Alwyn G. Davies

Organotin Chemistry

Organotin Chemistry, Second Edition. Alwyn G. Davies

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Alwyn G. Davies

Organotin Chemistry

Second, Completely Revised
and Updated Edition

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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*.

November 2003

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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]

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

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.

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

$$2\mathrm{Et_2Zn} + \mathrm{SnCl_4} \longrightarrow \mathrm{Et_4Sn} + 2\mathrm{ZnCl_2} \tag{1-3}$$

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.

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

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.

$$\mathrm{Et_2Zn} + \mathrm{SnCl_2} \longrightarrow \mathrm{Et_4Sn} + \mathrm{ZnCl_2} \tag{1-5}$$

Up to 1900, some 37 papers were published on organotin compounds, making use of these two basic (direct and indirect) reactions.

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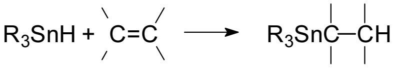
In 1900, Grignard published his synthesis of organomagnesium halides in ether solution. These reagents were much less sensitive to air than Frankland's solvent-free organozinc compounds, and they rapidly replaced and extended the scope of the zinc reagents as a source of nucleophilic alkyl and aryl groups. 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 crystallogrraphy 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.

$$\mathrm{R_3SnH + R'X \longrightarrow R_3SnX + R'H} \qquad (1\text{-}6)$$



$$\mathrm{R_3SnH + {>}C{=}C{<} \longrightarrow R_3Sn\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}H} \qquad (1\text{-}7)$$

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:	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**:** 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≡ by stannylidyne.

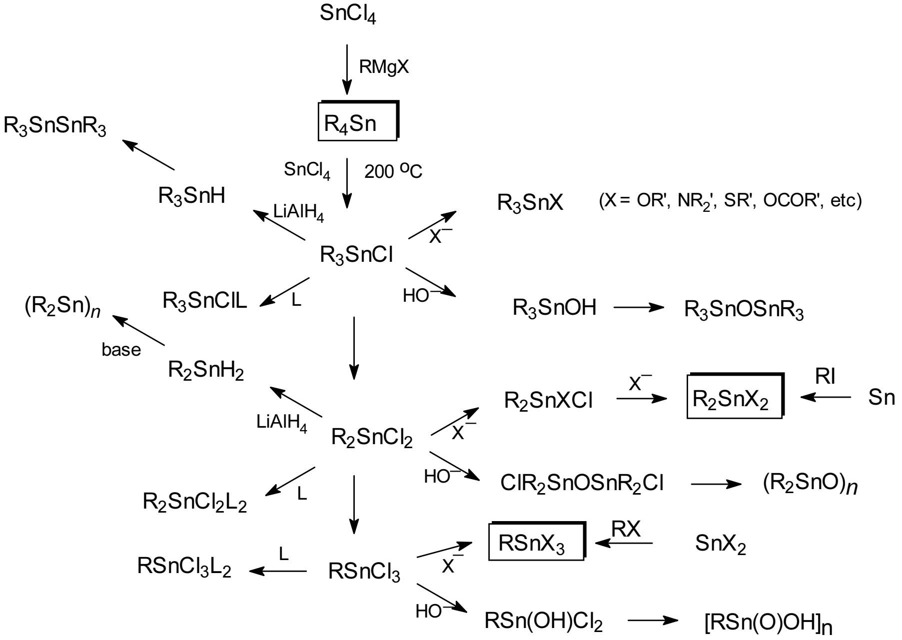
Some illustrative examples are as follows.

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.

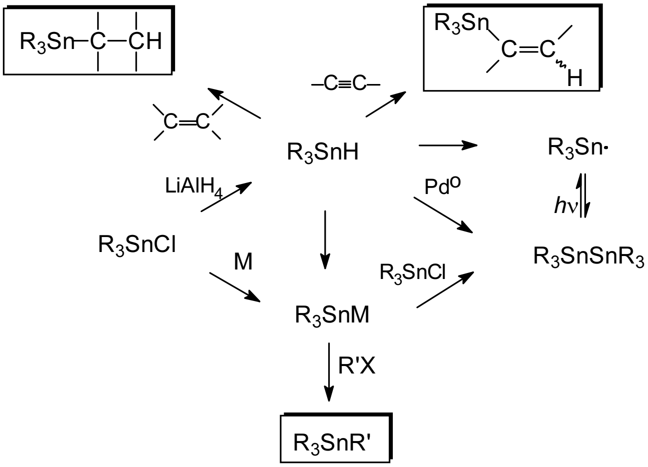
If there is doubt, the correct name can usually be found through the formula index.

1.3 Overview of Synthesis

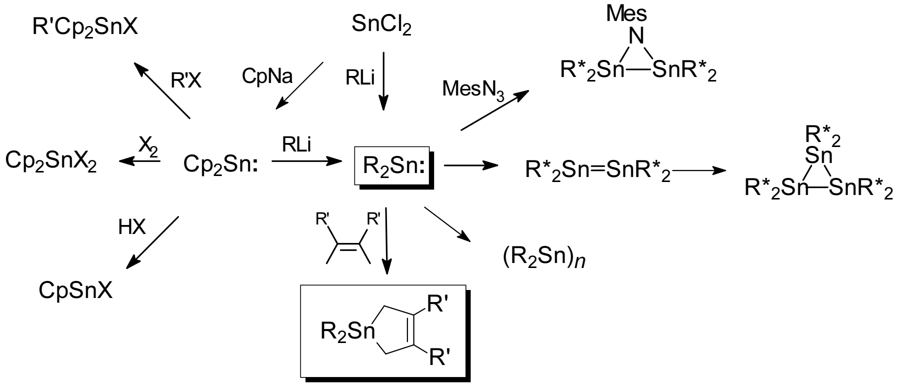
An overview of the principal groups of organotin compounds and their interconversions is given in Scheme 1-1, which deals mainly with tin(IV) compounds, and Schemes 1-2 and 1-3 which cover compounds related to tin(III) and tin(II) species, respectively. It



Scheme 1-1 Organotin synthesis based on the Grignard and Kocheshkov reactions.



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, $R_3Sn^\bullet$, provide the second way of generating the tin-carbon bond (Scheme 1-2).

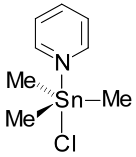
Under the influence of a base or a platinum catalyst, the triorganotin hydrides and dialkyltin dihydrides eliminate hydrogen to give the distannanes (R_3SnSnR_3) and the oligostannanes $(R_2Sn)_n$, respectively. The halides, hydrides, or distannanes can be converted into the metallic derivatives R_3SnM, 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.

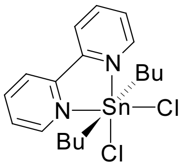
1.4 Overview of Structures

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.

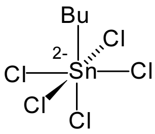
Simple tetraalkyl- and tetraaryl-tin(IV) compounds exist under all conditions as tetrahedral monomers, but in derivatives R_nSnX_{4-n} ($n = 1$ to 3), where X is an electronegative group (halide, carboxylate *etc.*), the Lewis acid strength of the tin is increased, and Lewis bases form complexes with 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**)

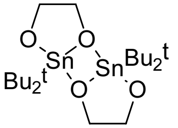


(**1-2**)

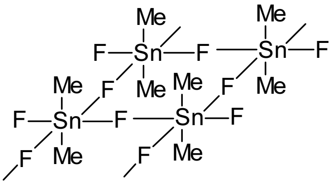


(**1-3**)

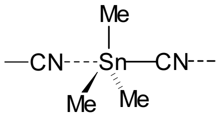
The groups X, however, usually carry unshared electron pairs, and can themselves act as Lewis bases, resulting in intermolecular self-association to give dimers, oligomers, or polymers. Some examples are shown in formulae **1-4**–**1-6**.



(**1-4**)



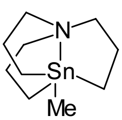
(**1-5**)



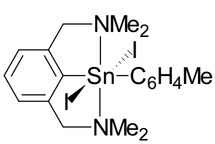
(**1-6**)

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.

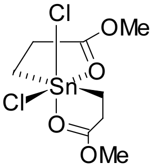
If R or X carries a functional substituent Y beyond the α-position, the alternative of intramolecular coordination can occur leading to the formation of monomers with 5-, 6-, 7-, or 8-coordinated tin. Some examples are shown in formulae **1-7**–**1-10**.



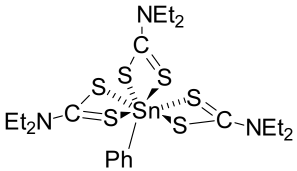
(**1-7**)



(**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 $[(Me_3Si)_2CH]_2Sn(II)$ (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, $Ar_2Sn(II)$, and their corresponding distannenes, $Ar_2Sn{=}SnAr_2$, 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]

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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.

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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
$(HC{\equiv}C)_4Sn$	504	447		2043
$(CH_2{=}CHCH_2)_4Sn$	487	474		1624
$(CH_2{=}CHCH_2)_2SnMe_2$	454			2016
Ph_4Sn	268, 263	221		

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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 ν_sSnC 221 cm^{-1}.[10]

Organotin hydrides, R_nSnH_{4-n}, are also tetrahedral monomers under normal conditions. Me_3SnH Shows ν(SnH) 1834 cm^{-1}, δ(SnH) 545 cm^{-1}, and in Me_3SnD, ν(SnD) is 1337 cm^{-1}. The value of ν(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 ν(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	$\nu SnX/cm^{-1}$	Compound	$\nu SnX/cm^{-1}$
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		

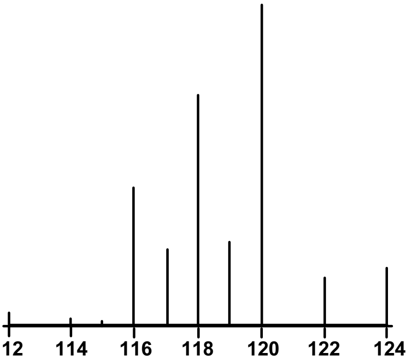
In inorganic tin compounds, an increase in coordination number is usually associated with a decrease in isomer shift, and this is interpreted in terms of changes of *s*-electron density on rehybridisation. As always, care must be taken to ensure that structures are unambiguous, but in organic compounds, 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	

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.

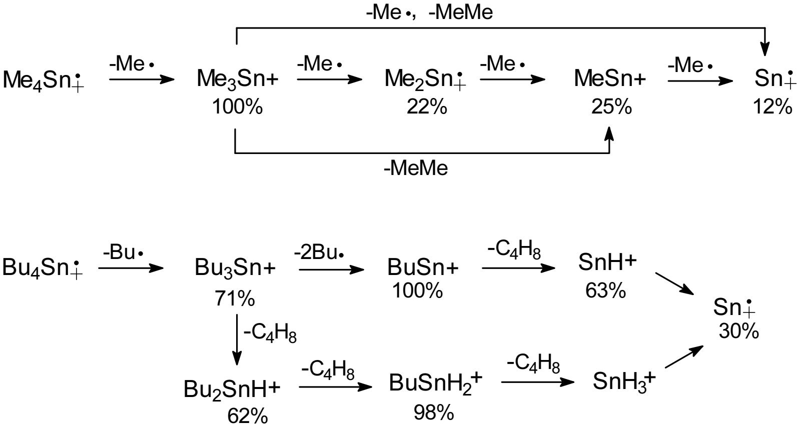


Figure 2-1 Fragmentation of tetramethyltin and tetrabutyltin radical cations.

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]

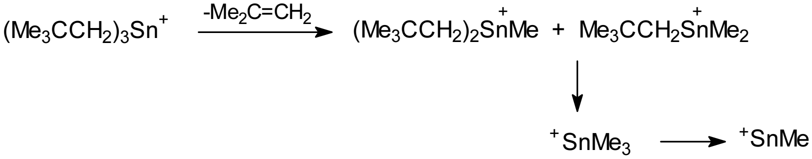


Figure 2-2 Fragmentation of the trineopentyltin cation.

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]

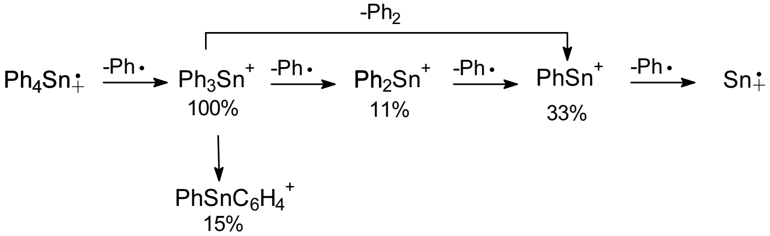


Figure 2-3 Fragmentation of the tetraphenyltin radical cation.

