Alwyn G. Davies

Organotin Chemistry

Second, Completely Revised
and Updated Edition

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Organotin Chemistry

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Organotin Chemistry

Second, Completely Revised
and Updated Edition

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The cover picture of a double-ladder tetraorganodistannoxane and its solid state ^{119}Sn NMR spectrum was kindly provided by Jens Beckmann and Dainis Dakternieks of Deakin University.

Preface

Organotin compounds have been claimed to have been studied by more techniques, and to have found more applications, than the organic derivatives of any other metal. This has resulted in an extensive literature that continues to grow at an ever-increasing rate, and provides the justification for this second edition of *Organotin Chemistry*.

I have again tried to provide an analysis of and guide to that literature. Some chapters have simply been revised and brought up to date, but most have been completely rewritten, and new sections have been added. Publications are covered up to the beginning of 2003.

This account is supplemented by the literature database on the accompanying CD, which I hope readers will use to find their way around the organotin literature and to counteract the severe compression and selection that is necessary in a book of this size. Further details are given below.

I am very grateful to Peter Smith (UCL) and Fred Armitage (KCL) who read all of the text, and to Mike Lappert, David Cardin, and Gerry Lawless (University of Sussex), Dainis Dakternieks, Andrew Duthie, and Jens Beckmann (Deakin University), and Sarah Wilsey (ICL) who read selected chapters. Peter Smith, Fred Armitage, and Sarah Wilsey also helped to check the proofs. They did much to reduce the numbers of errors and omissions, and to improve the text, but I would appreciate any comments from readers on the book or on the database. My thanks are also due to Gudrun Walter (Wiley-VCH) who saw the book through to publication, and to my wife for all help non-chemical.

The Organotin Database

The accompanying CD carries a database of more than 5,500 references on which this book is based, but only a fraction of which appear in the text. It is in the form of an EndNote® library (*2Edtinlib.enl*) and of a tagged text file in Refer format (*2Edtinlib.txt*).

Each reference carries details of the author, title, and journal, and also keywords, usually a brief abstract, and always a note of the relevant section or sections in the book. For example, references to papers on compounds containing a tin-silicon bond can be retrieved by searching for the keyword *SnSi* or the section number 19.5.0.0. Further details are given on the files *readme.txt* and *keywords.txt* on the CD.

The text file can be read on any word-processor and searched in the usual way, and it can also be imported into other reference-managing programs (Refer, BibIX, ProCite, Reference Manager, etc). The EndNote library provides more flexibility than the textfile: the individual fields (author, title, abstract, keywords, notes etc.) can be searched and edited, and the program also automatically compiles the bibliography of a paper. A demonstration program can be downloaded from *www.endnote.co.uk*.

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Contents

1   Introduction

1.1   History

The first organotin compound was prepared over 150 years ago. In 1849, in a paper devoted largely to the reaction which occurred when ethyl iodide and zinc were heated together in a sealed tube, Frankland says:[1] "In conclusion, I will describe, very briefly, the behaviour of iodide of ethyl in contact with several other metals, at elevated temperatures ... Tin also effected the decomposition of iodide of ethyl at about the same temperature (150 °C to 200 °C); the iodide became gradually replaced by a yellowish oily fluid, which solidified to a crystalline mass on cooling: no gas was evolved either on opening the tube or subsequently treating the residue with water ... It would be interesting to ascertain what combination the radical ethyl enters in the last ... decomposition". This paper is often held to mark the first systematic study in organometallic chemistry.[2, 3]

$$2\,EtI \;+\; Sn \;\longrightarrow\; Et_2SnI_2 \tag{1-1}$$

Frankland subsequently showed that the crystals were diethyltin diiodide (equation 1-1).[4–6] In independent work,[7] Löwig established that ethyl iodide reacted with a tin/sodium alloy to give what is now recognised to be oligomeric diethyltin, which reacted with air to give diethyltin oxide, and with halogens to give diethyltin dihalides (though through using incorrect atomic weights, the compositions that he ascribed to these compounds are wrong).

As an alternative to this so-called direct method, an indirect route was devised by Buckton in 1859,[8] who obtained tetraethyltin by treating tin tetrachloride with Frankland's diethylzinc.

$$2EtI \;+\; 2Zn \;\longrightarrow\; 2EtZnI \;\longrightarrow\; Et_2Zn \;+\; ZnI_2 \tag{1-2}$$

$$2Et_2Zn \;+\; SnCl_4 \;\longrightarrow\; Et_4Sn \;+\; 2ZnCl_2 \tag{1-3}$$
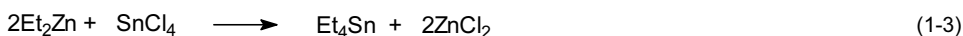
This direct route was developed by Letts and Collie,[9] who were attempting to prepare diethylzinc by reaction 1–2, and instead isolated tetraethyltin which was formed from tin which was present as an impurity in the zinc. They then showed that tetraethyltin could be prepared by heating ethyl iodide with a mixture of zinc and tin powder.

$$EtI \;+\; Zn/Sn \;\longrightarrow\; Et_4Sn \;+\; ZnI_2 \tag{1-4}$$

The indirect route was improved by Frankland who showed that the tin(IV) tetrachloride could be replaced by tin(II) dichloride which is easier to handle and reacts in a more controllable fashion.

$$Et_2Zn \;+\; SnCl_2 \;\longrightarrow\; Et_4Sn \;+\; ZnCl_2 \tag{1-5}$$
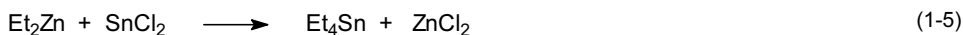
Up to 1900, some 37 papers were published on organotin compounds, making use of these two basic (direct and indirect) reactions.

In 1900, Grignard published his synthesis of organomagnesium halides in ether solution. These reagents were much less sensitive to air than Frankland's solvent-free organozinc compounds, and they rapidly replaced and extended the scope of the zinc reagents as a source of nucleophilic alkyl and aryl groups. In 1903, Pope and Peachey described the preparation of a number of simple and mixed tetraalkylstannanes, and of tetraphenyltin, from Grignard reagents and tin tetrachloride or alkyltin halides,[10] and reactions of this type soon became the standard route to alkyl- and aryl-tin compounds.

This early work is summarised in Krause and von Grosse's *Organometallische Chemie* which was published first in 1937,[11] and which described examples of tetraalkyl- and tetraaryl-stannanes, and of the organotin halides, hydrides, carboxylates, hydroxides, oxides, alkoxides, phenoxides, $R_2Sn(II)$ compounds (incorrectly), distannanes (R_3SnSnR_3), and oligostannanes ($R_2Sn)_n$.

Tin played a full part in the great increase of activity in organometallic chemistry which began in about 1949, and this was stimulated by the discovery of a variety of applications. Structural studies have always been prominent in organotin chemistry, and particularly the structural changes which occur between the solution and solid states. Mössbauer spectroscopy was extensively used during the 1960s and 1970s for investigating structures in the solid state, but it has now largely given place to X-ray crystallography and high resolution solid state tin NMR spectroscopy.

In 1962, Kuivila showed that the reaction of trialkyltin hydrides with alkyl halides (hydrostannolysis) (equation 1-6) was a radical chain reaction involving short-lived trialkyltin radicals, $R_3Sn\bullet$,[12] and in 1964, Neumann showed that the reaction with non-polar alkenes and alkynes (hydrostannation) (equation 1-7) followed a similar mechanism,[13, 14] and these reactions now provide the basis of a number of important organic synthetic methods.

$$R_3SnH + R'X \longrightarrow R_3SnX + R'H \tag{1-6}$$

$$R_3SnH + \; \underset{\diagup \quad \diagdown}{\overset{\diagdown \quad \diagup}{C=C}} \; \longrightarrow \; R_3Sn\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}H \tag{1-7}$$

Salts of the free R_3Sn^- anion and R_3Sn^+ cation have been examined by X-ray crystallography. The formation of short-lived stannylenes, $R_2Sn{:}$, has been established, and by building extreme steric hindrance into the organic groups, long-lived stannylenes have been isolated, and stable compounds with double bonds to tin, e.g. $R_2Sn=CR'_2$, $R_2Sn=SiR'_2$, $R_2Sn=SnR'_2$, and $R_2Sn=NR'$ have been prepared.

The various species of mononuclear organotin compounds with only carbon-bonded ligands, which are known, are summarised in Table 1-1. The best evidence which is available at the present time for the existence of these species, and the section where they are discussed, are listed in Table 1-1.

It is convenient to denote the number of valence electrons m, and the number of ligands n, by the notation m-Sn-n. For example the radical $R_3Sn^\bullet$ would be a 7-Sn-3 compound.

A major development in recent years has been the increasing use of organotin reagents and intermediates in organic synthesis, exploiting both their homolytic and heterolytic reactivity.[15]

In parallel with these developments, organotin compounds have found a variety of applications in industry, agriculture, and medicine, though in recent years these have been circumscribed by environmental considerations. In industry they are used for the stabilization of poly(vinyl chloride), the catalysis of the formation of the polyurethanes, and the cold vulcanisation of silicone polymers, and also as transesterification catalysts.

Table 1-1   Organotin species R_nSn

Formula	No. of electrons m	No. of ligands n	Evidence	Name	Location
R_4Sn	8	4	X-Ray	stannane	Chaps. 5-10
$R_4Sn^{\bullet+}$	7	4	ESR	stannane radical cation	Section 20.3
$R_4Sn^{\bullet-}$	9	4	ESR	stannane radical anion	Section 20.4
R_5Sn^-	10	5	NMR	hypervalent stannate anion	Sections 5.3.5 and 22.1
$R_2Sn=CR'_2$	8	3	X-Ray	stannene	Section 21.4
R_3Sn^+	6	3	X-Ray	stannylium ion	Section 7.2
$R_3Sn^{\bullet}$	7	3	ESR	stannyl radical	Section 20.1
R_3Sn^-	8	3	X-Ray	stannate anion	Section 19.1
$R_2Sn\text{:}$	6	2	X-Ray	stannylene	Section 21.1 and 21.5

Their biological properties are made use of in antifouling paints on ships (though this is now curtailed by legislation; see Chapter 23), in wood preservatives and as agricultural fungicides and insecticides, and in medicine they are showing promise in cancer therapy and in the treatment of fungal infections.[16]

1.2   Nomenclature

Attempts to reconcile the practices of organic and inorganic chemists in the meeting ground of organometallic chemistry have led to IUPAC sanctioning a number of alternative systems of nomenclature.

(1) Under the extended coordination principle, the names of the attached ligands are given, in alphabetical order, in front of the name of the central metal; anionic ligands are given the -o suffix. Thus Me_2SnCl_2 would be dichlorodimethyltin, and $Me_3SnSnMe_3$ would be hexamethylditin.

