formed.

Structures of Sn(II) compounds   Structures of Sn(IV) compounds
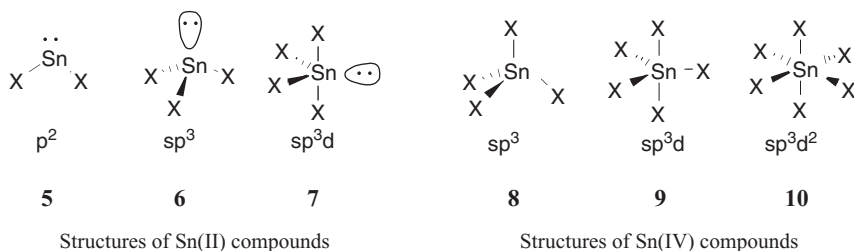
The X groups themselves may act as these further ligands, resulting in intramolecular coordination, or, particularly in condensed phases, intermolecular association, to give oligomers or polymers. A variety of techniques are available for determining these structures [^{119m}Sn Mössbauer spectroscopy, ^{117}Sn or ^{119}Sn NMR spectroscopy in the solid or liquid state (see Chapter 2.1),[6] IR spectroscopy, X-ray diffraction etc.] and structural studies have been a major aspect of inorganic and organic tin chemistry.

For example, in the vapor phase, Sn(II)F$_2$ is a monomer with an FSnF angle of 94° (**11**),[7] whereas, in the solid state, it exists as cyclic tetramers, held together by weaker Sn–F interactions (**12**).[8] Within the ring, the average FSnF angle is 83.7°, and outside the ring it is 82.8°. In the gas-phase, Me$_3$SnCl is a tetrahedral monomer with rSnCl 2.306(3) Å; in solution, the monomer is in equilibrium with oligomers, but in the crystal it is associated into a zig-zag polymer (**13**), with approximately trigonal bipyramidal tin, and rSnCl 2.43 and 3.27 Å.[9]

11   **12**   **13**
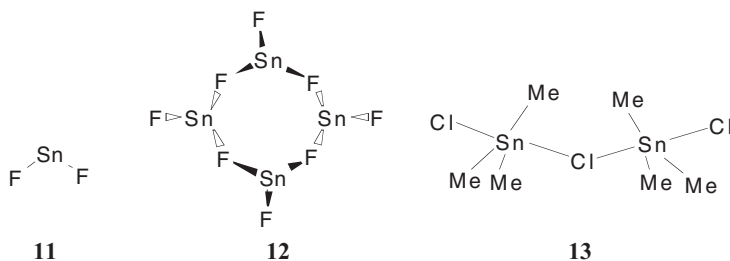
Some values of bond lengths and bond dissociation energies are given in Table 1.1.3, but it must be emphasized that these are only indicative values, which are dependent on the physical state.

1.1.4   Organotin Compounds, R$_n$Sn$_m$

The various known organotin species and their structures, where the tin is bonded to only carbon or tin, and without functional groups, are shown in Table 1.1.4.

Stannane radical cations SnMe$_4^{\bullet+}$ (and SnH$_4^{\bullet+}$) have been generated in frozen Freon matrices by irradiation with γ-rays. The ESR spectra, with the backing of MNDO and PM3 calculations, have been interpreted as implying distortion of the tetrahedral structure of the stannane into a C$_{3v}$ configuration, with an almost planar trigonal base, and one long one-electron SnMe bond. Alkylstannane radical anions can be prepared by γ-irradiation of the stannane in a matrix of Me$_4$Si, and arylstannane radical anions by reduction with an alkali metal. The radical anion, Me$_4$Sn$^{\bullet-}$, appears to have a trigonal bipyramidal structure, with the unpaired electron located in an equatorial, largely sp^2, orbital.