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 $R^\bullet$, or R_3Sn^+ and $R_3Sn^\bullet$, 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.

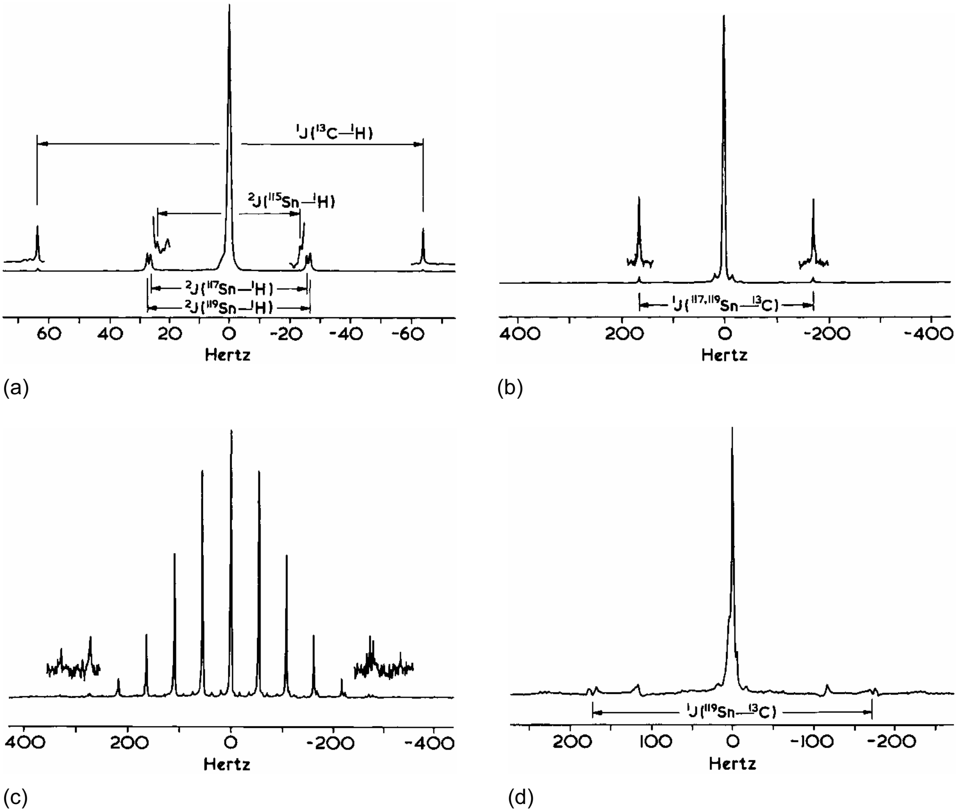


Figure 2-4 ^{1}H, ^{13}C, and ^{119}Sn NMR spectra of Me_4Sn. (a) ^{1}H Spectrum showing the characteristic satellite doublets due to $^2J(^{117}Sn–H)$ and $^2J(^{119}Sn–H)$ coupling. (b) ^{13}C Spectrum showing unresolved satellites due to $^1J(^{117/119}Sn–^{13}C)$ coupling. (c) ^{119}Sn Spectrum showing 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] sometimes 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.

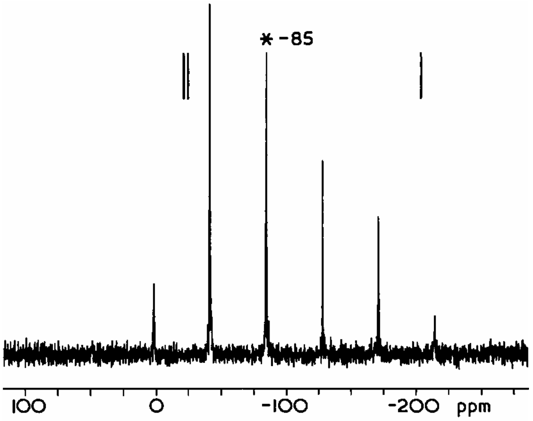


Figure 2-5 High resolution solid state ^{117}Sn NMR spectrum of $(Bu^t_2SnO)_3$ recorded on a Bruker MSL300 spectrometer operating at 106.940 MHz and a spinning speed of 4617 Hz. The isotropic shift is marked with an asterisk and the components of the shift tensor with vertical bars.

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-$Mes_2C_6H_3$)($GeBu^t_3$)Sn**:** and –2247 ppm in $Me_5C_5SnBF_4$. 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	Me_3SnCl (DMSO)	+6.5
Pr_4Sn	–17	Me_3SnBr	+128
Bu_4Sn	–12	Me_3SnI	+39
$(CH_2{=}CHCH_2)_4Sn$	–48	Me_2SnCl_2	+137
$(CH_2{=}CH)_4Sn$	–157	Me_2SnBr_2	+70
$(HC{\equiv}C)_4Sn$	–356	Me_2SnI_2	–159
Ph_4Sn	–137	$MeSnCl_3$	+21
$(PhCH_2)_4Sn$	–36	$MeSnBr_3$	–165
Cp_4Sn	–24	$MeSnI_3$	–700
$Me_5Sn^-\ Li^+$	–277	Bu_3SnCl	+141
$Ph_5Sn^-\ Li^+$	–303	Bu_3SnBr	+134
		Bu_2SnCl_2	+123
Me_3SnH	–105	$BuSnCl_3$ ($CDCl_3$	
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
		$Me_2Sn(OMe)_2$	–126
Me_3SnOH	+118	Bu_3SnOMe	+83
Cy_3SnOH	+2	$Bu_2Sn(OMe)_2$	+183
Ph_3SnOH	–86	$BuSn(OEt)_3$	+432
$(Me_3Sn)_2O$	+110		
$(Bu_3Sn)_2O$	+85	$Me_3SnOCOH$ ($CDCl_3$, 3 M)	+2.5
$(Cy_3Sn)_2O$	–8	($CDCl_3$, 0.05 M)	+150
$(Ph_3Sn)_2O$	–86		
$(Bu^t_2SnO)_3$	–84	Me_3SnNMe_2	+76
$(Bu_2SnO)_n$ (solid)	–177	$(Me_3Sn)_2NMe$	+81
$[(Bu_2SnCl)_2O]_2$	–140	$(Me_3Sn)_3$	
		$Me_2Sn(NMe_2)_2$	+59
$(Me_3Sn)_2S$	+94	$(Me_2SnNMe)_3$	+92
$(Bu_3Sn)_2S$	+82	$MeSn(NMe_2)_3$	–15
$(Ph_3Sn)_2S$	–53.7		
$(Me_2SnS)_3$	+128	$Me_3SnSnMe_3$	–109
$(Bu_2SnS)_3$	+127	$Bu_3SnSnBu_3$	–80
$(Ph_2SnS)_3$	+17	$Me_3SnSnBu_3$	–109, –82
		$Ph_3SnSnPh_3$	–144
$(Me_3Sn)_2Se$	+45	$(Ph_2Sn)_6$	–208
$(Me_3Sn)_2Te$	–60		
		Cp_2Sn	–2199
		$[(Me_3Si)_2CH]_2Sn$	+2325
		$\{[(Me_3Si)_2CH]_2Sn\}_2$	+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.

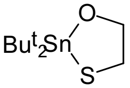
The most obvious conclusion that can be drawn concerning the chemical shift values of organotin compounds is that δ moves upfield by more than 40 ppm as the coordination of the tin increases 4 → 5 → 6 → 7. Some examples are given in Table 2-9.

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

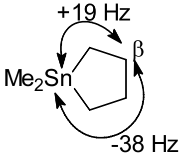
Compound	Coordn.	δ^{119}Sn	Compound	Coordn.	δ^{119}Sn
Me_4Sn	4	0	Me_5Sn^-	5	–277
Ph_4Sn	4	–137	Ph_5Sn^-	5	–303
Me_3SnCl	4	+160	Me_3SnCl,py	5	–9
$[Bu_2Sn(OCH_2)_2]_2$	5	–189	$[Bu_2Sn(OCH_2)_2]_\infty$	6	–230
$Me_2Sn(SCH_2)_2$	4	+194	$[Me_2Sn(SCH_2)_2]_\infty$	5	+94

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.

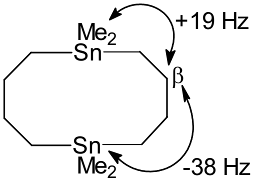
The coordination number may also be increased by autoassociation. For example, 2,2-di-t-butyl-1,3,2-oxathiastannolane (**2-1**) in $CDCl_3$ solution at 0.02 *M* concentration, when it is present principally as the monomer, shows δ +52. The signal progressively moves upfield as the concentration increases, 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 (*sp*C) –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.

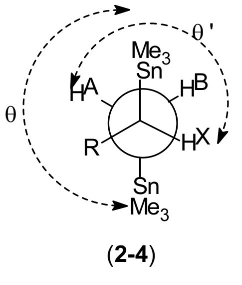
$$\theta = 0.0161[^2J(^{119}Sn,^1H)]^2 - 1.32[^2J(^{119}Sn,^1H)] + 133.4 \qquad (2\text{-}1)$$

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]

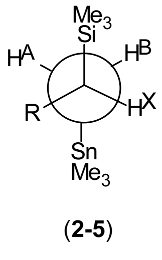
The presence of $^2J(^{119}Sn^{117}Sn)$ coupling in distannoxanes can be used to distinguish them from the corresponding tin hydroxides.[65] In the distannoxanes, the value of ^2J(SnSn) in benzene varies from 421 to 916 Hz, and this has been correlated with the Sn−O−Sn angle.

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

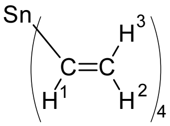
$$^{3}J(\mathrm{HH}) = 7 - \cos\theta + 5\cos 2\theta \tag{2-2}$$

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

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

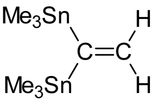
If 2-dimensional $^{119}\mathrm{Sn}/^{1}\mathrm{H}$ shift correlations can be established for long range coupling constants $^{n}J(^{119}\mathrm{Sn}/^{1}\mathrm{H})$, $n = 4$ or 6, the absolute signs of the coupling constants $J(\mathrm{SnSn})$ can be determined.[68]

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



$^{2}J(\mathrm{SnH}^{1})$ 99 Hz
$^{3}J(\mathrm{SnH}^{3})$ 100 Hz
$^{3}J(\mathrm{SnH}^{2})$ 183 Hz

(**2-6**)



$^{3}J(\mathrm{SnH})_{cis}$ 124 Hz
$^{3}J(\mathrm{SnH})_{trans}$ 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:

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

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 $h\nu$ 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, $HC\equiv CH$ 11.4, $MeC\equiv CH$ 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	rSn–C	rSn–X	Compound	rSn–X
Me_4Sn	214.4		$Mes_3Sn{-}OH$	196
$(CH_2=CH)_4Sn$	211.6		$(Ph_2Sn{-}S)_3$	237
$(HC\equiv C)_4Sn$	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
$(Me_3Sn{-}F)_\infty$	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

is often assessed by comparing the atomic separation with the sum of the van der Waals radii, when the van der Waals radius of tin is accepted to be about 217 pm.