(2) More commonly, the organic groups plus the metal are cited as one word, and the anionic component(s) as another. Thus Me_2SnCl_2 is usually called dimethyltin dichloride, and the common $(Bu_3Sn)_2O$ (tributyltin oxide or TBTO) is bis(tributyltin) oxide.

(3) Under the substitutive scheme, monotin compounds can be named by citing replacement of hydrogen in the appropriate tin hydride. Stannane is SnH_4, and Me_2SnCl_2 would be called dichlorodimethylstannane. The compounds $Bu_3SnSnBu_3$ can similarly be called hexabutyldistannane as a derivative of distannane, H_3SnSnH_3, and $(Bu_3Sn)_2O$ is hexabutyl distannoxane.

(4) The organotin group can itself be treated as a substituent, the H_3Sn group being stannyl, and the $H_2Sn=$ group being stannio. This is useful in compounds with more complicated structures, e.g. $Me_3SnCH_2CH_2CO_2H$ is 3-(trimethylstannyl)propanoic acid, and $Et_2Sn(C_6H_4OH\text{-}p)_2$ is 4,4′-diethylstanniodiphenol.

(5) The suffix 'a' can be added to the stem of the substituent (giving stanna) and used to indicate replacement of carbon. This is most useful with cyclic compounds, thus cyclo-$(CH_2)_5SnMe_2$ is 1,1-dimethylstannacyclohexane. Doubly bonded compounds are similarly named as alkenes with one or two of the doubly-bonded atoms replaced by tin: the compound $R_2Sn=CR_2$ is a stannene, and $R_2Sn=SnR_2$ is a distannene.

(6) By analogy with alkyl radicals and carbenes (methylenes), the species $R_3Sn^{\bullet}$ are stannyl radicals, and the species $R_2Sn\text{:}$ are stannylenes or stannyldiyls.

Chemical Abstracts indexing practice is summarised in the 1992 Index Guide, page 199, and is as follows.

(1) Acyclic compounds are named as derivatives of the acyclic hydrocarbon parents (see item 3 above), with an "ane" modification to indicate the presence of a chalcogen, for example H_4Sn, stannane; $H_3Sn(SnH_2)_{11}SnH_3$, tridecastannane; $(H_3SnO)_2SnH_2$, tristannoxane.

(2) Heterocyclic compounds are named as stanna replacement of carbon (see item 5 above).

(3) As substituent prefixes, H_3Sn- is indicated by stannyl, $H_2Sn=$ by stannylene, and $HSn\equiv$ by stannylidyne.

Some illustrative examples are as follows.

Bu_2SnO stannane, dibutyloxo

Bu_2Sn^{2+} stannanediylium, dibutyl

Me_3SnCN stannacarbonitrile, trimethyltin cyanide

$ClSnMe_2OSnMe_2Cl$ distannoxane, 1,3-dichloro-1,1,3,3,-tetramethyl

$Me_3SnCH=CHCH=CHSnMe_3$ stannane, 1,3-butadiene-1,4-diylbis[trimethyl

cyclo-$BrPhSn(CH_2)_6SnBrPh(CH_2)_6$-, 1,8-distannacyclotetradecane, 1,8-dibromo-1,8-diphenyl.

If there is doubt, the correct name can usually be found through the formula index.

1.3   Overview of Synthesis

An overview of the principal groups of organotin compounds and their interconversions is given in Scheme 1-1, which deals mainly with tin(IV) compounds, and Schemes 1-2 and 1-3 which cover compounds related to tin(III) and tin(II) species, respectively. It
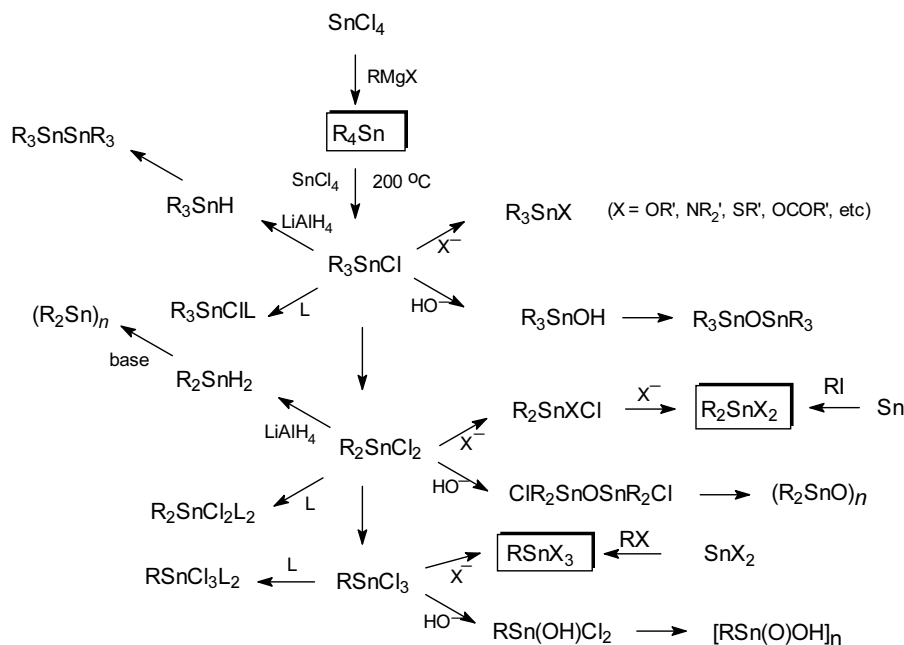
Scheme 1-1   Organotin synthesis based on the Grignard and Kocheshkov reactions.

$$R_3Sn-C-CH \quad\quad R_3Sn\text{ }C=C \text{ }H$$
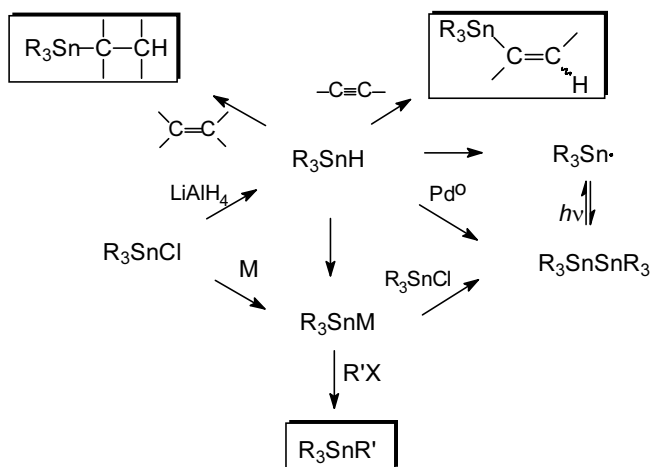
Scheme 1-2 Organotin synthesis based on reactions of SnH and SnM compounds.
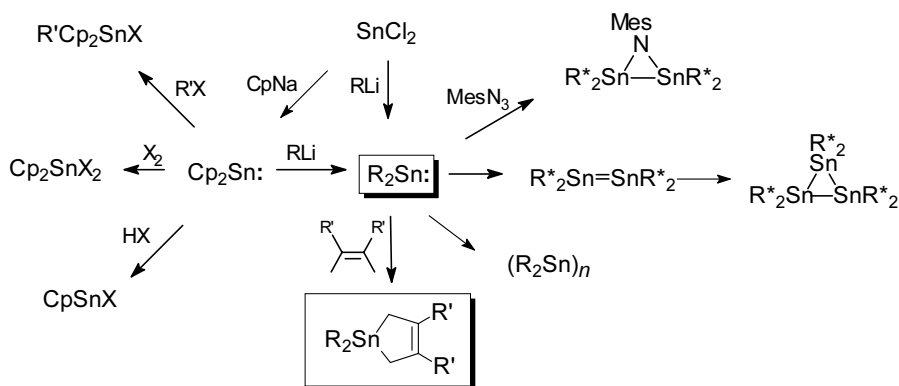
Scheme 1-3 Routes to lower valence state organotin compounds.

should be emphasised that, particularly with respect to Scheme 1-3, some of the reactions shown are as yet known only for specific organotin compounds, and are not necessarily general reactions.

Products which result from the formation of a new tin-carbon bond are boxed in the Schemes. The four principal ways in which this can be accomplished are the reaction of metallic tin or a tin(II) compound with an organic halide, of an organometallic reagent RM (M = lithium, magnesium, or aluminium) with a tin(II) or tin(IV) halide, of a trialkyltin hydride with an alkene or alkyne, or of a triorganotin-lithium reagent (R_3SnLi) with an alkyl halide.

The reaction which is most commonly used is that of a Grignard reagent with tin tetrachloride; complete reaction usually occurs to give the tetraorganotin compound (Scheme 1-1). This is then heated with tin tetrachloride when redistribution of the groups R and Cl occurs to give the organotin chlorides, R_nSnCl_{4-n} (n = 3, 2, or 1) (the Kocheshkov comproportionation). Replacement of the groups Cl with the appropriate nucleophile X (HO^-, RCO_2^-, RO^- etc.) then occurs readily to give the derivatives R_nSnX_{4-n}.

With a metal hydride as the nucleophile, the organotin hydrides, R_nSnH_{4-n} are formed, which, by addition to an alkene or alkyne (hydrostannation), usually by a radical chain mechanism involving stannyl radicals, $R_3Sn^•$, provide the second way of generating the tin-carbon bond (Scheme 1-2).

Under the influence of a base or a platinum catalyst, the triorganotin hydrides and dialkyltin dihydrides eliminate hydrogen to give the distannanes (R_3SnSnR_3) and the oligostannanes ($R_2Sn)_n$, respectively. The halides, hydrides, or distannanes can be converted into the metallic derivatives R_3SnM, where M is an alkali metal, and these act as sources of nucleophilic tin, which, by reaction with alkyl halides, provide a further way of creating a tin-carbon bond.

Recent years have seen important developments in the chemistry of tin(II) compounds and compounds with multiple bonds to tin (Scheme 1-3). The cyclopentadienyltin(II) compounds, which are formed from CpM and $SnCl_2$, are pentahapto monomers. When R is a simple alkyl or aryl group, the stannylenes $R_2Sn(II)$ are known only as short-lived reactive intermediates, but when the organic group is bulky [*e.g.* bis(trimethylsilyl)methyl or 2,4,6-trisubstituted aryl], as indicated by R* in Scheme 1-3, the monomeric stannylenes, $R*_2Sn$:, have been isolated, and have provided routes to the stannenes ($R*_2Sn=CR_2$) and distannenes ($R*_2Sn=SnR*_2$), and other compounds with a multiple bond to tin.

1.4   Overview of Structures

This description of the various types of organotin compounds must be supplemented by a description of the structures of the compounds, which are seldom as simple as the above formulae might indicate, and which frequently depend on the physical state of the sample.