Table 1.1.3   *SnX bond lengths, dissociation energies, and stretching frequencies*

Bond	r/pm	BDE/ kJ mol^{-1}	ν/cm^{-1}
Me$_3$Sn—H	171	322 ±17	1846
Me$_3$Sn—Me	218	295 ±17	526, 506
Me$_3$Sn—Et	220	281	—
Me$_3$Sn—CH=CH$_2$	212^a	340	—
Me$_3$Sn—Ph	214^b	358	241
Me$_3$Sn—SnMe$_3$	277.6	291	192
R$_2$Sn=SnAr$_2$	ca. 280	90^c	—
RSn≡SnR	267–307	—	—
Me$_3$SnCl	235.1	425 ±7	331
Me$_3$SnBr	249	381 ±17	234
Me$_3$SnI	272	320 ±17	189
Me$_3$SnOH	196	488 ±17	3620 (OH)

^{a}For (CH=CH$_2$)$_4$Sn. ^{b}For Ph$_4$Sn. ^{c}For R = (Me$_3$Si)$_2$CH

Hypervalent pentaorganostannate anions, such as Me$_5$Sn$^-$, are formed when an organolithium compound is added to a tetraorganostannane in the presence of a ligand to solvate the lithium cation. The ^{119}Sn NMR signal occurs about 300 ppm upfield from that of the parent stannane. The six isomeric Ph$_n$Me$_{5-n}$Sn$^-$ anions can be observed in equilibrium, and the NMR spectra imply that the anions have a trigonal bipyramidal structure, with the phenyl groups in the apical positions.[10] These anions are formed particularly readily from the stannacyclopentanes and stannacyclopentadienes, perhaps because ring strain is relieved by rehybridization of the tin.

The UV spectra of the oligostannanes, (R$_2$Sn)$_n$, show a strong absorption maximum, with a red shift with increasing chain length. Conjugation between the σ_{SnSn} bonds produces a series of molecular orbitals analogous to the π-orbitals of a conjugated polyene. The bonding orbitals have no nodes at the midpoints of bonds, and an increasing number of nodes at the tin atoms; the antibonding orbitals have nodes at the midpoints of bonds, and again an increasing number of nodes at tin. The HOMO has a node at each tin atom, as shown in Table 1.1.4. A metal-like electronic band is formed, with the implication of useful electronic and optical properties (see Chapter 3.8).[11]

The three-coordinate anion Ph$_3$Sn$^-$ is pyramidal, with an average CSnC angle of 96.9°, and the electron pair in a predominantly sp^3 orbital.[12] The hindered SnSi-bonded anion, (Bu$_2^t$MeSi)$_3$Sn$^-$, is less pyramidal, with average SiSnSi angles of 111.6°, presumably because of the increased steric hindrance.[13]

Prolonged attempts to characterize free organotin cations culminated in 2003, in the isolation of the tris(2,4,6-triisopropylphenyl)stannyl cation by the reaction shown in Equation (1.2) (see Chapter 2.7).[14]

$$\text{Ar}_3\text{Sn}\diagdown\diagup + E^+ [B(C_6F_5)_4]^- \longrightarrow Ar_3Sn^+ [B(C_6F_5)_4]^- + \diagup\diagdown E$$
$$E^+ = Et_3Si(C_6H_6)^+ \text{ or } Et_3SiCH_2CPh_2^+$$

$$(1.1.2)$$
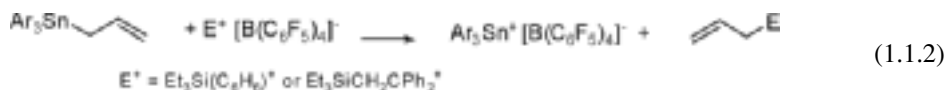
The cation is planar about the tin, with the aryl rings twisted out of the plane, propeller-fashion, by an average of 61.1°; In the NMR spectrum, the value of δSn is 714. The SiSn-bonded cation (Bu$_2^t$MeSi)$_3$Sn$^+$ is similarly planar, and shows δSn at 2653 ppm.[15]