Enthalpies of formation have been determined for about 70 organotin compounds, principally by static bomb calorimetry, and are listed in the reviews by Pilcher and Skinner,[77] Tel'noi and Rabinovich,[78] Harrison,[79] and Simões, Libman, and Slayden.[80, 81] The enthalpies of formation of the radicals of $Me_3Sn^{\bullet}$, $Et_3Sn^{\bullet}$, and $Bu_3Sn^{\bullet}$ have been measured to be ΔH°_f (g) = 130 ± 17, 99.7 ± 17.6, and -36 kJ mol^{-1}, respectively,[80] (that for $Bu_3Sn^{\bullet}$ by photoacoustic calorimetry) and from these values and the enthalpies of formation of the organotin compounds, *bond dissociation enthalpies, D*(M–L), for the reaction 2-6 can be derived from equation 2-7.

$$\mathrm{M{-}L} \rightarrow \mathrm{M}^{\bullet} + \mathrm{L}^{\bullet} \tag{2-6}$$

$$D(\mathrm{M{-}L}) = \Delta H^{\circ}_{\mathrm{f}}\,(\mathrm{M}^{\bullet}, \mathrm{g}) + \Delta H^{\circ}_{\mathrm{f}}\,(\mathrm{L}^{\bullet}, \mathrm{g}) - \Delta H^{\circ}_{\mathrm{f}}\,(\mathrm{M{-}L}) \tag{2-7}$$

Table 2-14 lists values of ΔH°_f (M-L, g)[80] and of ΔH°_f ($L^{\bullet}$, g),[81] and of *D*(M–L) derived by equation 2-7, using the above values for the enthalpies of formation of the stannyl radicals. These figures should be viewed with caution, particularly when they depend on the values of ΔH°_f(g) $Me_3Sn^{\bullet}$ and $Et_3Sn^{\bullet}$ which are accompanied by substantial uncertainties. Most of the values for organotin compounds are Simões' selected values in the NIST Chemistry Web Book.[70]

Table 2-14 Bond dissociation enthalpies (kJ mol^{-1}). [a]

M–L	ΔH°_f(M–L, g)	ΔH°_f($L^{\bullet}$, g)	*D*(M–L)
Me_3Sn–H	25	218	325
Me_3Sn–Me	–20	147	299
Me_3Sn–Et	–30	119	281
Me_3Sn–Pr^i	–47	84	263
Me_3Sn –Bu^t	–67	48	247
Me_3Sn–CH_2Ph	83	207	256
Me_3Sn–CH=CH_2	91	299	340
Me_3Sn –Ph	113	339	358
Me_3Sn–OH	–318	39	488
Me_3Sn–Cl	–317	121	570
Me_3Sn–Br	–138	112	382
Me_3Sn–I	–83	107	322
Me_3Sn–$SiMe_3$	–208	26	366
Me_3Sn–$GeMe_3$	–166	88	386
Me_3Sn–$SnMe_3$	–27	132	291
Et_3Sn–H	2	218	319
Et_3Sn–Et	–42	119	267
Et_3Sn–CH=CH_2	88	289	304
Et_3Sn–$SnEt_3$	–148	103	354
Bu_3Sn–H		218	308
Bu_3Sn–Bu	–219	74	257
Bu_3Sn–Br	–273	112	349

[a] 1 kJ = 0.2390 kcal. 1 kcal = 4.184 kJ

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3 The Stannyl Group as a Substituent

3.1 Tin as a Hydrogen Equivalent

When hydrogen in an organic molecule RH is replaced by a Main Group organometallic substituent, M, the product RM frequentily shows chemical properties similar to those of the parent, and often to an enhanced degree. The metal M can be bonded to the organic moiety through carbon or through a heteroatom, and M can be regarded as a hydrogen equivalent, or as a surrogate for hydrogen.[1]

In this context, an organotin group acts as a hydrogen equivalent. The enhanced reactivity of the R-Sn bond compared with the R–H bond that is usually observed, and which underlies most of the synthetic utility of organotin compounds, is not due to any single factor, but can be ascribed variously to the availability of *d* orbitals on the metal, the higher σ and $\sigma*$ C–Sn bond energy levels in the organotin group M (which result in strong C–Sn hyperconjugation), the longer and weaker C–Sn bonds, and the polarity of the bond, which enhances the electrophilicity of Sn and the nucleophilicity of R.

Recognition of this principle can help in the understanding of established organic reactions and the design of new ones. The theme is outlined here (Sections 3.1.1 and 3.1.2), and specific examples are dealt with in more detail in the appropriate sections of subsequent chapters.

In the equations that follow, the symbol M can represent either hydrogen or a stannyl group.

3.1.1 Chemical Reactions

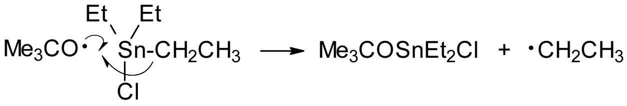
Homolytic Substitution at H or Sn

$$X^{\bullet} + \text{M-R} \longrightarrow \text{X-M} + R^{\bullet} \qquad (3\text{-}1)$$

Free radicals, such as t-butoxyl radicals, react with hydrocarbons by bimolecular homolytic substitution (S_H2) at hydrogen centres (equation 3-1, M = H), for example, equation 3-2.

$$Me_3CO^{\bullet}\ \text{H-}CH_2CH_3 \longrightarrow Me_3COH + {}^{\bullet}CH_2CH_3 \qquad (3\text{-}2)$$

Most tetraalkylstannanes similarly usually react by S_H2 at a hydrogen centre, but alkyltin halides and similar derivatives react by an S_H2 process at the tin centre, for example reaction 3-3. These reactions are useful for generating specific alkyl radicals for ESR and similar studies,[2] and are discussed in Section 5.3.6 and 11.4. Photoexcited carbonyl compounds react in the same way.



$$Me_3CO^{\bullet}\ \text{Sn}(Et)_2(Cl)\text{-}CH_2CH_3 \longrightarrow Me_3COSnEt_2Cl + {}^{\bullet}CH_2CH_3 \qquad (3\text{-}3)$$

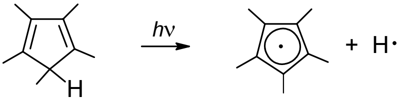
Organotin Chemistry, Second Edition. Alwyn G. Davies

ISBN: 3-527-31023-1

Photoinduced C-H or C-Sn Homolysis

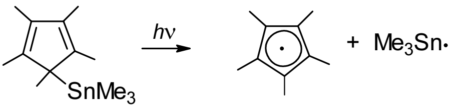
$$\text{R-M} \xrightarrow{h\nu} \text{R}\cdot + \cdot\text{M} \tag{3-4}$$

Irradiation of pentamethylcyclopentadiene with UV light generates the cyclopentadienyl radical and a hydrogen atom.



(3-5)

Cyclopentadienyltin compounds undergo the same reaction, but much more readily, to generate the cyclopentadienyl and stannyl radicals.[3] These reactions have been used for studying substitutent effects in cyclopentadienyl ([5]annulene) radicals (see Sections 9.3.3 and 20.1.1).

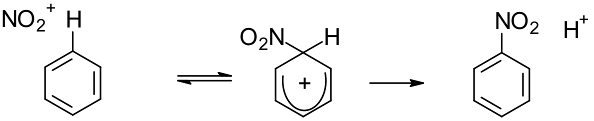


(3-6)

Electrophilic Aromatic Substitution of H or Sn

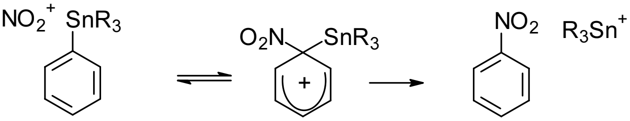
$$\text{E}^+ + \text{ArM} \longrightarrow \text{EAr} + \text{M}^+ \tag{3-7}$$

Electrophilic aromatic substitution of hydrogen occurs through the formation of a Wheland intermediate, followed by loss of a proton.



(3-8)

Arylstannanes react by the same mechanism, much more rapidly, by *ipso* substitution,[4] and this is exploited for introducing a substituent regiospecifically into an arene or heteroarene under mild conditions (see Section 7.1).[5] Whether M = H or R_3Sn, the Wheland intermediate is stabilised by symmetry-enhanced hyperconjugation (see below).

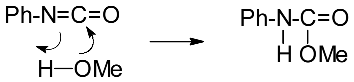


(3-9)

Nucleophilic Addition by HX or SnX

$$\text{M-X} + \text{A=B} \longrightarrow \text{M-A-B -X} \tag{3-10}$$

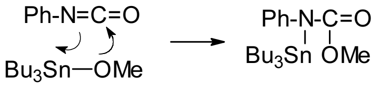
Protic reagents such as water, or alcohols, or amines, in which hydrogen is bonded to an electronegative group, will add, often reversibly, to a variety of polar multiple bonded compounds, such as aldehydes, isocyanates, or carbon dioxide, for example:



$$\mathrm{Ph{-}N{=}C{=}O} \quad \mathrm{H{-}OMe} \longrightarrow \mathrm{Ph{-}\underset{H}{N}{-}\underset{OMe}{C}{=}O}$$

(3-11)

Organotin compounds, R_3SnX, R_2SnX_2, etc., react in the same way, again much more rapidly, to give the stannyl equivalents of the protic products (see Section 14.1.3).[6] In the example shown here (equation 3-12), the addition of a tin alkoxide to an isocyanate can be part of a catalytic cycle by which polyurethanes are prepared commercially.



$$\mathrm{Ph{-}N{=}C{=}O} \quad \mathrm{Bu_3Sn{-}OMe} \longrightarrow \mathrm{Ph{-}\underset{Bu_3Sn}{N}{-}\underset{OMe}{C}{=}O}$$

(3-12)

Nucleophilic Substitution by HX or SnX

$$\mathrm{M\text{-}X} + \mathrm{A\text{-}B} \longrightarrow \mathrm{M\text{-}A} + \mathrm{B\text{-}X} \qquad (3\text{-}13)$$

Similarly the polarity of the $Sn^{\delta+}{-}X^{\delta-}$ bond enhances the nucleophilicity of X in substitution reactions.[6] A simple example is the reaction of bis(tributyltin) oxide with a dialkyl carbonate, which gives the alkyltin carbonate, which then eliminates CO_2 by the reverse of the above reaction to provide the easiest route to tributyltin alkoxides (see Section 14.1.1).

$$\begin{array}{c} \mathrm{(Bu_3Sn)_2O} \\ + \\ \mathrm{(MeO)_2C{=}O} \end{array} \longrightarrow \begin{array}{c} \mathrm{Bu_3SnOC({=}O)OMe} \\ + \\ \mathrm{Bu_3SnOMe} \end{array} \xrightarrow[-\mathrm{CO_2}]{\Delta} \mathrm{2Bu_3SnOMe} \qquad (3\text{-}14)$$

Metallation of RH and Transmetallation of R_4Sn

$$\mathrm{LiBu} + \mathrm{M\text{-}R} \longrightarrow \mathrm{BuM} + \mathrm{LiR} \qquad (3\text{-}15)$$

Acidic hydrocarbons such as alkynes or cyclopentadienes can be metallated with butyllithium. For less acidic hydrocarbons, the nucleophilicity has to be enhanced with a ligand such as TMEDA or potassium t-butoxide

$$\mathrm{CH_2{=}CH\text{-}H} + \mathrm{BuLi} \longrightarrow \mathrm{CH_2{=}CH\text{-}Li} + \mathrm{BuH} \qquad (3\text{-}16)$$

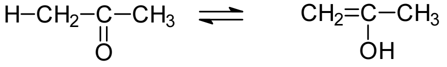
Alternatively, the stannyl derivative of the hydrocarbon can be treated with butyllithium, when the reaction occurs readily under mild conditions (see Section 22.1).

$$\mathrm{CH_2{=}CH\text{-}SnBu_3} + \mathrm{BuLi} \longrightarrow \mathrm{CH_2{=}CH\text{-}Li} + \mathrm{Bu_4Sn} \qquad (3\text{-}17)$$

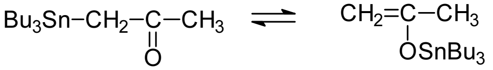
Prototropy of H–C–C=O and Stannylotropy of Sn–C–C=O

$$\mathrm{M{-}C{-}C{=}O} \rightleftharpoons \mathrm{C{=}C{-}O{-}M} \qquad (3\text{-}18)$$

Tautomeric shift of the proton (prototropy) in a carbonyl compound has its equivalent in the tautomeric shift of tin (metallotropy, stannylotropy) in an α-stannylcarbonyl compound.



$$\mathrm{H{-}CH_2{-}\underset{\overset{\|}{O}}{C}{-}CH_3} \rightleftharpoons \mathrm{CH_2{=}\underset{\overset{|}{OH}}{C}{-}CH_3} \qquad (3\text{-}19)$$



$$\mathrm{Bu_3Sn{-}CH_2{-}\underset{\overset{\|}{O}}{C}{-}CH_3} \rightleftharpoons \mathrm{CH_2{=}\underset{\overset{|}{OSnBu_3}}{C}{-}CH_3} \qquad (3\text{-}20)$$

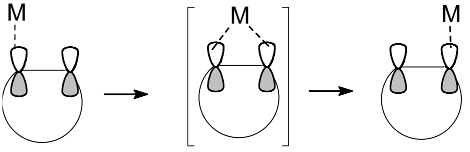
The position of the keto-enol equilibrium depends on the structure, solvent, temperature, and ligands about the metal, but in general the presence of the metal tends to increase the proportion of enolate present (see Section 14.3).