Simple tetraalkyl- and tetraaryl-tin(IV) compounds exist under all conditions as tetrahedral monomers, but in derivatives R_nSnX_{4-n} ($n = 1$ to 3), where X is an electronegative group (halide, carboxylate *etc.*), the Lewis acid strength of the tin is increased, and Lewis bases form complexes with a higher coordination number. The compounds R_3SnX usually give five-coordinate complexes R_3SnXL which are approximately trigonal bipyramidal, and the compounds R_2SnX_2 and $RSnX_3$ usually form six-coordinate complexes $R_2SnX_2L_2$ and $RSnX_3L_2$ which are approximately octahedral. The first such complex to have its structure determined by X-ray crystallography was Me_3SnCl,py (**1-1**) and some further examples of such complexes are shown in structures **1-2** and **1-3**.
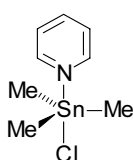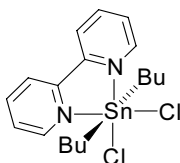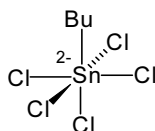
(**1-1**)   (**1-2**)   (**1-3**)

The groups X, however, usually carry unshared electron pairs, and can themselves act as Lewis bases, resulting in intermolecular self-association to give dimers, oligomers, or polymers. Some examples are shown in formulae **1-4**–**1-6**.

(**1-4**)   (**1-5**)   (**1-6**)
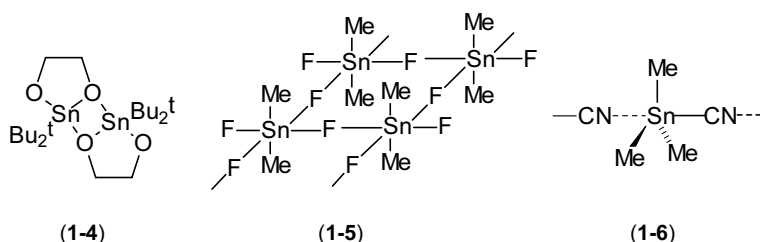
This self-association is governed by the nature of the ligands L and also by the steric demands of R, X, and L, and it is common for the degree of association to increase in the sequence gas < solution < solid.

If R or X carries a functional substituent Y beyond the α-position, the alternative of intramolecular coordination can occur leading to the formation of monomers with 5-, 6-, 7-, or 8-coordinated tin. Some examples are shown in formulae **1-7** − **1-10**.

(**1-7**)   (**1-8**)   (**1-9**)   (**1-10**)
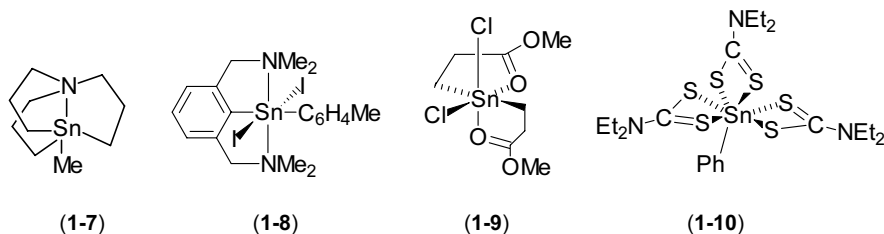
The structures of these intramolecularly self-associated monomers, oligomers, and polymers are seldom those of regular polyhedra, and the determination of their structures, and the steric and electronic factors which govern them, has been an important feature of organotin chemistry since the early 1960s. Initially the evidence came largely from proton NMR spectra and IR spectra on solutions, and IR and Mössbauer spectra on the solid state, supported by a few X-ray studies of single crystals.[17–19] More recently, comparison of the high resolution ^{119}Sn (or ^{117}Sn) NMR spectra in solution and the solid state has proved to be a very sensitive indicator of changes in structure, and single crystal X-ray studies are now commonplace.[20–22]

Systematic studies of organotin(II) compounds (Chapter 21) are much less extensive than those of tin(IV) compounds, but already it is apparent that there is a wide variety of structures. In bis(cyclopentadienyl)tin(II), the two rings are pentahapto-bonded, but the lone pair is stereochemically active and the rings are non-parallel. Other cyclopentadienyltin compounds, however, are known in which the rings are parallel, or the hapticity may change, or the CpSn$^+$ ion may be present. The discovery of the σ-bonded stannylene [(Me$_3$Si)$_2$CH]$_2$Sn(II) (Lappert's stannylene) in 1973 has stimulated a lot of studies. In the vapor phase it is monomeric, but in the solid state a dimer of C_{2h} symmetry is formed. Many further diarylstannylenes, Ar$_2$Sn(II), and their corresponding distannenes, Ar$_2$Sn=SnAr$_2$, with sterically hindering *ortho* substitutents have subsequently been prepared.

No Sn(III) radicals have yet been isolated (Chapter 20), though some are known which are stable in solution, in equilibrium with their dimers. Evidence regarding their structures comes mainly from ESR spectroscopy, which shows that, in contrast to carbon-centred radicals which are planar, tin-centred radicals are pyramidal even when the tin carries aryl ligands.

These topics are dealt with in detail in subsequent chapters.

1.5   Bibliography

This section lists, largely chronologically, the more important general reviews of organotin chemistry, with some comments as to their contents. More specialised reviews are referred to at the appropriate sections in the text. Extensive bibliographies are also given in the volume of Houben Weyl, in volumes 1, 5, 8, 9, 11, 14, 16, 17, 18, 19, and 20 of Gmelin, and in Science of Synthesis, which are referred to below.

The *Chemical Review* by Ingham, Rosenberg, and Gilman (1960),[23] and the three volumes of *Organotin Chemistry* edited by Sawyer (1971),[24] provide an extensive if not comprehensive listing of the organotin compounds which were known at those dates. Reprints of the *Chemical Review* were widely circulated and did much to stimulate interest in the subject. The various volumes of Gmelin give a thorough coverage of the compounds known at the date the material went to press; thereafter, one is dependent on Chemical Abstracts.

E. Krause and A. von Grosse, *Die Chemie der Metal-organischen Verbindungen*, (1937, reprinted 1965). Pages 311-372 relate to organotin chemistry.[11]

M. Dub, *Organometallic Compounds, Literature Survey, 1937-1959*, Vol. II *Organic Compounds of Germanium, Tin, and Lead* (1961).[25] A non-critical compendium listing preparations and physical and chemical properties, compiled from Chemical Abstracts. Pages 79-253 relate to organotin chemistry. This supplements the data given in Krause and von Grosse's book.

W.P. Neumann *Die Organische Chemie des Zinns*, (1967),[26] and its revised and translated edition: W.P. Neumann *The Organic Chemistry of Tin*, (1970).[19]

K.A. Kocheshkov, N.N. Zemlyanskii, N.I. Sheverdina, and E.M. Panov, *Metodi Elemento-organicheskoi Khimii. Germanii, Olovo, Svinesh*, (1968).[27] Pages 162-530 give a thorough coverage of organotin chemistry, though in Russian.

R.C. Poller, *The Chemistry of Organotin Compounds*, 1970.[18]

Organotin Compounds, ed. A.K. Sawyer, (1971), vols. 1, 2, 3. Comprehensive coverage in fourteen chapters by a variety of authors, with extensive lists of compounds; written at a time before organotin compounds were used extensively in organic synthesis.[24]

P.J. Smith, A Bibliography of X-ray Crystal Structures of Organotin Compounds (1981).[28]

B.J. Aylett. Organometallic compounds, 4th. Edn. Vol. 1 The Main Group Elements, Part 2. Groups IV and V. (1979).[29] Pages 177-276 deal with organotin chemistry.

Organotin Compounds: New Chemistry and Applications, ed. J.J. Zuckermann (1976).[30] Based on lectures given at the centenary meeting of the ACS.

G. Bähr and S. Pawlenko, in *Methoden der Organischen Chemie* (Houben Weyl), vol. 13/6, (1978), pp. 181-251.[31] Emphasises preparative methods, with brief experimental details.

A.G. Davies and P.J. Smith, *Adv. Inorg. Chem. Radiochem.*, 1980, **23**, 1.[32]

A.G. Davies and P.J. Smith, *Tin* in *Comprehensive Organometallic Chemistry*, (1982); reprints of this were widely circulated.[33]

M. Pereyre, J.-P. Quintard and A. Rahm, *Tin in Organic Synthesis*, (1987). Still the only book on this increasingly important aspect of organotin chemistry, though there is an excellent supplement in the 2nd edition of *Chemistry of Tin* (1998), which is noted below.

Organotin Compounds in Organic Synthesis, Tetrahedron Symposia in Print No. 36, Ed. Y. Yamamoto (1989).[34]

Organometallic Synthesis, ed. J.J. Eisch and R.B. King, Vol. 2, 1981;[35] Vol. 3, 1986;[36] Vol. 4, 1988.[37] Give tested experimental details for the synthesis of some 40 organotin compounds.

Chemistry of Tin, ed. P.G. Harrison, (1989).[38] Covers both inorganic and organic aspects. Chapters on organotin chemistry are as follows. General trends (P.G. Harrison). Spectroscopy (P.G. Harrison). Formation of the tin-carbon bond (J.L. Wardell). Organic compounds of Sn(IV) (K.C. Molloy). Organic compounds of Sn(II) (P.D. Lickiss). Tin-metal bonded compounds (F. Glockling). Radical chemistry of tin (A.G. Davies). Organotin compounds in organic synthesis (J.L. Wardell). Biological chemistry of tin (M.J. Selwyn). Industrial uses (C.J. Evans).

I. Omae, *Organotin Chemistry*, (1989), 355 pages. A then up-to-date survey of the field.[39]

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H. Nozaki, *Organotin Chemistry* in *Organometallics in Synthesis* Ed. M. Schlosser, (1994).[41] Volume 2 (2002) contains articles on organotin chemistry by J.A. Marshall, and on the Stille reaction by L.S. Hegedus.

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H. Ali and J.E. van Lier, *Synthesis of Radiopharmaceuticals via Organotin Intermediates*. [45] Organotin compounds react rapidly and chemo-, regio-, and stereo-selectively with a variety of reagents, and this has been exploited in the synthesis of pharmaceuticals with a radioactive label, particularly when the radioisotope has a short half-life. A second review covering similar ground is included in Patai's volume, as noted below.

M.I. Bruce, *Structures of Organometallic Compounds Determined by Diffraction Methods*, in *Comprehensive Organometallic Chemistry II*, ed. E.W. Abel, F.G.A. Stone, and G. Wilkinson, (1995), vol. 13.[46] Pages 1107-1149 give a comprehensive listing of organotin compounds (ca. 1500 entries) which have had their structure determined by electron diffraction or X-ray diffraction.

The Chemistry of Organic Germanium, Tin and Lead Compounds ed. S. Patai, (1995).[47] Many of the articles emphasise the comparison between the three metals. Chapters which cover tin are as follows. The nature of the C-M bond (H. Basch and T. Hoz). Structural aspects (K.M. Mackay). Stereochemistry and conformation (J.A. Marshall and J.A. Jablonowski), Thermochemistry (J.A.M. Simões, J.F. Liebman, and S.W. Slayden). ESR spectra (J. Iley). PES (C. Cauletti and S. Stranges). Analytical aspects (J. Zabicky and S. Grinberg). Synthesis of M(IV) organometallic compounds (M = Ge, Sn, Pb) (J.M. Tsangaris, R. Willem and M. Gielen). Acidity, complexing, basicity and H-bonding (A. Schulz and T.A. Klapötke). Substituent effects of Ge, Sn and Pb groups (M. Charton). Electrochemistry (M. Michman). Photochemistry (C.M. Gordon and C Long). Isotopically labelled organic derivatives (K.C. Westway and H. Joly). Environmental methylation (P.J. Craig and J.T. van Elteren). Organotin toxicology (L.R. Sherman). Safety and environmental effects (S. Maeda).

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I. Omae, *Applications of Organometallic Compounds,* (1998).[51]

Gmelin Handbuch der Anorganischen Chemie, Tin.[52] Part 1: Tin Tetraorganyls SnR_4 (1975). Part 2: Tin Tetraorganyls R_3SnR' (1975). Part 3: Tin Tetraorganyls $R_2SnR'_2$, $R_2SnR'R$, $RR'SnRR'$, Heterocyclics and Spiranes (1976). Part 4: Organotin Hydrides (1976). Part 5: Organotin Fluorides. Triorganotin Chlorides (1978). Part 6: Diorganotin Dichlorides. Organotin Trichlorides (1979). Part 7: Organotin Bromides (1980). Part 8: Organotin Iodides, Organotin Pseudohalides (1981). Part 9: Triorganotin Sulphur Compounds (1982). Part 10: Mono- and Diorganotin Sulphur Compounds. Organotin-Selenium and Tellurium Compounds (1983). Part 11: Trimethyltin- and Triethyltin-Oxygen Compounds (1984). Part 12: Tripropyltin- and Tributyltin-Oxygen Compounds (1985). Part 13: Other R_3Sn-Oxygen Compounds. $R_2R'Sn$- and $RR'RSn$-Oxygen Compounds (1986). Part 14: Dimethyltin-, Diethyltin-, and Dipropyltin-Oxygen Compounds (1986). Part 15: Di-n-butyltin-Oxygen Compounds (1988). Part 16: Diorganytin-Oxygen Compounds with R_2Sn, $RR'Sn$, or Cyclo(RSn) Units and with Identical or Different Oxygen-Bonded Groups (1988). Part 17: Organotin-Oxygen Compounds of the Types $RSn(OR')_3$, $RSn(OR')_2OR$; $R_2Sn(X)OR'$, $RSnX(OR')_2$ and $RSnX_2(OR')$ (1989). Part 18: Organotin-Nitrogen Compounds. R_3Sn-N Compounds with R = Methyl, Ethyl, Propyl, and Butyl (1990). Part 19: Organotin-Nitrogen Compounds (concluded). Organotin-Phosphorus, -Arsenic, -Antimony, and -Bismuth Compounds (1991). Part 20: Compounds with Bonds Between Tin and Main Group IV to Main Group I–IV Elements (1993). Part 21: Compounds with Bonds Between Tin and Transition Metals of Groups III to IV (1994). Part 22: Compounds with Bonds Between Tin and Transition Metals of Groups VIII, I, and II (1995). Part 23. Tin-centred radicals, tin(II) compounds, compounds with tin-element double bonds, tin(II) complexes with aromatic systems, stannacarboranes, and other organotin compounds (1995).

All these have been collated by Herbert and Ingeborg Schumann. The Gmelin handbooks cover comprehensively the organometallic compounds of tin. They are available in rather few libraries, but the database can be accessed and searched by computer.

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2 Physical Methods and Physical Data

2.1 Physical Methods

The remark has been made that compounds of tin can be studied by more techniques than those of any other element. The fact that it has more stable isotopes that any other element gives it very characteristic mass spectra, and isotopic labelling can be used to interpret vibrational spectra, and for spiking samples in trace analysis; two of the isotopes have spin 1/2 and are suitable for NMR spectroscopy, and their presence adds information to the ESR spectra of radical species. Further, the radioactive isotope ^{119m}Sn is appropriate for Mössbauer spectroscopy. The structural complications that are referred to in the previous chapter have therefore been investigated very thoroughly by spectroscopic and diffraction methods, and structural studies have always been prominent in organotin chemistry.

In the sections that follow, the basic theory of these techniques will be discussed only insofar as it is specially relevant to organotin compounds. It must always be borne in mind that the structures of organotin compounds which carry functional groups may be dependent on the physical state (gaseous, solid, or liquid), and, when the compounds are in solution, on the nature of the solvent and on the concentration. For example, the Sn–Cl stretching frequency in the far IR spectra of trimethyltin chloride in solution can be correlated with the donor number of the solvent. Caution must therefore always be exercised in attempting to quote "typical" values for properties such as vibrational frequences or NMR chemical shifts.

2.1.1 Infrared and Raman Spectroscopy[1–3]

Typical vibrational frequencies for organotin compounds are tabulated by Neumann,[4] Poller,[5] Omae,[6] Harrison,[2] and Nakamoto[3] and data on individual compounds can be found in the relevant volumes of Gmelin.[7]

Tetraorganotin compounds, R_4Sn, show little tendency to be other than tetrahedrally 4-coordinate, and their vibrational frequencies are not dependent on the physical state (Table 2-1). The force constants in Me_4Sn are fSn–C 2.19, and fC–H 4.77 N cm^{-1}.[8] The CF_3–Sn bond is longer and weaker than the CH_3–Sn bond [220.1(5) pm in $(CF_3)_4Sn$ and

Table 2-1 Sn–C And C≅C vibrational frequencies (cm^{-1}) in tetraorganostannanes.

Compound	ν_{as}SnC	ν_sSnC	δCSnC	νC≅C
Me_4Sn	529	508	157	
Et_4Sn	508	490	132, 86	
$(CF_3)_4Sn$		211		
$(CH_2=CH)_4Sn$	531	490		1583
$(HC≡C)_4Sn$	504	447		2043
$(CH_2=CHCH_2)_4Sn$	487	474		1624
$(CH_2=CHCH_2)_2SnMe_2$	454			2016
Ph_4Sn	268, 263	221		

214.3(3) pm in $(CH_3)_4Sn$], and the force constant is reduced to 1.86 N cm^{-1}.[9] Isotopic labelling with ^{116}Sn and ^{124}Sn in Ph_4Sn has been used to identify $\nu_{as}SnC$ at 268 and 263 respectively, and $\nu_s SnC$ 221 cm^{-1}.[10]

Organotin hydrides, R_nSnH_{4-n}, are also tetrahedral monomers under normal conditions. Me_3SnH Shows $\nu(SnH)$ 1834 cm^{-1}, $\delta(SnH)$ 545 cm^{-1}, and in Me_3SnD, $\nu(SnD)$ is 1337 cm^{-1}. The value of $\nu(SnH)$ varies from about 1780 cm^{-1} (in Cy_3SnH) to 1910 cm^{-1} (in Vin_3SnH), but it is always strong and convenient for monitoring reactions by IR spectroscopy.

The third class of compounds that are not prone to increase their coordination numbers are the hexaalkyldistannanes, R_3SnSnR_3, and the related oligostannanes. The Sn–Sn stretch is infrared inactive, but Raman active, and $Me_3SnSnMe_3$ shows $\nu(SnSn)$ 192 cm^{-1}. If the phenyl groups in hexaphenylditin are alkylated in the *ortho* positions, steric hindrance weakens the Sn–Sn bond, and the vibration frequency and force constant are reduced (see Table 18-2).

In many types of triorganotin compounds, R_3SnX, self association to give an oligomer $(-R_3SnX-)_n$ places the two groups X in the axial position, and the three groups R coplanar in the equatorial position, in a trigonal bipyramidal arrangement about tin. The symmetrical vibration of the R_3Sn moiety is therefore rendered infrared inactive (though it remains Raman active) and the absence of the ν_s band in the IR spectrum at *ca*. 510 cm^{-1} was used a lot in the early days of organotin structural chemistry as evidence for the oligomerisation.[5] Similarly the presence of two Sn–O stretching frequencies at ca. 1570 and 1410 cm^{-1} in solid and molten trialkyltin carboxylates shows that the CO_2 group has C_{2v} symmetry with equivalent C–O bonds, confirming the oligomeric structure $(-SnR_3-O-CR=O-)_n$.

Vibrational frequencies which have been assigned to SnX bonds in compounds of known structure are given in Table 2-2.

Table 2-2   Vibrational frequencies of Sn–X bonds.

Compound	vSnX/cm^{-1}	Compound	vSnX/cm^{-1}
R_3SnH	1777–1846	R_3SnNR_2	520–620
R_2SnH_2	1820–1863		
$RSnH_3$	1855–1880	R_3SnSR'	320–370
R_3SnF	340–377	$Me_3SnSnMe_3$	192
R_3SnCl	318–336	$Ph_3SnSnPh_3$	138
R_3SnBr	222–234	$(Me_3Sn)_4Sn$	159, 198
R_3SnI	176–204		
$Me_3SnCl_2^-$	227		
$Me_3SnBr_2^-$	140	$(2,4,6\text{-}Et_3C_6H_2)_6Sn_2$	92
$Me_3SnI_2^-$	134		
Me_3SnOH	531–576		
$(Bu_3Sn)_2O$	770		
$(Ph_3Sn)_2O$	770		

2.1.2   Mössbauer Spectroscopy [11, 2, 12–17]

When the complexity of organotin structures was first becoming appreciated, Mössbauer spectroscopy played a major part in elucidating the structures in the solid state. However, the spectra usually consist of singlets or doublets which are broad (typically

0.4 mm s^{-1}) compared with the normal range of isomer shifts [ca. 4 mm s^{-1} for organotin(IV) compounds], and data from different laboratories on the same compounds may vary by ca. 0.2 mm s^{-1}. The technique is used less now that the more discriminating technique of high resolution solid state NMR spectroscopy has been developed, and X-ray diffraction is more generally available for investigating crystalline samples. A thorough, recent, review is available, which gives diagrams correlating the isomer shift and quadrupole coupling with structural types.[17]

The source of the γ-rays is the ^{119m}Sn isotope which is prepared by the (n,γ) reaction of ^{118}Sn. It decays with a half life of 245 days to give the nuclear excited ^{119}Sn*. This has a spin *I* of ± ^{3}/2, and a half life of 1.84 × 10^{-8} s, and emits a γ-ray of 23.875 keV in its transition to the ground state with spin *I* of ± ^{1}/2 . It is usually incorporated into barium or calcium stannate, which give a line-width of about 0.33 mm s^{-1}. Measurements are usually carried out at 77 K, to increase the recoil-free fraction of the emission and absorption; for $BaSnO_3$, this is 0.8 at 77 K, and 0.55 at 300 K.