Nucleophilic Reactions of Enols C=C–OH and Stannylenolates C=C–OSn

$$\mathrm{M{-}O{-}C{=}C} + \mathrm{E}^+ \longrightarrow \mathrm{M}^+ + \mathrm{O{=}C{-}C{-}E} \qquad (3\text{-}21)$$

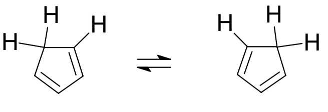
Stannyl enolates (equation 3-21, $M = R_nSnX_{3-n}$) will take part in substitution or addition reactions with electrophiles under milder conditions than will the protic enols (M = H; see Section 14.3.2).[7]

Sigmatropic Rearrangements of H and Sn

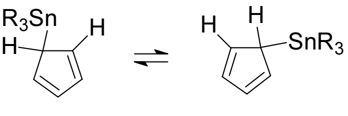


(3-22)

The sigmatropic shift of hydrogen in, for example, cyclopentadiene (equation 3-23), has its equivalent in the much faster shift of the stannyl substitutent in a stannylcyclopentadiene (equation 3-24).[8]



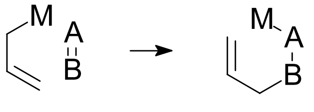
(3-23)



(3-24)

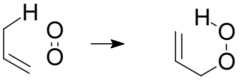
By assembling suitable ligands about the tin, it is possible to investigate the mechanism of the rearrangement in a way that is not possible with the protic parent (see Section 9.3.2).

H-Ene and Sn-Ene Reactions

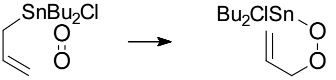


(3-25)

The principle that metals behave as hydrogen equivalents suggested that the familiar hydrogen-ene reactions (e.g. equation 3-25, M = H) should have their metallic counterparts (M = SnR_3), and indeed allylstannanes do react in the same way with the same eneophiles, and very much more rapidly (see Section 9.1.3.4),[9] for example:



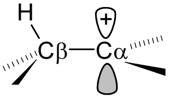
(3-26)



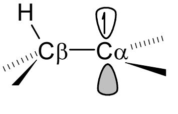
(3-27)

3.1.2 C–Sn Hyperconjugation[10]

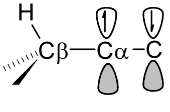
Hyperconjugation between a C–H σ bond and an unoccupied or singly occupied *p* orbital in a carbon cation (**3-1**) or radical (**3-2**), respectively, is recognised to be important, but it is usually accepted to be negligible when it involves the filled π system of an alkene or alkyne or arene (**3-3**).



(**3-1**)



(**3-2**)



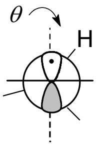
(**3-3**)

Hyperconjugation by a C–Sn σ bond (and indeed by most carbon-metal σ bonds) is much more effective than C–H hyperconjugation, and it is an important factor in determining the structure and stability of not only radicals and cations, but also of compounds with filled π systems such as allyl-, benzyl-, and cyclopentadienyl-stannanes. The importance of vinyl-, allyl-, and aryl-stannanes in organic synthesis owes much to the stabilisation of radical and cation intermediates by a stannyl substituent, and under suitable conditions this can accelerate a reaction by a factor of more than 10^{14}.

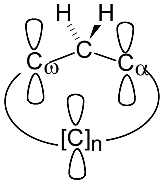
The stabilisation of carbon cations by a β-C–Si bond (the "beta effect") was the first carbon-metal hyperconjugation to be recognised, and provided the basis for extending the concept further down Group 14. The most direct evidence for hyperconjugation, however, comes from the ESR spectroscopy of radicals.

The magnitude, $a_{H\beta}$, of the hyperfine coupling to a proton in the β-position to an unpaired electron is given by the Heller-McConnell equation (3-28), where $\rho_{C\alpha}$ is the unpaired electron spin density, c_α is the LCAO coefficient on the α carbon atom, and θ is the dihedral angle between the β-C–H bond and the axis of the 2*p* orbital carrying the unpaired electron (**3-4**). In a localised alkyl radical, where $\rho_{C\alpha}$ is essentially unity, the value of *B* is about 6.0 mT (60 G), but in an ethyl radical, with free rotation about the C_α–C_β bond, the average value of θ is 45°, $\cos^2\theta$ is 0.5, and the measured value of $a_{H\beta}$ is 2.75 mT. The magnitude of the coupling thus provides a quantitative relative measure of the hyperconjugation.

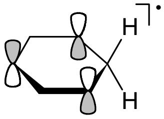
$$a_{H\beta} = \rho_{C\alpha}(A + B\cos^2\theta) = c_\alpha^2(A + B\cos^2\theta) \qquad (3\text{-}28)$$



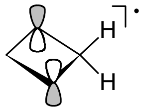
(3-4)



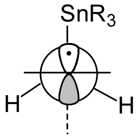
(3-5)



(3-6)



(3-7)



(3-8)

This ability of ESR to quantify hyperconjugation showed that the magnitude of the effect is subject to symmetry control, and can be enhanced or forbidden when the CH group is bonded to both ends of a conjugated system which carries the unpaired electron, in what is known as the Whiffen effect (**3-5**).[10, 11] The hyperfine coupling is now given by the equation 3-29, where c_α and c_ω are the coefficients at the two flanking ends of the π system.

$$a_{H\beta} = (c_\alpha + c_\omega)^2 (A + B \cos^2\theta) \tag{3-29}$$

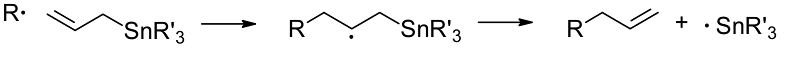
If c_α and c_ω have the same sign and magnitude, the spin density term when the two act in concert ($c_\alpha^2 + c_\omega^2 + 2c_\alpha c_\omega$) is twice what it would be if they acted independently ($c_\alpha^2 + c_\omega^2$) and the hyperfine coupling is double what would otherwise be expected. If c_α and c_ω have the opposite sign and magnitude, the spin density term is zero, and the hyperfine coupling is negligible. For example, the observed values of $a_{H\beta}$ in the cyclohexadienyl radical (**3-6**), where c_α and c_ω are both positive, and in the cyclobutenyl radical (**3-7**), where c_α and c_ω have opposite signs, are 4.77 and 0.445 mT, respectively, compared with predicted values, using the simple Heller-McConnell equation, and ignoring the Whiffen effect, of *ca.* 2.8 and *ca.* 4.2 mT, respectively.

How does C-Sn hyperconjugation fit into this pattern?

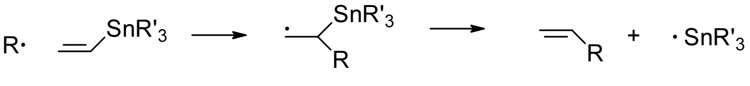
3.1.2.1 Carbon Radicals

The temperature-dependence of the ESR spectrum of the 2-stannylethyl radical shows that it is most stable in the conformation **3-8,** in which the C–Sn bond eclipses the axis of the singly occupied 2*p* orbital. The rotational barrier about the C_α–C_β bond, which is probably a reasonable measure of the C–Sn hyperconjugation, is *ca.* 8 kJ mol^{-1}.[12–14]

C–Sn Hyperconjugation in an intermediate β-stannyl radical is also important in the conjugative homolytic substitution of an allylstannane (equation 3-30)[15, 16] (see Section 9.1.3.3), and in the *ipso* substitution of a vinylstannane (equation 3-31; see Section 8.1.2).



(3-30)

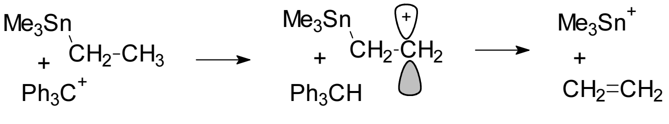


(3-31)

3.1.2.2 Carbon Cations: the β-Tin Effect

The hyperconjugative effect between a C–Sn bond and a β-positive charge is greater in a cation than in a radical, and there are many examples of the enhancement of the rate of both nucleophilic and electrophilic reactions resulting from the introduction of a stannyl substituent. The effect is general amongst the Group 14 metals and has been identified with other metals, notably mercury; it has been studied most thoroughly with organosilanes,[17, 18] and it increases down Group 14.

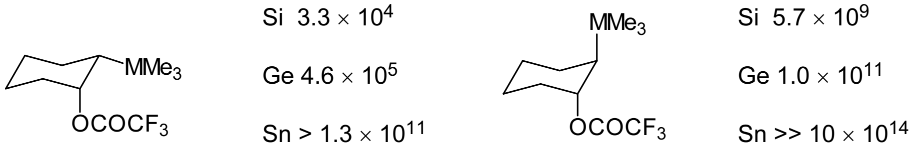
The stabilisation of a carbocation by hyperconjugation by a β-C−Sn bond is sometimes referred to simply as the β-tin effect. It is apparent in the abstraction of hydride by Ph_3C^+ BF_4^- from alkyltin compounds.[19] Tetramethyltin is unreactive, but ethyltin compounds undergo elimination.



(3-32)

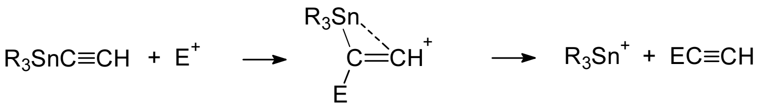
With *threo*-$Me_3SnCHMeCHDMe$, the reaction takes place with 99% *anti* stereoselectivity.[20] The stabilising effect increases down the series Si < Ge < Sn < Pb, and the rate constants for the reaction of $M(CH_2CH_3)_4$ with Ph_3C^+ at 29.8 °C (except for tin, at 25 °C) are Si 6.8×10^{-7}, Ge 4.8×10^{-5}, Sn 1.0×10^{-2}, Pb 5.9 $M^{-1}s^{-1}$.

The same effect is apparent in the rates of ionisation of the *cis*- and *trans*-*2*-metallocyclohexyl trifluoroacetates (Scheme 3-1),[21] in accord with calculations.

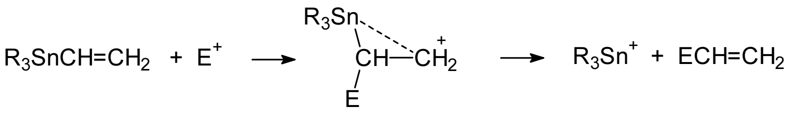


Scheme 3-1 First order rate constants for ionisation, relative to cyclohexyl trifluoroacetate; 97% CF_3CH_2OH solvent at 25.0 °C.

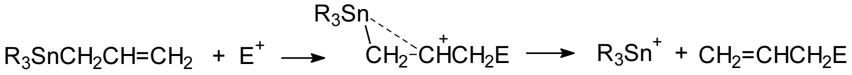
The β-effect similarly enhances the reactivity of alkynyl- (Section 8.2.2), alkenyl- (Section 8.1.2), allyl- (Section 9.1.3.2), and aryl- (Section 7.1) stannanes in their reactions with electrophiles (equations 3-33−3-36), and its effect can be recognised in other contexts such as the ene reactions of allylstannanes (Section 9.1.3.4), and the charge-transfer reactions and ring-substitution reactions of benzylstannanes.[22]



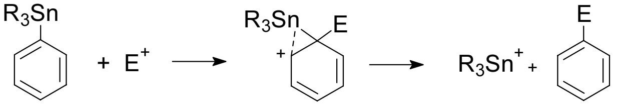
(3-33)



(3-34)



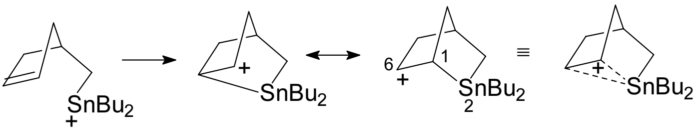
(3-35)



(3-36)

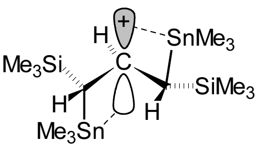
By an addition reaction similar to reaction 3-35, the first stable *sec*-alkyl carbocations have been isolated and characterised. The allylstannane $Me_3SiCH{=}CHCH(SiMe_3)(SnMe_3)$ reacts with Me_3SnCl in the presence of $ZrCl_4$ or HfF_4 to give $(Me_3Si)(Me_3Sn)CHCH^+CH(SiMe_3)(SnMe_3)\ M_2Cl_9^-$ as colourless crystals, m.p. 109 °C, that are stable under nitrogen at room temperature for days. In the crystal, the C−Sn bonds eclipse the vacant *p*-orbital, and the Sn−C bonds are lengthened [to 221.3(2) pm] and the Cα−Cβ bonds are shortened [to 142.2(8) pm] by C-Sn hyperconjugation (**3-9**). The ^{29}Si NMR chemical shift (δ +1.0) is normal for a tetraalkylsilane, but the ^{119}Sn resonance (δ +144.0) is strongly deshielded.[23]

The 2-dialkylstannanorbornyl cation (δSn +334) that has recently been reported by Müller can similarly be represented in terms of the β-tin effect (Scheme 3-2). Low temperature NMR shows that the C(1)−Sn(2) and C(6)−Sn(2) bonds remain equivalent at −40 °C, suggesting a non-classical rather than an equilibrating structure.[24] Wrackmeyer's example of intramolecular bonding between a stannyl cation and an alkyne (equation 8-53 and formulae **8-1** and **8-2**) can be modelled in a similar way.