The principal source of useful chemical information is the isomer shift (IS or δ) and the quadrupole coupling (QC or Δ). Compilations of these data are available,[2, 12–18] and a complete listing is given in the *Mössbauer Effect References and Data Journal*.[19, 20] The symbols IS and QC are used in this text to avoid confusion with NMR chemical shifts. Values of IS are usually referenced against SnO_2 or $BaSnO_3$, which are the same within experimental error (and all data in this book are quoted on this standard). For isomer shifts which are given in the literature against other standards, the following corrections should be applied: grey (α) tin, +2.10; white (β) tin, +2.70; Mg_2Sn, +1.82; Pd/Sn +1.52 mm s^{-1}. It is common practice now to analyse the spectra, particularly when peaks overlap, by computer curve-fitting programmes. Values for IS and QC (± ca. 0.2 mm s^{-1}) for a selection of organotin compounds are given in Table 2-3.

The *isomer shift* gives a measure of the *s*-electron density at the tin nucleus. As the nucleus emits or absorbs the γ-ray, its radius changes, and the interaction with the *s*-electrons which are close to the nucleus affects the separation between the ground state and the excited state. A decrease in the *s*-electron density at the nucleus corresponds to a more positive isomer shift.

The *quadrupole coupling* arises because the excited state with *I* of 3 + 2 has quadrupolar charge separation, and this can interact with a local electric field gradient due to the ligands about the tin. For example, a tetrahedral compound R_4Sn, with zero field gradient at the tin, will show only a singlet signal, but a compound R_3SnX, with only axial symmetry, will show the signal split into a doublet.

Thus organotin(II) compounds (Table 2-3) which frequently have the unshared electron pair in an orbital with substantial 5*s* character, usually show isomer shifts in the range 2 to 4 mm s^{-1}, whereas tin(IV) compounds show shifts in the range –0.5 to 2.5 mm s^{-1}. An elegant example of this is provided by bis(trimethylstannylcyclopentadienyl)tin(II) ($Me_3Sn^{IV}C_5H_4)_2Sn^{II}$,[21] which presumably has an open-sandwich structure similar to that of $(C_5H_5)_2Sn$: itself, with C_{2v} symmetry. For the Sn(IV) centre it shows a singlet with IS 1.30, QC 0 mm s^{-1} (cf. Me_4Sn, IS 1.30, QC 0 mm s^{-1}) and for the Sn(II) centre it shows a doublet of half the intensity, with IS 3.58, QC 0.89 mm s^{-1} (*cf*. Cp_2Sn, IS 3.72, QC 0.81 mm s^{-1}).

Isomer shift values also depend on the electronegativity of the ligands, on the coordination number, and on the stereochemistry. Thus the series of alkylpentahalogenostannates, $BuSnX_nY_{5-n}$ $^{2-}$ shown in Table 2-4, may all be assumed to have similar octahedral structures, and the value of IS falls with increasing electronegativity of X and Y, i.e. as the ligand attracts electrons away from the tin.[22] A similar trend can be distinguished as the alkyl groups are varied in, for example, the tetrahedral compounds R_4Sn, indicating that the electron releasing power increases in the sequence Me < Et < Pr < Bu.

Table 2-3   Mössbauer data for organotin compounds.

Compound	IS/mm s^{-1}	QC/mm s^{-1}	Compound	IS/mm s^{-1}	QC/mm s^{-1}
Cp_2Sn	3.73	0.65	Me_3SnH	1.24	0.0
$Cp*_2Sn$	3.53	0.99	Ph_3SnH	1.39	0.0
$(C_5Ph_5)_2Sn$	3.74	0.58			
$CpSnCl$	3.71	1.04	$Ph_3SnSnPh_3$	1.35	0.0
$CpSnBr$	3.40	0.99	$(Ph_2Sn)_6$	1.56	0.0
$CpSnI$	3.90	0			
$(Me_3SnC_5H_4)_2Sn$	3.58	0.89	Bu_3SnF	1.48	3.74
	1.30	0	Bu_3SnCl	1.58	4.40
$[(Me_3Si)_2CH]_2Sn$	2.16	2.31	Bu_3SnBr	1.60	3.30
Me_4Sn	1.20	0.0	Bu_3SnI	1.47	2.71
Bu_4Sn	1.37	0.0	Bu_2SnCl_2	1.60	3.25
Ph_4Sn	1.22	0.0	$BuSnCl_3$	1.31	1.83
$(C_6F_5)_4Sn$	1.04	0.0			
Me_3SnPh	1.25	0.0	Bu_3SnOAc	1.40	3.40
$Me_3Sn(C_6Cl_5)$	1.32	1.09	$(Bu_3Sn)_2O$	1.10	2.10
$Et_3SnC{\equiv}CSnEt_3$	1.30	1.00	Bu_2SnO	0.94	2.08

Table 2-4   Isomer shift and ligand electronegativity.

Compound	IS/mm s^{-1}	Compound	IS/mm s^{-1}
$BuSnF_5^{2-}$	0.27	Me_4Sn	1.20
$BuSnF_4Cl^{2-}$	0.47	Et_4Sn	1.30
$BuSnCl_5^{2-}$	1.03	Pr_4Sn	1.30
$BuSnCl_4Br^{2-}$	1.08	Bu_4Sn	1.37
$BuSnCl_3Br_2^{2-}$	1.15		
$BuSnCl_2Br_3^{2-}$	1.20	Ph_4Sn	1.15
$BuSnBr_5^{2-}$	1.38		

In inorganic tin compounds, an increase in coordination number is usually associated with a decrease in isomer shift, and this is interpreted in terms of changes of *s*-electron density on rehybridisation. As always, care must be taken to ensure that structures are unambiguous, but in organic compounds, the reverse trend can sometimes be identified, for example, values for the isomer shifts are $Me_2SnCl_3^-$, 1.40; $Me_2SnCl_4^{2-}$, 1.59; and $Ph_2SnCl_3^-$, 1.38; $Ph_2SnCl_4^{2-}$, 1.44 mm s^{-1}.

In the period when Mössbauer spectroscopy provided one of the few techniques that were available for determining organotin structures in the solid state, many attempts were made to correlate particular regular geometries with certain ranges of quadrupole splitting. However, the increasing availability of single crystal X-ray diffraction has provided a more direct way of determining structures, and has made it apparent that few structures are as regular as were thought.

2.1.3   Mass Spectrometry

Tin has ten naturally occurring isotopes, more than any other element. The relative abundances are given in Table 2-5. In the mass spectrum, these isotopes give rise to the characteristic pattern of peaks which is illustrated in the Table.

Table 2-5 Naturally occurring isotopes of tin.

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

112 114 116 118 120 122 124

Rather limited use has been made of mass spectrometry in the study of organotin compounds,[23, 24] though MS linked to gas-liquid chromatography is now being used for the identification of organotin compounds, particularly in environmental studies. Most of the early work involved electron ionisation (EI), but in recent years, other techniques such as chemical ionisation (CI),[25] fast atom bombardment (FAB),[26, 27] field desorption,[28] surface ionisation,[29] and, particularly, electrospray (ES),[30, 31] have been used.

The usual pattern of behaviour was established in the early studies which were by EI,[32–35] and the reaction paths have been analysed more recently by MS-MS and ES. Typical modes of fragmentation are illustrated for Me_4Sn and Bu_4Sn, with relative abundances of the ions, in Figure 2-1.
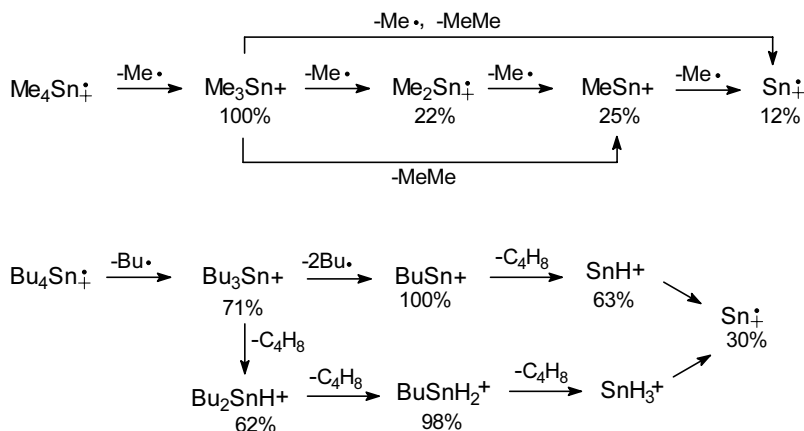
Figure 2-1 Fragmentation of tetramethyltin and tetrabutyltin radical cations.

Very little of the molecular ion $R_4Sn^{\bullet+}$ is usually detected by EI MS at 70 eV.

$Me_4Sn^{\bullet+}$ Decays by progressive loss of $Me^{\bullet}$ and MeMe, but with β-H available in the alkyl group, the alkene R(–H) is eliminated, and the hydrides Bu_2SnH^+ and $BuSnH_2^+$, and $Sn^{\bullet+}$ are major products from Bu_4Sn.

R_3Sn^+ Is the principal ion fragment in the spectra of Me_4Sn, Et_4Sn, Vin_4Sn, Ph_4Sn, Et_6Sn_2, and Ph_2SnEt_2. With mixed groups, alkyl is lost more readily than aryl. If the skimmer voltage is progressively increased in ES MS, this allows the fragmentation pathway to be determined, and trineopentyltin triflate has been shown to fragment by elimination of isobutene and migration of a methyl group from carbon to tin (Figure 2-2).[36]

$$(Me_3CCH_2)_3Sn^+ \xrightarrow{-Me_2C=CH_2} (Me_3CCH_2)_2\overset{+}{Sn}Me + Me_3CCH_2\overset{+}{Sn}Me_2$$

$$^+SnMe_3 \longrightarrow {}^+SnMe$$
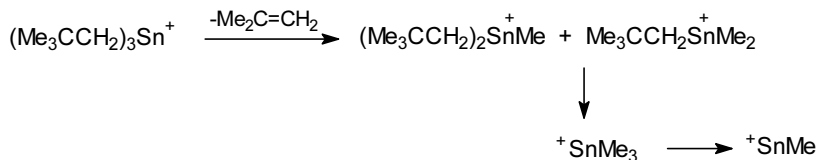
Figure 2-2 Fragmentation of the trineopentyltin cation.

Groups R such as hydrogen, phenyl (Figure 2-3), or vinyl, which cannot eliminate an alkene, lose instead the dimer R–R, but substituents in the phenyl rings may have a substantial effect on the disintegration patterns.[27]

$$Ph_4Sn^{\cdot}_+ \xrightarrow{-Ph\cdot} Ph_3Sn^+ \xrightarrow{-Ph\cdot} Ph_2Sn^+ \xrightarrow{-Ph\cdot} PhSn^+ \xrightarrow{-Ph\cdot} Sn^{\cdot}_+$$

with $-Ph_2$ from Ph_3Sn^+ (100%) to $PhSn^+$ (33%); Ph_2Sn^+ 11%; and

$$PhSnC_6H_4^+$$
15%
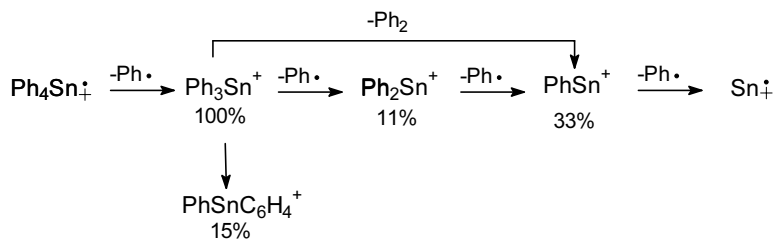
Figure 2-3 Fragmentation of the tetraphenyltin radical cation.

Distannanes such as $Et_3SnSnEt_3$ and $Ph_3SnSnPh_3$ show rather more of the molecular ion under EI at 70 eV, and can then fragment to give $R_3SnSnR_2^+$ and $R^{\cdot}$, or R_3Sn^+ and $R_3Sn^{\cdot}$, or, in the case of Et_6Sn_2, loss of C_2H_4 to give alkyltin hydride fragments.[33]

2.1.4   NMR Spectroscopy [37–39]

The ^{115}Sn, ^{117}Sn, and ^{119}Sn nuclei each have spin ½ and are in principle suitable for NMR studies. Their properties are shown in Table 2-6. It will be seen that for the ^{117}Sn and ^{119}Sn isotopes the receptivity is some powers of ten less than that of a proton, but some 20 times better than that of ^{13}C. With respect to both receptivity and abundance, ^{119}Sn has some advantange over ^{117}Sn, and most measurements have been made with ^{119}Sn, although ^{117}Sn has been used when external circumstances have rendered ^{119}Sn inconvenient (e.g. interference by radiotransmitters associated with London Heathrow airport),[40] or when coupling by tin isotopes has been studied. Satellites due to coupling by the ^{117}Sn and ^{119}Sn isotopes can be observed in the ^1H and ^{13}C NMR spectra and it will be noted that the ratio $J(^{119}Sn)/J(^{117}Sn)$ should be that of the two magnetogyric ratios, namely 1.0462; frequently, the values quoted in the literature do not meet this requirement. The ^1H, ^{13}C, and ^{119}Sn NMR spectra of Me_4Sn are illustrated in Figure 2-4.

Table 2-6 Properties of ^{115}Sn, ^{117}Sn, and ^{119}Sn nuclei.

Property	^{115}Sn	^{117}Sn	^{119}Sn
Natural abundance (%)	0.35	7.61	8.58
Magnetic moment (μ/μ_N)	−1.582	−1.723	−1.803
Magnetogyric ratio ($\gamma/10^7$ rad T^{-1} s^{-1})	−8.014	−9.589	−10.0318
NMR frequency (MHz)[a]	32.718780	35.632295	37.290665
Relative receptivity $D^{p\ b}$	1.24×10^{-4}	3.49×10^{-3}	4.51×10^{-3}
$D^{c\ c}$	0.7	19.5	25.2

[a] With respect to ^{1}H = 100 MHz. [b] Relative to ^{1}H. [c] Relative to ^{13}C.
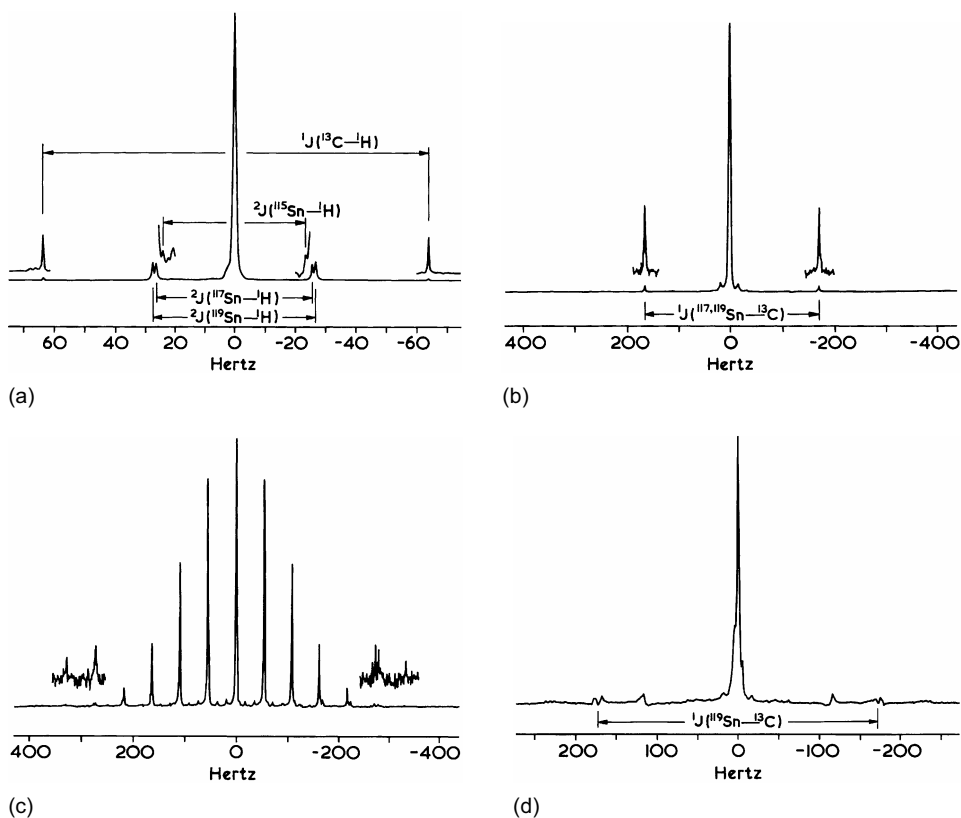
Figure 2-4 ^{1}H, ^{13}C, and ^{119}Sn NMR spectra of Me$_4$Sn. (a) ^{1}H Spectrum showing the characteristic satellite doublets due to $^2J(^{117}$Sn–H) and $^2J(^{119}$Sn–H) coupling. (b) ^{13}C Spectrum showing unresolved satellites due to $^1J(^{117/119}$Sn–^{13}C) coupling. (c) ^{119}Sn Spectrum showing 13-line multiplet due to $^2J(^{119}$Sn–H) coupling. (d) Proton decoupled ^{119}Sn spectrum, showing satellites due to $^1J(^{119}$Sn–^{13}C) coupling. (Taken with permission from *Chemistry of Tin*, by P.G. Harrison, Blackie, 1989.)

Early studies were made by continuous wave ^{119}Sn NMR, and later by internuclear ^{1}H{^{119}Sn} double resonance (INDOR), in which a tin satellite line in the proton NMR spectrum is monitored as the region of the tin resonance frequency is simultaneously swept.[41, 42] Since the introduction of pulsed Fourier transform NMR, direct observation of the ^{119}Sn resonance has become the standard technique for measurements,[37, 39] some-

times enhanced by polarisation transfer methods such as INEPT, but 2D proton detected $^1H\{^{119}Sn\}$ spectroscopy gives a further increase in sensitivity.[43, 44] Experimental details for the use of the technique in solution measurements are given by Wrackmeyer.[37] All the multidimensional techniques that have been developed for ^{13}C NMR can be used for $^{117/119}Sn$.

The first high resolution solid state NMR spectra of organotin compounds were obtained in 1978,[45] and the technique has proved to be invaluable, particularly for investigating the structural changes which occur when organotin compounds solidify.[46, 47, 48] Typical conditions are an operating frequency of 106.940 MHz for ^{117}Sn or 119.914 MHz for ^{119}Sn (on an instrument operating at 300 MHz for proton NMR), a spinning rate of ca. 4500 Hz, a pulse delay of ca. 10 s, a contact time of $1-10$ ms, and collection of $200-500$ transients. A convenient compound for setting up the cross-polarization match is tetrakis(trimethylstannyl)methane, $(Me_3Sn)_4C$, which gives a signal with no spinning side bands because the tin is in a near-perfect tetrahedral environment. It has a chemical shift δ +48.2 with respect to Me_4Sn, and is often used also for calibrating chemical shifts.

If the site-symmetry of the tin is lower than cubic, the anisotropy of the chemical shift is frequently more in frequency terms, particularly at high fields, than the spinning frequency (typically $5-10$ kHz), and the spectrum appears as an assembly of lines separated by the spinning frequency, their contour being characteristic of the anisotropy of δ. The line which represents the isotropic chemical shift is then usually identified by running a second spectrum at a different spinning rate, when only this line maintains its position. A typical simple spectrum, for $(Bu^t_2SnO)_3$, is illustrated in Figure 2-5. In the solid state, δ Sn is −85, and in $CDCl_3$ solution it is −84.9, confirming that in solution the compound retains the same cyclic trimeric structure established in the crystal by X-ray diffraction.
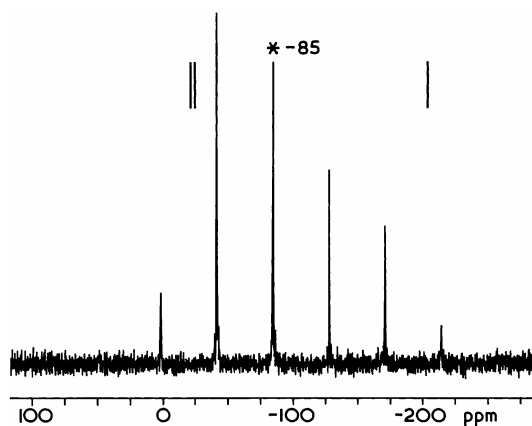
Figure 2-5   High resolution solid state ^{117}Sn NMR spectrum of $(Bu^t_2SnO)_3$ recorded on a Bruker MSL300 spectrometer operating at 106.940 MHz and a spinning speed of 4617 Hz. The isotropic shift is marked with an asterisk and the components of the shift tensor with vertical bars.

NMR Parameters are listed in the various volumes of Gmelin, and a number of compilations of data are available.[37, 39, 49-54] Chemical shifts are quoted against tetramethyltin as zero, upfield shifts being negative; care must be taken in using some of the earlier literature (e.g. ref. 49), where an opposite sign convention was followed. Many of the data that follow are taken from the two reviews by Wrackmeyer.[37, 39]

The chemical shift

[119]Sn Chemical shifts in organotin compounds cover a range of about 4500 ppm, the current extremes apparently being +2966 ppm in $(2,6\text{-Mes}_2C_6H_3)(\text{GeBu}^t_3)\text{Sn}$: and –2247 ppm in $\text{Me}_5C_5\text{SnBF}_4$. The data for a selection of some key compounds in non-interacting solvents are given in Table 2-7; the solvents are usually not specified in the table, as

Table 2-7 [119]Sn Chemical shifts of some organotin compounds.