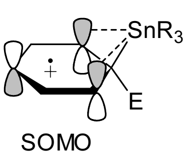


Scheme 3-2 The 2-stannanorbornyl cation.

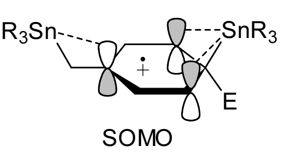
The Wheland intermediates that are formed in reaction 3-36 are important as their pentadienyl cation LUMO (**3-10**) has the appropriate symmetry for (Whiffen) enhanced hyperconjugation, which is in large part responsible for the high *ipso* reactivity, and the relative reactivities of compounds $C_6H_5MEt_3$, compared with benzene, towards electrophiles, as M varies, are approximately: (benzene 1), Si, 5×10^4, Ge 10^6, Sn 5×10^{11}, Pb 10^{20}. [25] The 4-stannylbenzyltin compounds should further benefit from both the Whiffen effect at the *ipso* position and the simple C−Sn hyperconjugation at the 4-position (**3-11**) .



(3-9)

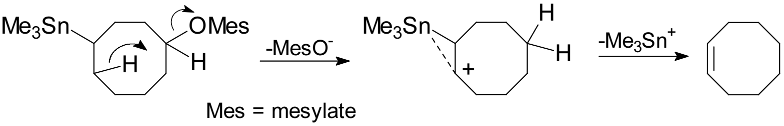


(3-10)



(3-11)

The β-tin effect is also active in promoting 1,5-hydrogen shift in cyclooctyl and cyclodecyl systems (equation 3-37).[26]



(3-37)

Mes = mesylate

3.1.2.3 Filled π-Systems

Whereas C–H hyperconjugation with a filled π-system is, at best, small, the equivalent C–Sn hyperconjugation is important in determining the structure and stability of organotin compounds. The effect is sometimes called neutral hyperconjugation, though this term might apply also to hyperconjugation in neutral radicals.

Allyltin compounds are most stable in the conformation in which the C–Sn bond lies parallel with the axis of the π-system, so that the σ–π* overlap is maximised (see Section 9.1.2).[27]

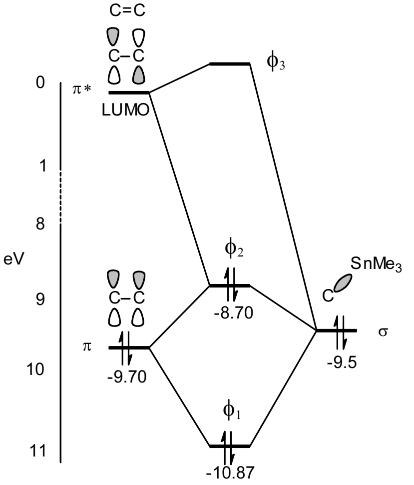
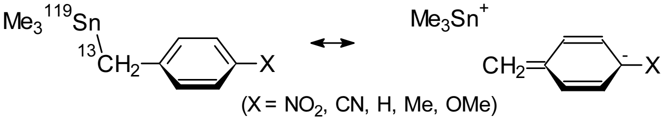


Figure 3-1 Correlation diagram for $Me_3SnCH_2CH{=}CH_2$.

The correlation diagram for hyperconjugation in allyltrimethyltin is given in Figure 3-1, with the energy levels as determined by PES (1 eV = 23.06 kcal mol^{-1} = 96.49 kJ mol^{-1}).[28-30] The C–Sn σ-orbital (–9.5 eV) interacts with the π-C=C orbital (–9.70 eV) to give two new MOs, ϕ_1 and ϕ_2. This, alone, would be a net destabilising interaction, and the conformation in which the Sn–C bond eclipsed the olefin π-orbital would be unstable, but the upper energy level is brought down by interaction of the C–Sn σ-orbital also with the vacant π^*-C=C orbital, so that the net result of the two interactions is stabilising by 2.17 eV, although the new HOMO ϕ_2 has been raised in energy above that of the original π-bond, so that the ionisation energy is reduced to 8.70 eV.

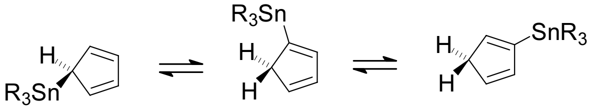
Evidence for C–Sn hyperconjugation with a filled π-system also comes from the NMR spectra of ring-substituted benzyltin compounds (**3-12**).[31, 32]



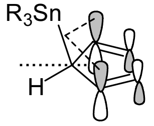
(**3-12**)

In the NMR spectra, the value of ^1J (^{119}Sn−^{13}C) correlates inversely with the ability of X to stabilise a negative charge (e.g. OMe 294, H 278, CN 239 Hz), which may be ascribed to the reduction of the C−Sn σ-bond order by hyperconjugation.

The Whiffen effect of enhanced hyperconjugation is apparent in the structures of stannylcyclopentadienes and related compounds. Consideration of the dissociation energies of the sp^2C−H, sp^3C−H, sp^2C−Sn and sp^3C−Sn bonds suggests that the vinylic isomers **3-14** and **3-15** should be more stable than **3-13**, but all structural studies indicate that in the gaseous, liquid, or solid state, the sp^3C-bonded isomer **3-13** is the most stable. Only when the metal is at the 5(sp^3)-position can the molecule benefit from C−Sn hyperconjugation with the symmetrical butadiene LUMO (**3-16**).



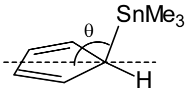
(**3-13**) (**3-14**) (**3-15**)



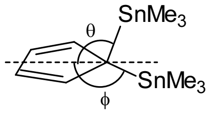
(**3-16**)

Thus trimethylstannylcyclopentadiene has the structure (**3-17**) in which the C−Sn bond is 216(1) pm, about 2 pm longer than a normal sp^3C−Sn bond, and the angle θ that the C−Sn bond forms with the ring is 111.6° rather than the 125° that would be expected for an undistorted structure.[33] Bis(trialkylstannyl)cyclopentadienes have a geminal structure, so that both C-Sn bonds can hyperconjugate, but electron diffraction and X-ray diffraction show that, in both the gas phase[33] and in the crystal,[34] for bis(trimethylstannyl)cyclopentadiene the angles θ and ϕ are about 116° and 128° (**3-18**). The reason for this lack of symmetry is not clear, but the structure of bis(trimethylsilyl)cyclopentadiene is similar;[10] in the benzenium ion, $C_6H_7^+$, the equivalent angles involving the sp^3CH_2 group are equal, both by experiment and by calculation.[35]

In the crystal, Cp_4Sn has a distorted tetrahedral structure in which the cyclopentadienyl rings are planar and η^1-bonded, and the tin is bent towards the cyclopentadienyl rings by an average of 5.1°.[34]



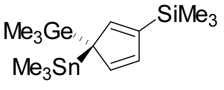
(**3-17**)



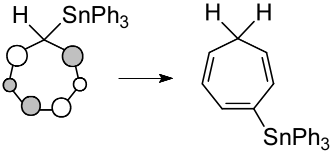
(**3-18**)

When there is a variety of metal substituents on the ring, they are arranged with the two heaviest metals on the 5-position (e.g. **3-19**), which maximises the hyperconjugation.[36]

Cycloheptatriene has an antisymmetric LUMO, so that hyperconjugation with a stannyl group on the 7-position should be symmetry-forbidden, and a stannylcycloheptatriene should be more stable with the tin on an sp^2-hybridised carbon (bond dissociation energies: H–CH_3 438, H–CH=CH_2 444, Me_3Sn–CH_3 297, Me_3Sn–CH=CH_2 327 kJ mol^{-1}). Indeed, at 160 °C, 7-triphenylstannylcycloheptatriene (**3-20**) undergoes rapid (degenerate) [1,5]-shift of tin with $E^{\#}$ 42.2 kJ mol^{-1}, and slower (non-degenerate) shift of hydrogen to give, at 160 °C, the 3-stannyl isomer (**3-21**).[37]



(**3-19**)

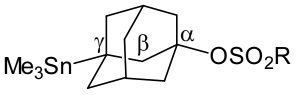


(**3-20**) (**3-21**)

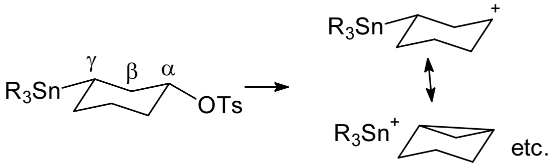
3.1.2.4 Carbon Cations: the γ-, δ-, ε-Effects

With an appropriate structure, one might expect that overlap between a C–Sn σ-orbital and a vacant *p*-orbital would be significant over a more extended framework, leading to effects further down the Greek alphabet.

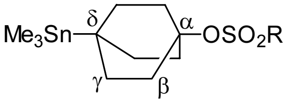
Shiner showed that the γ-trimethylstannyl substituent accelerated the solvolysis of 5-(trimethylstannyl)-1-adamantyl sulfonates (**3-22**),[38] and Lambert showed that the effect was apparent in 3-trialkylstannylcyclohexyl tosylate (**3-23**), but only when the two groups are *cis* so that the Sn–C and C–O bonds are in a W-geometry; the solvolysis in 97% CF_3CH_2OH was then accelerated by a factor of $> 2 \times 10^3$.[39]



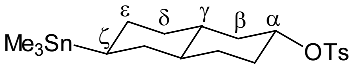
(**3-22**)



(**3-23**)



(**3-24**)



(**3-25**)

By intermolecular competition of an allylsilane and a homoallylstannane for reaction with an electrophile, the β-effect of silicon has been shown to be more effective than the γ-effect of tin in activating the double bond towards addition.[40, 41]

In the 1,4-substituted bicyclooctyl system (**3-24**), the stannyl substituent shows a substantial δ-effect,[42] but no evidence could be found for a ζ-effect in (**3-25**).[43]

3.2 Stannyl Substituent Constants

3.2.1 Electronic Effects

From photophysical measurements, the recommended "best" values for the σ^+ values of stannyl methyl groups are: Ph_3SnCH_2 –0.73(2), Me_3SnCH_2 –0.81, and $(Me_3Sn)_2CH$ –1.06.[44] However, no systematic studies of chemical reactions or physical properties of organotin compounds appear to have been carried out with the aim of determining electronic substituent constants for stannyl groups, SnXYZ. In the absence of such experimental studies, Charton's method of estimating the constants as functions of the Allred-Rochow electronegativity of the metal, and the substitutent constants of the ligands XYZ, offers a useful approach.[45] A selection of the values so derived, expressed in terms of the usual variants of σ, is shown in Table 3-1. σ_m And σ_p are Hammett's *meta* and *para* constants, $\sigma_p{}^o$ is Wepster and Taft's constant, and $\sigma_p{}^+$ and $\sigma_p{}^-$ are Hammett's constants for charged sites. No constants ($\sigma\bullet$) are available for the properties of radicals.

Table 3-1 Estimated values of electronic stannyl substituent constants.