Compound	δ	Compound	δ
Me_4Sn	0	Me_3SnCl	+164
Et_4Sn	+1	$\text{Me}_3\text{SnCl (DMSO)}$	+6.5
Pr_4Sn	–17	Me_3SnBr	+128
Bu_4Sn	–12	Me_3SnI	+39
$(\text{CH}_2\text{=CHCH}_2)_4\text{Sn}$	–48	Me_2SnCl_2	+137
$(\text{CH}_2\text{=CH})_4\text{Sn}$	–157	Me_2SnBr_2	+70
$(\text{HC}{\equiv}\text{C})_4\text{Sn}$	–356	Me_2SnI_2	–159
Ph_4Sn	–137	MeSnCl_3	+21
$(\text{PhCH}_2)_4\text{Sn}$	–36	MeSnBr_3	–165
Cp_4Sn	–24	MeSnI_3	–700
$\text{Me}_5\text{Sn}^-\,\text{Li}^+$	–277	Bu_3SnCl	+141
$\text{Ph}_5\text{Sn}^-\,\text{Li}^+$	–303	Bu_3SnBr	+134
		Bu_2SnCl_2	+123
Me_3SnH	–105	$\text{BuSnCl}_3\text{ (CDCl}_3)$	+6
Me_2SnH_2	–225	(DMSO)	–457
MeSnH_3	–346	Ph_3SnCl	–45
Bu_3SnH	–91	Ph_2SnCl_2	–32
Bu_2SnH_2	–202	PhSnCl_3	–63
Bu_2SnHCl	–18		
Ph_3SnH	–165	Me_3SnOMe	+129
		$\text{Me}_2\text{Sn(OMe)}_2$	–126
Me_3SnOH	+118	Bu_3SnOMe	+83
Cy_3SnOH	+2	$\text{Bu}_2\text{Sn(OMe)}_2$	+183
Ph_3SnOH	–86	BuSn(OEt)_3	+432
$(\text{Me}_3\text{Sn})_2\text{O}$	+110		
$(\text{Bu}_3\text{Sn})_2\text{O}$	+85	$\text{Me}_3\text{SnOCOH (CDCl}_3\text{, 3 M)}$	+2.5
$(\text{Cy}_3\text{Sn})_2\text{O}$	–8	$(\text{CDCl}_3\text{, 0.05 M)}$	+150
$(\text{Ph}_3\text{Sn})_2\text{O}$	–86		
$(\text{Bu}^t_2\text{SnO})_3$	–84	$\text{Me}_3\text{SnNMe}_2$	+76
$(\text{Bu}_2\text{SnO})_n\text{ (solid)}$	–177	$(\text{Me}_3\text{Sn})_2\text{NMe}$	+81
$[(\text{Bu}_2\text{SnCl})_2\text{O}]_2$	–140	$(\text{Me}_3\text{Sn})_3\text{N}$	+86
		$\text{Me}_2\text{Sn(NMe}_2)_2$	+59
$(\text{Me}_3\text{Sn})_2\text{S}$	+94	$(\text{Me}_2\text{SnNMe})_3$	+92
$(\text{Bu}_3\text{Sn})_2\text{S}$	+82	$\text{MeSn(NMe}_2)_3$	–15
$(\text{Ph}_3\text{Sn})_2\text{S}$	–53.7		
$(\text{Me}_2\text{SnS})_3$	+128	$\text{Me}_3\text{SnSnMe}_3$	–109
$(\text{Bu}_2\text{SnS})_3$	+127	$\text{Bu}_3\text{SnSnBu}_3$	–80
$(\text{Ph}_2\text{SnS})_3$	+17	$\text{Me}_3\text{SnSnBu}_3$	–109, –82
		$\text{Ph}_3\text{SnSnPh}_3$	–144
$(\text{Me}_3\text{Sn})_2\text{Se}$	+45	$(\text{Ph}_2\text{Sn})_6$	–208
$(\text{Me}_3\text{Sn})_2\text{Te}$	–60		
		Cp_2Sn	–2199
		$[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}$	+2325
		$\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}\}_2$	+725, +740

solvent effects are small compared with the chemical shifts unless there is some coordinative interaction with the tin. Values of δ have been rounded off to the nearest integers, as values quoted in the literature often vary by ±2 ppm, even when self-interaction or interaction with the solvent is not a problem.

Organotin compounds which carry ligands with unshared electrons, particularly oxygen and nitrogen, often associate into oligomers in solution when the chemical shift increases with increasing concentration. The chemical shift of the monomer can then often be obtained by extrapolation back to zero concentration. At the other extreme, the solid state NMR spectrum gives the chemical shift for the highest oligomer which is formed, the structure of which is often known from X-ray crystallography.

The sensitivity of the chemical shift to structure, and the use to which this can be put,[55] is illustrated by the spectra of the diastereoisomeric tetra-2-butylstannanes, (MeEtHC*)$_4$Sn, which are listed in Table 2-8, where *R* and *S* refer to the *R*- and *S*-2-butyl groups, respectively.[56, 57] ^{1}H Or ^{13}C NMR cannot differentiate between the various isomers, but the ^{119}Sn NMR spectrum shows three well resolved signals with relative intensities close to the statistical values.

Table 2-8 ^{119}Sn Chemical shifts for the diastereoisomers of tetra-2-butyltin.

Isomer	S_2R_2Sn	$(S_3RSn + R_3SSn)$	$(S_4Sn + R_4Sn)$
δ ^{119}Sn	−45.20	−45.34	−45.76
Rel. intensity (%)	35.8	49.0	15.2
Calc. intensity (%)	37.5	50.0	12.5

The chemical shifts are sensitive to a number of competing factors, in which the paramagnetic term due to the electrons in the inner shells of the tin predominates. The effects of these various factors are difficult to separate. Within a closely related family of compounds R$_3$SnX, there is a linear correlation between δ and the electronegativity of X,[49] but in general no correlation appears to hold with any other any simple group parameter. This is illustrated by the familiar "sagging" contour of the plot which is often obtained when values of δ are plotted against *n* for compounds Me$_{4-n}$SnX$_n$. A similar plot is obtained for compounds of silicon, germanium, and lead, and indeed linear correlations exist between the chemical shift values for the metals ^{119}Sn and ^{29}Si (r = 0.990),[58] ^{119}Sn and ^{73}Ge (*r* = 0.991),[59] and ^{119}Sn and ^{207}Pb (*r* = 0.975)[58, 60] in compounds of similar structure.

The prediction of shifts is still best done by correlation with the data that have been tabulated for closely related compounds. The correlations with the chemical shifts of the corresponding compounds of silicon, germanium, and lead which are referred to above, may also be useful.

The most obvious conclusion that can be drawn concerning the chemical shift values of organotin compounds is that δ moves upfield by more than 40 ppm as the coordination of the tin increases 4 → 5 → 6 → 7. Some examples are given in Table 2-9.

Table 2-9 ^{119}Sn Chemical shift and coordination number.

Compound	Coordn.	δ^{119}Sn	Compound	Coordn.	δ^{119}Sn
Me$_4$Sn	4	0	Me$_5$Sn$^-$	5	−277
Ph$_4$Sn	4	−137	Ph$_5$Sn$^-$	5	−303
Me$_3$SnCl	4	+160	Me$_3$SnCl,py	5	−9
[Bu$_2$Sn(OCH$_2$)$_2$]$_2$	5	−189	[Bu$_2$Sn(OCH$_2$)$_2$]$_\infty$	6	−230
Me$_2$Sn(SCH$_2$)$_2$	4	+194	[Me$_2$Sn(SCH$_2$)$_2$]$_\infty$	5	+94

The extra ligand(s), L, may be a polar solvent and the chemical shifts of compounds such as organotin halides are very solvent-dependent, due to the formation of complexes R_nSnX_{4-n},L and R_nSnX_{4-n},L_2 in equilibrium. For example, δSn values for Me_3SnCl in various solvents are as follows: CCl_4 +160; PhH +158; DMSO +3; pyridine –9; HMPT –48.

The coordination number may also be increased by autoassociation. For example, 2,2-di-t-butyl-1,3,2-oxathiastannolane (**2-1**) in $CDCl_3$ solution at 0.02 *M* concentration, when it is present principally as the monomer, shows δ +52. The signal progressively moves upfield as the concentration increases, reaching a value of –25 at 0.45 *M*, when a substantial amount of the dimer is present. In the solid state, where X-ray crystallography confirms that the compound exists as the dimer, the value of δ is –100.[61]

(**2-1**)   (**2-2**)   (**2-3**)
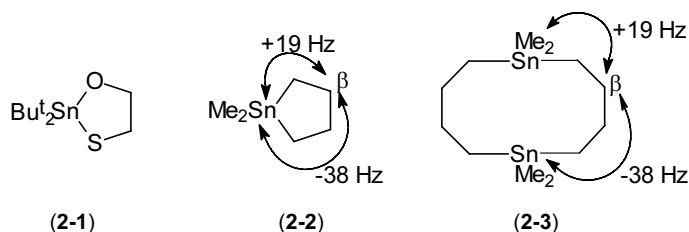
The extreme range of chemical shifts is to be found in the tin(II) compounds, R_2Sn**:**. When R is an alkyl or aryl group, the doubly occupied and the vacant orbital on tin appear to be close in energy, and the induced circulation of electrons between these two orbitals deshields the tin. When R is cyclopentadienyl, the HOMO is close to an sp^2 hybrid, and the LUMO has almost pure *p* character; the energy separation is too large to permit efficient circulation of charge, and the tin is highly shielded.

Nuclear spin coupling

Methods of measuring nuclear coupling by tin have been reviewed by Wrackmeyer.[62] Coupling to the lighter elements appears to be mainly by the Fermi contact mechanism, which increases with increasing *s*-character of the bonds. Thus the values of ^1J(SnC) and ^2J(Sn,H) for methyltin chlorides are shown in Table 2-10.

Table 2-10   Values of $^1J(^{119}Sn,^{13}C)$ for methyltin chlorides.

	Me_4Sn	Me_3SnCl	Me_2SnCl_2	Me_3SnCl,py
$^1J(^{119}Sn,^{13}C)$/Hz	–338	–380	468	–472
$^2J(^{119}Sn,^1H)$/Hz	54.7	58.1	69.0	

In Me_4Sn, each SnC bond is an sp^3 hybrid. In Me_3SnCl and Me_2SnCl_2, the tin makes an enhanced *p* contribution to the polar Sn–Cl bonds, and therefore the remaining Sn–C bonds have an enhanced *s* character, and transmit spin polarisation by the Fermi mechanism more effectively, and ^1J(SnC) is increased. In Me_3SnCl,py, the pyridine and Cl are apical ligands in a trigonal bipyramid in which the Me_3Sn group is essentially sp^2 hybridized, and ^1J(SnC) is large.

The effect on $^1J(^{119}Sn,^{13}C)$ of increase in the contribution to the *s* character of the Sn–C bond by change of the carbon hybridization is apparent in the series tetraethyltin (sp^3C) –330, tetravinyltin (sp^2C) –520, tetraphenyltin (sp^2C) –531, and tetraethynyltin (spC) –1176 Hz.