Substituent	σ_m	σ_p	$\sigma_p{}^\circ$	$\sigma_p{}^+$	$\sigma_p{}^-$
$SnMe_3$	–0.06	0.00	–0.02	–0.13	–0.12
$Sn(CF_3)_3$	0.63	0.92	0.84	0.75	1.29
$SnEt_3$	–0.06	0.00	–0.02	–0.12	–0.12
$SnBu_3$	–0.06	0.02	0.00	–0.12	0.15
$Sn(CH{=}CH_2)_3$	0.08	0.28	0.23	0.07	0.52
$Sn(C{\equiv}CH)_3$	0.36	0.63	0.56	0.42	0.96
$SnPh_3$	0.06	0.25	0.20	0.04	0.48
$Sn(C_6F_5)_3$	0.45	0.72	0.65	0.53	1.07

The data in Table 3-1 indicate that a trialkylstannyl group should have only a weak electron attracting or electron releasing effect whatever the skeleton the group is attached to, or the phenomenon which is being studied.

In 4-trimethylstannylbenzoic acid, with an observed pK_a of 5.98 (estimated with the above data, 6.12) compared with benzoic acid, pK_a 4.20, the stannyl substituent is electron releasing. On the other hand, the ESR spectra of the trimethylstannylcyclopentadienyl radical (see Section 20.2), and of the trimethylstannylbenzene radical anion (see Section 20.4) indicate that, under these conditions, the stannyl group is weakly electron attracting.

3.2.2 Steric Effects

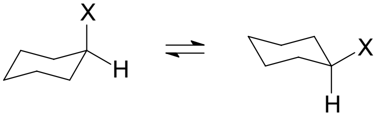
Again, the largest set of steric substituent constants for stannyl groups are estimated rather than measured ones, and are based on van der Waals radii.[45] Steric parameters ν_X are defined as $\nu_X = r_X - r_H$, where r_X and r_H are the van der Waals radii of the groups X and H in Ångstrom units. The substituent is regarded as being segmented into each atom, with its attached atoms, of the group's skeleton, and the segment is considered to have that conformation which presents its smallest face to the active site. Values of the segmental steric parameters, ν_i, where i is the segment number counting from the leading atom of the group skeleton, are given in Table 3-2.

Table 3-2 Estimated values of steric stannyl substituent constants.

Substituent	ν_1	ν_2	ν_3
$SnMe_3$	1.55	0.52	0
$Sn(CF_3)_3$		0.90	0.27
$SnEt_3$	1.55	0.52	0.52
$SnBu_3$	1.55	0.52	0.52
$Sn(CH{=}CH_2)_3$		0.57	0.57
$Sn(C{\equiv}CH)_3$		0.58	0.58
$SnPh_3$		0.57	0.57
$Sn(C_6F_5)_3$			0.57

The preference of a substituent X for the less sterically hindered equatorial position in monosubstituted cyclohexanes can be measured by variable temperature NMR spectroscopy, and expressed as an A value (equation 3.38) which is the free energy difference, in calories, between the two conformers.

$$A = -\Delta G^\circ = RT \ln K \tag{3-38}$$



(3-39)

Values for some organotin substituents and for Me_3C, Me_3Si, Me_3Ge, and Me_3Pb groups are shown in Table 3-3.[46] The steric effect of the substituent decreases down the Periodic Group, which is probably largely the result of the increasing length of the C−M bond. In 2-tributylstannyl-*N*-methylpiperidine, the value of A is only 73 cal mol^{-1}; NMR coupling constants suggest that this may be caused by conformational distortion of the ring.[47]

Table 3-3 *A* Values (kcal mol^{-1}) for Group 14 substituents.

R_3M	Me_3C	Me_3Si	Me_3Ge	Me_3Sn	Me_2PhSn	$MePh_2Sn$	Ph_3Sn	$i\text{-}Pr_3Sn$	Me_3Pb
A	4.9	2.5	2.1	1.0	1.1	1.2	1.1	1.1	0.67

MM2 Force field calculations accurately reproduce the above A value for the Me_3Sn group in trimethylstannylcyclohexane.[46, 48]

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4 Formation of the Carbon–Tin Bond[1, 2]

The principal methods for forming the carbon-tin bond involve the reaction of organometallic reagents with tin compounds (equation 4-1), the reaction of stannylmetallic compounds with organic halides (equation 4-2), the reaction of tin or tin(II) compounds with alkyl halides (equation 4-3), the hydrostannation of alkenes or alkynes (equation 4-4), the reaction of acidic hydrocarbons with Sn–O and Sn–N bonded compounds (equation 4-5), and carbonyl-forming eliminations (equation 4-6); the symbol sn represents ¼Sn.

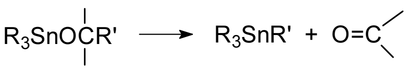
$$\mathrm{RM} + \mathrm{snX} \longrightarrow \mathrm{snR} + \mathrm{MX} \tag{4-1}$$

$$\mathrm{snM} + \mathrm{RX} \longrightarrow \mathrm{snR} + \mathrm{MX} \tag{4-2}$$

$$\mathrm{Sn\ or\ SnX_2} + \mathrm{RX} \longrightarrow \mathrm{R_2SnX_2\ or\ RSnX_3} \tag{4-3}$$

$$\mathrm{snH} + \mathrm{C{=}C\ or\ C{\equiv}C} \longrightarrow \mathrm{snC\text{-}CH\ \ or\ \ snC{=}CH} \tag{4-4}$$

$$\mathrm{R^{\delta-}H^{\delta+}} + \mathrm{snO\ or\ snN} \longrightarrow \mathrm{snR} \tag{4-5}$$



(4-6)

4.1 Reaction of Organometallic Reagents with Tin Compounds

The nucleophilic alkylation of a tin compound with an organometallic reagent is the most common route to organotin compounds.

$$4\text{-}n\mathrm{R'M} + \mathrm{R}_n\mathrm{SnX}_{4\text{-}n} \longrightarrow \mathrm{R}_n\mathrm{SnR'}_{4\text{-}n} + 4\text{-}n\mathrm{MX} \tag{4-7}$$

The metal M is commonly magnesium in a Grignard reagent, or lithium, or aluminium, and X is commonly halide. Selective partial alkylation of the tin is usually difficult to achieve, and the reaction is taken to completion to give R_4Sn (equation 4-8); if any organotin halides are present, they can be removed as the complexes which they form with dry ammonia, or as the insoluble fluorides which they form with sodium fluoride. Any subsequent dealkylation, if required, can then be achieved by the Kocheshkov reaction (Section 11.1.2).

$$4\mathrm{RMgX} + \mathrm{SnX_4} \xrightarrow{\text{ether}} \mathrm{R_4Sn} + 4\mathrm{MgX_2} \tag{4-8}$$

Thus tetraethyltin, tetrapropyltin, and tetrabutyltin are obtained from the alkylmagnesium bromide and tin tetrachloride in refluxing ether in 85–95% yield;[3, 4] tetravinyltin

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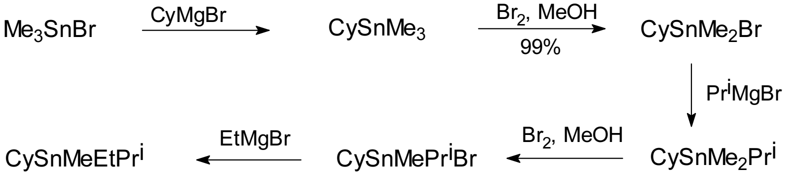
can be prepared in a similar way.[5] On the industrial scale, the reaction is carried out in toluene containing the minimum amount of ether which is necessary to allow the Grignard reagent to be formed.[6, 7] Tetramethyltin is better prepared (yield, 91%) in the higher-boiling dibutyl ether as solvent.[8] A process flow diagram for the industrial preparation of Bu_4Sn and $(Bu_3Sn)_2O$ is given in Omae's book.[9]

Grignard reagents derived from secondary and tertiary alkyl halides give rather lower yields of the products R_4Sn (e.g. s-Bu_4Sn, 65%[10]). neoPentylmagnesium chloride and tin tetrachloride (6:1) react to give a product consisting of about two thirds of trineopentyltin chloride and one third of hexaneopentylditin, but the Grignard reagent then reacts with trineopentyltin bromide to give tetraneopentyltin in 99% yield.

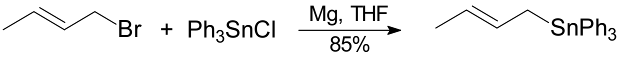
Tetraphenyltin and the corresponding tolyl and xylyl compounds are formed in 30–90% yield when the arylmagnesium halide and tin tetrachloride are heated under reflux in THF for 12 h.[11]

Similar reactions between Grignard reagents and organotin halides give tetraorganotin compounds with mixed organic groups. This is illustrated by the preparation of (methyl)(ethyl)(isopropyl)(cyclohexyl)tin:[12]



(4-9)

If there are problems in preparing the Grignard reagent, the reaction can be carried out under the Barbier conditions, where a mixture of the organic halide and the tin halide is treated with magnesium. For example, under normal conditions, crotyl bromide reacts with magnesium to give largely octa-2,6-diene, but a mixture of crotyl bromide and triphenyltin chloride in THF reacts with magnesium to give crotyltriphenyltin in 85% yield.[13]



(4-10)

Sn-O Bonded compounds, including the alkoxides R_3SnOR' [14] and the insoluble dialkyltin oxides $(R_2SnO)_n$, can be used in place of the halides. For example, allyltributyltin, which is a useful reagent in organic synthesis, can be prepared from allylmagnesium bromide and bis(tributyltin) oxide.[15]

$$CH_2{=}CHCH_2MgBr + (Bu_3Sn)_2O \xrightarrow[94\%]{} Bu_3SnCH_2CH{=}CH_2 \qquad (4\text{-}11)$$

A general method makes use of Barbier conditions combined with ultrasonication. The organic halide, RX, bis(tributyltin) oxide, and magnesium powder are caused to react in THF, in the presence of 1,2-dibromoethane, in an ultrasonic cleaning bath at about 35 °C for one hour.[16] The presence of a surface-active compound in the bath assists cavitation. The reactions proceed in good yield with alkyl, vinyl, allyl, benzyl, aryl, and heteroaryl halides (usually bromides).

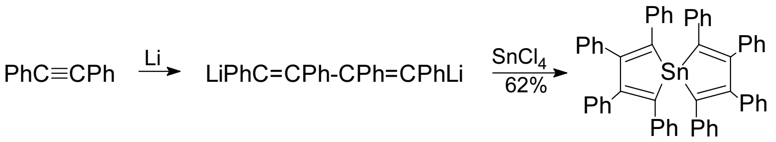
Tin halides can be alkylated also with organoaluminium reagents.[17] This method is seldom used in the laboratory, but it has been recommended as a method for removing organotin residues, R_3SnX, from reaction mixtures.[18] On the industrial scale, it has been used for making tetrabutyltin and tetraoctyltin, as the trialkylaluminum reagents are cheap and can be used in the absence of a solvent.[6, 7] The $AlCl_3$ and organotin halide which is formed may form a complex, and incomplete alkylation may occur, but this can be avoided by adding an amine or ether which complexes more strongly with the $AlCl_3$. By controlling the ratio of reagents, clean partial alkylation can be achieved (e.g. Et_4Sn, 97% yield, Et_3SnCl, 94% yield).

$$4R_3Al + 3SnCl_4 \longrightarrow 3R_4Sn + 4AlCl_3 \tag{4-12}$$

Organolithium compounds have the advantages over Grignard reagents that they can be prepared from reagents other than halides, many are commercially available, and they have a higher reactivity which can be further enhanced by adding a ligand which breaks up the oligomeric structure of the $(RLi)_n$, and increases the nucleophilicity of R. Some examples are shown in equations 4-13[19], 4-14,[20] and 4-15.[21]

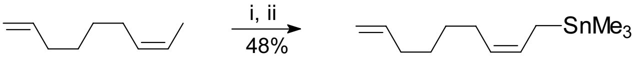
$$Bu^tLi + (Bu^t_2SnO)_3 \xrightarrow[99.6\%]{} Bu^t_3SnOLi \tag{4-13}$$

$$(Me_3Si)_3CH \xrightarrow{MeLi} (Me_3Si)_3CLi \xrightarrow{Me_3SnBr} (Me_3Si)_3CSnMe_3 \tag{4-14}$$



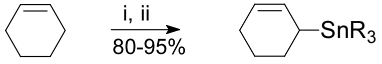
(4-15)

If the required reagent RLi cannot be obtained by lithiation of RH with, say, butyllithium, the metallation can sometimes be achieved by using a mixture of butyllithium and potassium t-butoxide (Schlosser's reagent or the LIKOR reagent) (e.g. equations 4-16 [22] and 4-17[13]). The precise nature of the reagent is uncertain, but it is probably best represented as the organopotassium reagent, BuK.



(4-16)

i $BuLi/KOBu^t$ ii Me_3SnCl



(4-17)

i. $BuLi/KOBu^t$ ii. R_3SnCl R = Me, Bu, Ph

Cyclopentadienyl-tin(II) and -tin(IV) compounds can be made from cyclopentadienyl sodium, and ethynyltin(IV) compounds have been obtained by treating a mixture of the alkyne and tin halide with a tertiary amine (equation 4-18).[23]

$$n\,PhC{\equiv}CH + SnCl_4 \xrightarrow{Bu_3N} (PhC{\equiv}C)_nSnCl_{4-n} \xrightarrow{R'CH=O} PhC{\equiv}CCH(OH)R' \tag{4-18}$$

There are a number of reports of the preparation of organotin compounds under Wurtz conditions, in which a mixture of the organic halide (RX) and tin halide is treated with metallic sodium (equation 4-19).[24] This method can be used for both alkyl and aryl compounds, and involves the formation of RNa as an intermediate. However, the formation of the RSn bond is accompanied by reduction of RX to RR and of tin(IV) to tin(II).[13] These problems can be reduced by working at high dilutions and with diorganotin dihalides rather than tin tetrahalides, or by dividing the reaction into its two constituent steps (equations 4-20 and 4-21),[25] but few examples of the use of this method are to be found in the recent literature.

$$4RX + SnX_4 + 8Na \longrightarrow R_4Sn + 8NaX \qquad (4\text{-}19)$$

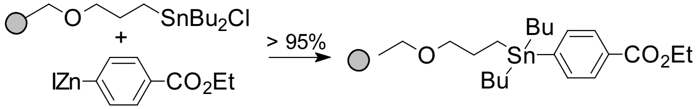
$$4RX + 8Na \longrightarrow 4RNa + 4NaX \qquad (4\text{-}20)$$

$$4RNa + SnX_4 \longrightarrow R_4Sn + 4NaX \qquad (4\text{-}21)$$

Frankland's preparation of the first organotin compound used diethylzinc as a reagent, but, as in most syntheses, Grignard reagents have largely supplanted the zinc reagents, which continue to be used only for those compounds in which the organic group carries a functional substituent which might be sensitive to a Grignard reagent. Thus Simmons and Smith's iodomethylzinc iodide (equation 4-22),[26] and compounds related to Reformatsky's α-bromoesters (equation 4-23)[27] have been used for making functionally substituted organotin compounds, and a chlorostannyl resin has been arylated with a variety of functionally-substituted arylzinc halides (equation 4-24).[28]

$$ICH_2ZnI + Me_2PhSnI \xrightarrow[94\%]{} Me_2PhSnCH_2I \qquad (4\text{-}22)$$

$$BrZnCH_2CONEt_2 + Ph_3SnCl \longrightarrow Ph_3SnCH_2CONEt_2 \qquad (4\text{-}23)$$



(4-24)

Organotin compounds R_nSnX_{4-n} are speciated in the analysis of environmental samples by alkylation to the tetraalkylstannanes such as R_nSnEt_{4-n}, which are then identified by GLC/MS or HPLC/MS, and tetraalkylborates (e.g. $NaBEt_4$), which are stable to water, are often used for this purpose in preference to Grignard reagents (Section 23.3).[29–31]

There are a few examples of trifluoromethyl-, or fluorovinyl-, or allyl-trimethylsilanes being used to alkylate $SnCl_4$, Bu_3SnCl, or $(Bu_3Sn)_2O$.[32–34]

The organic derivatives of various other metals have been used on occasion (e.g. Cu, Hg, Ga, Tl, Pb) for making the C-Sn bond, usually because the reactants were available *via* a hydrometallation reaction (e.g. Al, Zr [35]), or because they were constitutionally (e.g. CF_3Hg)[36] or stereochemically (e.g. $R_2C{=}CRCu$) more stable than the magnesium or lithium analogues. The arylcopper(I) compounds also have the characteristic that they will react with diorganotin dichlorides by monoarylation to give $R_2SnArCl$, whereas the magnesium and lithium compounds usually give R_2SnAr_2.[37] The Kocheshkov reaction, in which an alkyltin compound alkylates a tin halide (e.g. equation 4-25), can be placed in the same category as the above reactions, but the focus of interest is usually the formation of the tin-halogen bond, and these reactions are discussed in Section 11.1.2.

$$R_4Sn + SnCl_4 \longrightarrow 2R_2SnCl_2 \qquad (4\text{-}25)$$

4.2 Reaction of Stannylmetallic Compounds with Organic Electrophiles

The reaction of a stannylmetallic compound with an organic halide or other organic electrophile (e.g. equation 4-26) is a versatile process.

$$R_3SnM + R'X \longrightarrow R_3SnR' + MX \tag{4-26}$$

Commonly, the metal M is lithium, when the reagents have been described as stannylanionoids. These reagents can readily be prepared from the tin halides and metallic lithium (equation 4-27), or the distannanes and an alkyllithium (equation 4-28), or the tin hydrides and LDA (equation 4-29) (see Section 19.1.1).

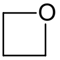
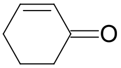
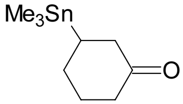
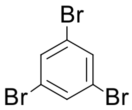
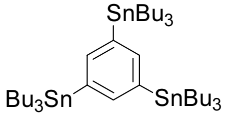
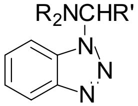
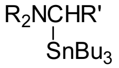
$$R_3SnX + 2Li \xrightarrow{THF} R_3SnLi + LiX \tag{4-27}$$

$$R_3SnSnR_3 + R'Li \longrightarrow R_3SnLi + R_3SnR' \tag{4-28}$$

$$R_3SnH + LiNPr^i_2 \longrightarrow R_3SnLi + HNPr^i_2 \tag{4-29}$$

Some typical reactions of stannylanionoids which result in the formation of a C–Sn bond are shown in Table 4-1. Primary and secondary alkyl halides react mainly by substitution, but tertiary alkyl halides give mainly elimination. Aryl halides can also give arynes through elimination reactions.

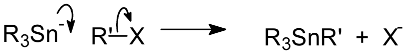
Table 4-1 Trialkylstannanes, R_3SnR', prepared from stannylmetallic compounds.

Reactant, R_3SnM	Reactant, R′X	Product	Ref.
Me_3SnLi	CCl_4	$(Me_3Sn)_4C$	38
$Bu_3SnMgCl$	$CH_2{=}O$	Bu_3SnCH_2OH	39
Bu_3SnLi	$C_7H_{15}CH{=}O$	$C_7H_{15}CH(OLi)SnBu_3$	40
$Bu_3SnMgCl$		$Bu_3SnCH_2CH_2OH$	41
$Bu_3SnMgCl$		$Bu_3SnCH_2CH_2CH_2OH$	41
Me_3SnLi			42
Bu_3SnLi	$N(CH_2CH_2CH_2Cl)_3$	$N(CH_2CH_2CH_2SnBu_3)_3$	43
Bu_3SnLi			44
Bu_3SnLi		 $R_2N\underset{SnBu_3}{\underset{\vert}{C}}HR'$	45

The kinetics of the reaction of Me_3SnLi and Vin_3SnLi with alkyl halides,[46] and of Bu_3SnK with s- and t-butyl bromides and iodides,[47] have been determined by the stopped flow method, and the reaction of $Ph_3Sn^- Bu_4N^+$ (generated by cathodic reduction of $Ph_3SnSnPh_3$) has been followed potentiometrically.[48] Second order kinetics are observed. The reactions are very fast; typical rate constants are, for $Ph_3Sn^- Bu_4N^+$ and EtBr in $(MeOCH_2)_2$, 22 M^{-1} s^{-1}, and for Me_3SnLi and BuCl in THF at 20 °C, 0.74 M^{-1} s^{-1}. The reactivity of the anionoids decreases down the Group, and relative rate constants towards alkyl bromides are Ph_3Ge^- 5.9, Ph_3Sn^- 1, Ph_3Pb^- 2.4×10^{-4}.

The rates of the reactions, however, depend on the structure of the stannyl anion and of the organic substrate, on the nature of the solvent, and on the presence or absence of radical initiators, particularly light. Four principal mechanisms have been identified.

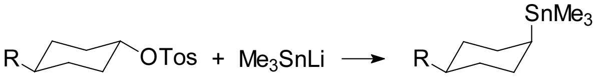
S_N2 at Carbon[46, 49–51]



$$R_3Sn^- \quad R'{-}X \longrightarrow R_3SnR' + X^-$$

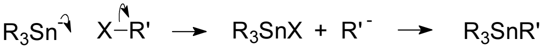
(4-30)

These reactions involve inversion at the reaction centre, for example:



(4-31)

S_N2 at Halogen[50, 52, 53]

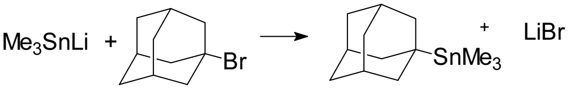


$$R_3Sn^- \quad X{-}R' \longrightarrow R_3SnX + R'^- \longrightarrow R_3SnR'$$

(4-32)

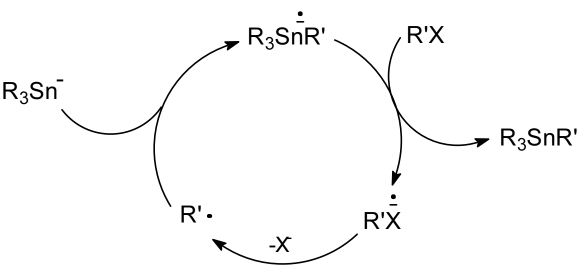
The tin halide and carbanion which are formed can react within the solvent cage to give the tetraalkyltin.

These reactions can occur with bridgehead halides which are unreactive by the S_N2 mechanism, for example:



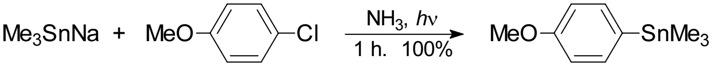
(4-33)

$S_{RN}1$[46, 53]

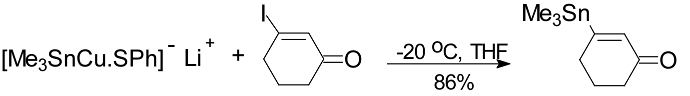


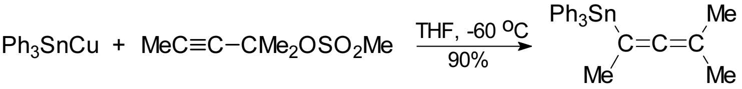
Scheme 4-1 $S_{RN}1$ reaction of stannyl anions.