In one-bond Sn-Sn coupling, the mutual atomic polarisability appears to be the dominant term. In R_3SnSnR_3 and $R_3SnSnR_2SnR_3$, ^1J(SnSn) correlates linearly with the Taft σ^* values of R. Electronegative substituents reduce the polarizability of the Sn nuclei, and the following values of ^1J(SnSn) are observed: $Me_3SnSnMe_3$ +4460 Hz, $Ph_3SnSnPh_3$ 4470 Hz, $(Me_3Sn)_4Sn$ 876 Hz, and $AcOBu_2SnSnBu_2OAc$ (which contains 5-coordinate tin) 14,980 Hz.

Values of ^2J(SnCH) usually parallel those of ^1J(SnC) which are discussed above. The change in hybridisation at tin is accompanied by a change in the bond angles, and in methyltin compounds, the equation 2-1 has been proposed for relating the Me−Sn−Me angle θ to the value of $^2J(^{119}Sn,^1H)$.[63] By this criterion, the values of $^2J(^{119}Sn,^1H)$ in Table 2-10 for Me_4Sn, Me_3SnCl, and Me_2SnCl_2, should correspond to Me−Sn−Me angles of 109.4°, 111.1°, and 119.0°, respectively, whereas the measured angles are 109.5°, 110.1°, and 117.9°, respectively. Caution must of course be exercised when coupling constants measured in solution are correlated with bond angles measured by X-ray crystallography.

$$\theta = 0.0161[^2J(^{119}Sn,^1H)]^2 - 1.32[^2J(^{119}Sn,^1H)] + 133.4 \tag{2-1}$$

Coupling to ^{13}C through more than one bond is illustrated by the value for ^nJ(SnC) in Bu_4Sn: ^1J 314, ^2J 20, ^3J 52, ^4J 0 Hz. ^2J And ^3J SnC coupling can distinguish a monostannacyclopentane (**2-2**) from the dimer, 1,6-distannacyclodecane (**2-3**). In the dimer, the β-carbon shows two sets of tin satellites resulting from coupling to two different tin atoms with ^2J +19 Hz and ^3J –38 Hz. In the monomer the single tin atom gives rise to one set of satellites, with the coupling constant resulting from the algebraic sum of the two paths of coupling, $^{2/3}J$ –19 Hz.[64]

The presence of $^2J(^{119}Sn^{117}Sn)$ coupling in distannoxanes can be used to distinguish them from the corresponding tin hydroxides.[65] In the distannoxanes, the value of ^2J(SnSn) in benzene varies from 421 to 916 Hz, and this has been correlated with the Sn−O−Sn angle.

Values of ^3J(SnCCH)[57] and of ^3J(SnCCC)[37] show Karplus-type dependency on the dihedral angle.[66] Representative values are ^3J(SnH) 0° 110, 60° 14, 120° 40, 180° 140 Hz, and ^3J(SnC) 0° 35, 90° 10, 180° 60 Hz.

The Karplus-type behaviour of ^3J(SnCCSn) is confirmed by coupling constants in the compounds $Me_3SnCH_2CHRSnMe_3$, shown in Newman projection in **2-4**.[67] The dihedral angles SnCCSn (θ) and H^ACCH^B (θ') will vary with R, but if there is no distortion of the tetrahedral angles about carbon, θ and θ' though unknown, will remain equal. The fact that there is a linear relationship between ^3J(SnCCSn) and $^3J(H^ACCH^B)$ shows that the dependence of ^3J on the dihedral angle in both is the same, and as the latter shows Karplus behaviour by definition, the former must also. The same argument applies to the value of $^3J(^{119}SnCC^{29}Si)$ in the compounds $Me_3SiCH_2CHRSnMe_3$ (**2-5**).
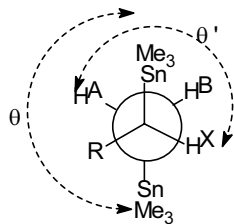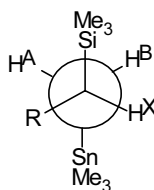
(2-4)   (2-5)

If the Karplus equation for $^3J(HCCH)$ is taken to be as shown in equation 2-2, this leads to the corresponding expressions for $^3J(SnCCSn)$ and $^3J(^{119}Sn^{29}Si)$ as shown in equations 2-3 and 2-4. The reliability of these equations will be improved as further data become available.

$$^3J(HH) = 7 - \cos \theta + 5 \cos 2\theta \tag{2-2}$$

$$^3J(SnSn) = 580 - 79 \cos \theta + 395 \cos 2\theta \tag{2-3}$$

$$^3J(SnSi) = 52 - 9 \cos \theta + 45 \cos 2\theta \tag{2-4}$$

If 2-dimensional $^{119}Sn/^1H$ shift correlations can be established for long range coupling constants $^nJ(^{119}Sn/^1H)$, $n = 4$ or 6, the absolute signs of the coupling constants $J(SnSn)$ can be determined.[68]

In vinylstannanes, $|^3J(^{119}Sn/^1H)|_{trans} > |^3J(^{119}Sn/^1H)|_{cis} \approx |^2J(^{119}Sn/^1H)|_{gem}$, and electropositive substituents at the double bond increase the coupling constants. Examples are given in formulae **2-6** and **2-7**.
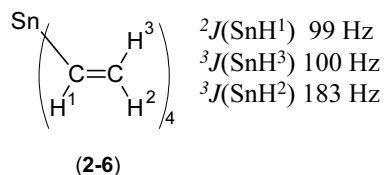
$^2J(SnH^1)$ 99 Hz	
$^3J(SnH^3)$ 100 Hz	
$^3J(SnH^2)$ 183 Hz	

(2-6)
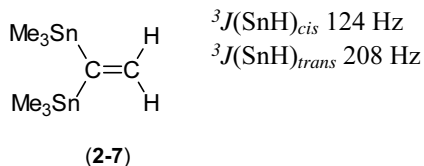
$^3J(SnH)_{cis}$ 124 Hz
$^3J(SnH)_{trans}$ 208 Hz

(2-7)

2.1.5 Photoelectron Spectroscopy[69]

In gas phase photoelectron spectroscopy (PES), a sample is irradiated with UV light (usually He I with $h\nu$ 21.22 eV or He II with $h\nu$ 40.81 eV). This leads to the ejection of an electron carrying an excess of kinetic energy (KE) which is related to the ionisation energy (IE) by the equation:

$$h\nu = IE + KE \tag{2-5}$$

Table 2-11 Vertical IEs of stannanes R_3SnR' (eV).

R_3SnR'	1 (dominant character)	2	3	Ref.
Me_3SnH	9.65	10.60	13.55	71
Me_2SnH_2	10.00	10.45	10.90	71
Me_3SnMe	9.76	ca. 13		72
Me_3SnBu	9.52	11.31		72
$H_3SnCH=CH_2$	10.1 ($\pi_{C=C} - \pi^*_{SnH3}$)	11.4	12.2	73
$H_3SnCH=CHMe$	9.6 ($\pi_{C=C} - \pi^*_{SnH3}$)	10.2	11.1	73
$H_3SnC\equiv CH$	10.6 ($\pi_{C\equiv C}$)	11.8	12.4	73
$Me_3SnCH_2CH=CH_2$	8.70 ($\sigma_{C-Sn} - \pi/\pi^*_{C=C}$)	9.76	10.87	72
$Me_3SnCH_2Cyclopropyl$	8.85	10.09	10.45	72
$Me_3SnCH_2CH_2CH=CH_2$	8.71	11.74		72
$Me_3SnCH_2CH_2CH_2CH=CH_2$	9.72	11.40	10.30	72
$Bu_3SnCH_2CH=CH_2$	8.40 ($\sigma_{C-Sn} - \pi/\pi^*_{C=C}$)	8.95		72
$Ph_3SnCH_2CH=CH_2$	8.33 ($\sigma_{C-Sn} - \pi/\pi^*_{C=C}$)	8.97	9.53	72
Ph_4Sn	9.04	9.77	11.55	74
$Me_3SnSnMe_3$	8.20 (σ_{Sn-Sn})	9.3	9.6	75

Measurement of KE and knowledge of *h*ν thus lead to the ionization energy, which, by Koopman's theorem, is equated to the energy level in which the electron resided. PES Therefore gives fundamental information of the energy levels of the various molecular orbitals.

Vertical IEs of a variety of stannanes are given in Table 2-11,[70] and their use in analysing the hyperconjugative effect in allylstannanes is given in Section 3.1.2.3. For comparison, IE values for simple organic compounds are: MeH 12.61, BuH 10.53, $CH_2=CH_2$ 10.51, $MeCH=CH_2$ 9.69, $HC≡CH$ 11.4, $MeC≡CH$ 10.4, Ph_4C 8.41 eV.

2.2   Physical Data[76]

Selected physical data which are relevant to the synthesis, structure, stability, and spectroscopic properties of organotin compounds are listed here. Further details are given in the appropriate chapters.

Atomic number 50. *Relative atomic mass* 118.710. The abundance of the ten naturally occurring isotopes is given in Table 2-5, and the properties of the spin-active isotopes are given in Table 2-6.

Valence electrons: [Kr] $4d^{10} 5s^2 5p^2$

Electronegativity values of the Group 14 elements (Table 2-12) are of limited value as there are disagreements between the various scales,[6, 76] and in polyatomic compounds the values vary with the ligands.

Table 2-12   Electronegativity of the Group 14 elements

	Pauling	Allred-Rochow	Sanderson
C	2.55	2.50	2.47
Si	1.90	1.74	1.74
Ge	2.01	2.02	2.31
Sn	1.96	1.72	2.02
Pb	2.33	1.55	2.01

(Taken from J.E. Huheey, Inorganic Chemistry, 3rd. ed., Harper and Row, New York, 1983.
For values of Mullikan group electronegativities, see S.G. Bratsch, *J. Chem. Educ.*, 1988, **65**, 34 and 223.)

Covalent bond lengths (*r*) derived from X-ray crystallography on organotin compounds are listed in Table 2-13; the covalent radius of tin can be taken to be about 140.5 pm. In crystalline organotin compounds, the absence or presence of bonding to tin

Table 2-13   Covalent bond lengths (*r*, pm) to tin.

Compound	*r*Sn−C	*r*Sn−X	Compound	*r*Sn−X
Me_4Sn	214.4		$Mes_3Sn−OH$	196
$(CH_2=CH)_4Sn$	211.6		$(Ph_2Sn−S)_3$	237
$(HC≡C)_4Sn$	206.7			
Ph_4Sn	216.8		$Me_3Sn−SnMe_3$	277.6
$(CF_3)_4Sn$	216.8		$Ph_3Sn−SnPh_3$	279.1
$Me_3Sn−H$	214.9	171	$(−Ph_2Sn−)_6$	277
$(Me_3Sn−F)_∞$	210	210, 240	$[(Me_3Si)_2CH]_2Sn=Sn[CH(SiMe_3)]_2$	276
$Me_3Sn−Cl$	210.6	235.1	$[(Me_3Si)_2CH]_2Sn=C(BBu^t)_2(SiMe_3)_2$	203