This mechanism occurs particularly with aryl halides, phosphates, and ammonium salts, and with geminal dihalides. The reactions can be stimulated by light, or inhibited by *p*-dinitrobenzene, and aryl halides can react exclusively by the $S_{RN}1$ mechanism or by S_N2 on halogen, depending on the structures of R_3Sn and of ArX, and on the presence or absence of light. For example, *p*-methoxychlorobenzene shows no reaction with Me_3SnNa in liquid ammonia in the dark, but on irradiation at 350 nm it gives *p*-methoxyphenyltrimethyltin.[53]


(4-34)

For some of these reactions, the tin-copper reagents (equations 4-35 and 4-36) have some advantages.[54, 55] Thus, if reaction 4-35 is attempted with trimethylstannyllithium, 42% of the starting material is recovered, and only 32% of the required product is obtained.[54]


(4-35)



$$Ph_3SnCu + MeC{\equiv}C{-}CMe_2OSO_2Me \xrightarrow[90\%]{THF,\ -60\ ^{o}C} (Ph_3Sn)(Me)C{=}C{=}CMe_2$$

(4-36)

Non-chain Electron Transfer

$$R_3Sn^- + R'X \longrightarrow [R_3Sn\bullet + R'X^{\bullet-}] \longrightarrow [R_3Sn\bullet + R'\bullet + X^-] \longrightarrow R_3SnR' + X^- \qquad (4\text{-}37)$$

This mechanism has been proposed for the reaction of Bu_3SnK with s- and t-butyl bromides and iodides, in which a species absorbing at 400 nm, and believed to be the $R_3Sn\bullet$ radical, has been observed.[47] Proof of the involvement of radicals is given by the observation of a ^{119}Sn CIDNP effect in the reaction involving n-butyl bromide and iodide. The signal for Bu_4Sn shows strong emission, and that for the small amount of $Bu_3SnSnBu_3$ that is formed by the pairing of two $Bu_3Sn\bullet$ radicals shows enhanced absorption.[56]

4.3 Reaction of Tin or Tin(II) Compounds with Alkyl Halides[57]

Frankland's preparation of the first organotin compound involved heating ethyl iodide with metallic tin.[58]

$$2EtI + Sn \longrightarrow Et_2SnI_2 \qquad (4\text{-}38)$$

Despite the obvious attractions of this method (the direct reaction), particularly for industrial purposes, it is not widely used. Smith and Rochow[59, 60] showed that Me_2SnCl_2 and Me_2SnBr_2 could be prepared by passing the vapour of the appropriate methyl halide through molten tin, and that the reaction was catalysed by metallic copper.

$$2MeCl + Sn \longrightarrow Me_2SnCl_2 \qquad (4\text{-}39)$$

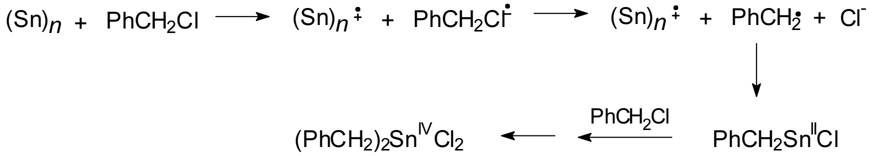
Under similar conditions, ethyl chloride gave only low yields of diethyltin dichloride, and attempts to alkylate tin, either in a sealed tube or under these flow conditions, with butyl chloride, butyl bromide, or bromobenzene were unsuccessful.

A similar process has been patented for extracting tin from ores and slags. For example, cassiterite ore is roasted, then reduced with hydrogen and heated in a stream of methyl chloride gas. 44% Of the tin can be recovered as the halides Me_nSnCl_{4-n} ($n = 1-3$), and this is raised to 60–75% if copper is added.[61]

Allyl bromide or benzyl chloride and various ring-substituted benzyltin chlorides however react with metallic tin in refluxing toluene (110 °C) to give good yields of the corresponding diorganotin dihalide (e.g. equation 4-40);[62] the tin can be activated with mercuric chloride and triethylamine.[63] Pentamethylcyclopentadienyl bromide similarly reacts with tin to give the pentamethylcyclopentadienyltin bromides.[64]

$$2PhCH_2Cl + Sn \xrightarrow[88\%]{PhMe,\ 111\ ^{o}C} (PhCH_2)_2SnCl_2 \qquad (4\text{-}40)$$

The reaction between benzyl chloride and tin is inhibited by nitrobenzene, suggesting that it involves electron transfer, and a reasonable mechanism for the formation of the tin-carbon bonds is shown in equation 4-41. A direct insertion of tin into the carbon-halogen bond has been proposed for the reaction of tin with a mixture of methyl iodide and water.[65]



(4-41)

A wide variety of additives have been proposed for promoting the reaction between the alkyl halides and tin. The extensive Japanese work in this field, by S. Matsuda, H. Matsuda, I. Omae, and others, which is published largely in Japanese in *Kogyo Kagaku Zasshi*, is summarised in English in Omae's book.[9]

The reactivity usually follows the sequence RI > RBr > RCl, and MeX > EtX > PrX > higher RX. The principal classes of catalyst are (i) a metal or metal halide in the presence of a ligand or polar solvent, (ii) the compounds R_3M or $R_4M^+ X^-$, where M = N, P, or Sb, and (iii) potassium iodide and a crown ether in a polar solvent.

A recent patent describes the preparation of organotin oxides by the gas phase reaction between primary alcohols and finely divided tin in the presence of a Lewis acid.[66] The alcohol vapour is passed under reduced pressure over a mixture of tin powder (200–400 mesh) and the catalyst ($SnCl_2$, $AlCl_3$, $ZnCl_2$ etc.) at 200–400 °C. For example, methanol was passed over 325 mesh tin powder and an $SnCl_2$ catalyst at 280 °C, giving a 91% yield of Me_2SnO in about 2 h. The preparation of Bu_2SnO, $(Me_3Sn)_2O$, $(Bu_3Sn)_2O$, and MeSn(O)OH by similar reactions is reported. Again, an electron-transfer mechanism can be written for these reactions.

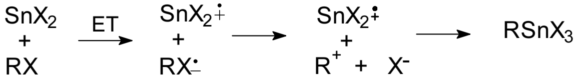
Trialkyltin chlorides, R_3SnCl (R = butyl, octyl, heptyl, and decyl), can also be prepared by the reaction between tin and the alkyl halide in a molten quaternary ammonium halide, R'_4NX.[67] The reactivity of the alkyl halides RX follows the usual sequence for their reaction with nucleophiles, and the Sn-C bonds are thought to be formed by reaction of the tin(II) nucleophiles $R_nSnBr_{5-n}^-$ with the RX.[68]

Following early work with benzyl halides,[62] a number of examples have been published of the reaction of tin with allyl halides in aqueous emulsions, to give allyltin halides which react *in situ* by carbonyl addition, often with ultrasonic assistance.[69–71]

Less work has been reported on the analogous reaction between tin(II) compounds and alkyl halides (equation 4-42).

$$RX + SnX_2 \longrightarrow RSnX_3 \qquad (4\text{-}42)$$

Again, it is likely that an electron transfer reaction (equation 4-43) is involved.



$$\begin{array}{c} SnX_2 \\ + \\ RX \end{array} \xrightarrow{ET} \begin{array}{c} SnX_2^{\cdot +} \\ + \\ RX^{\cdot -} \end{array} \longrightarrow \begin{array}{c} SnX_2^{\cdot +} \\ + \\ R^{+} + X^{-} \end{array} \longrightarrow RSnX_3 \qquad (4\text{-}43)$$

Reactivity follows the sequence RI > RBr > RCl, and $SnI_2 > SnBr_2 > SnCl_2$. The uncatalysed reaction of methyl iodide with stannous iodide at 160 °C has been reported,[72] but usually a catalyst is necessary. These catalysts are similar to those which are used for the "direct" reactions, and include dialkyl sulphides, amines, ammonium and phosphonium salts, and copper(II). The trialkylstibines appear to be particularly effective and the compounds $RSnX_3$, R = C_1 to C_{18}, have been prepared by this method. A similar reaction with the α,ω-dihalides, $X(CH_2)_nX$, $n = 4-5$, provides access to functionally substituted tetraorganotin compounds, but the aryl halides are unreactive.

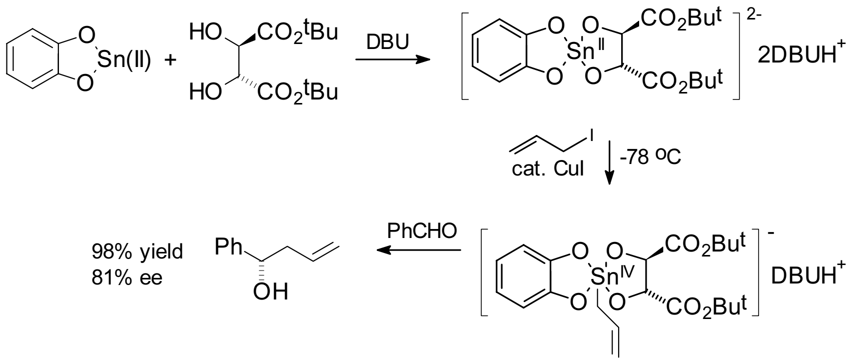
Allyl, propargyl, and cyclopentadienyl halides are more reactive than alkyl halides, and LiBr,[73] Cu(I),[74] Cu(II),[75, 76] and $R_4N^+ X^-$ salts have been used as promoters.[73, 74, 76]

There have been two recent developments that suggest that reactions of these types may be more widely used in the future.

First, the stannylene $:Sn[N(TMS)_2]_2$, which readily takes part in electron-transfer reactions, has been used to prepare compounds $RSnX[N(TMS)_2]_2$, where R = alkyl, allyl, allenyl, hexynyl, phenyl, or styryl, and then these can be used in further reactions such as Stille coupling (Section 22.2).[77–79]

$$Bu{-}{\equiv}{-}I + :Sn[N(TMS)_2]_2 \xrightarrow[30\ min]{THF/RT} Bu{-}{\equiv}{-}SnI[N(TMS)_2]_2 \qquad (4\text{-}44)$$

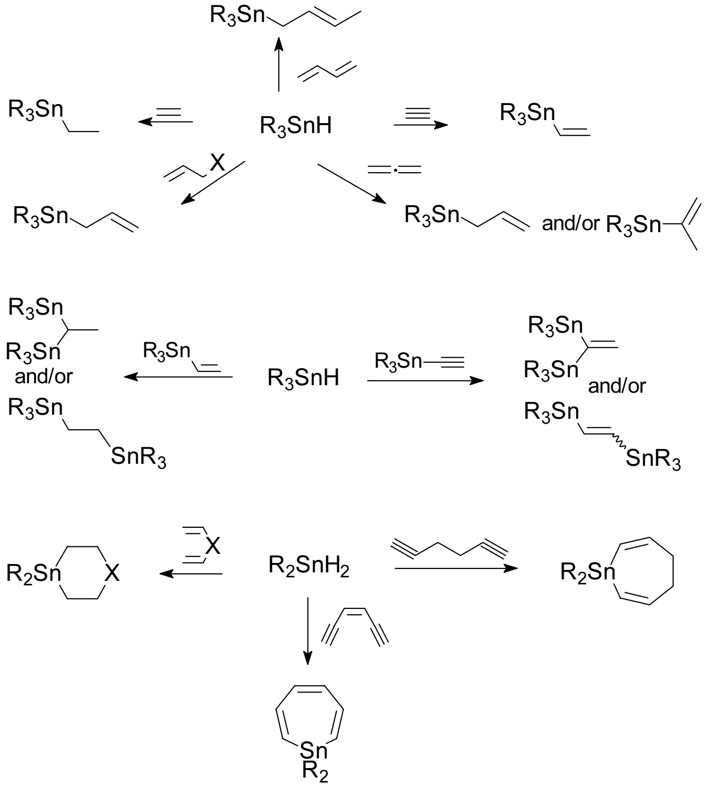
Second, if tin(II) catecholate is ligated by an optically active dialkyl tartrate, it will react with an allylic bromide or iodide and an aldehyde, in the presence of CuI as catalyst, to give the optically active homoallylic alcohol. The enantioselectivity is highest when the alkyl groups of the tartrate are bulky (t-butyl or cyclohexyl). Aromatic aldehydes give higher enantioselectivities than do aliphatic aldehydes, and the reaction is also successful with α-carbonylketones.[74]



(4-45)

4.4 Hydrostannation of Alkenes and Alkynes[80]

The hydrostannation of an alkene or alkyne by an organotin hydride provides a versatile way of preparing alkyl- and vinyl-tin compounds. Variations on this general theme are illustrated in Scheme 4-2.



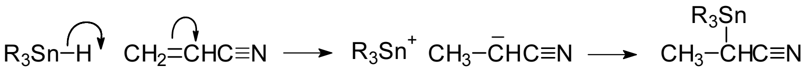
Scheme 4-2 Hydrostannations.

This section deals mainly with the hydrostannation of alkenes, and further details can be found in the appropriate subsequent sections on, for example, stannyl radicals (Section 20.1.3), and stannacycloalkanes (Chapter 10). The hydrostannation of alkynes, allyl compounds, and allenes, is dealt with in Sections 8.1.1 and 10.1. which cover the vinyl- and allyl-tin compounds which are produced.

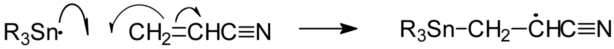
Four mechanisms are recognised for hydrostannation reactions, the tin hydride acting as a source of a tin-centred radical, $R_3Sn^•$, electrophile, R_3Sn^+, or nucleophile, R_3Sn^-, or as a ligand for a metal, R_3SnMH; the mechanism that is followed depends, *inter alia*, on the nature of the groups R and of the alkene, and on the absence or presence of catalysts. There are a few examples of reactions being carried out with a tin hydride in the presence of a Lewis acid such as ZrX_4 or HfX_4;[81] the detailed mechanisms of these reactions are not clear, but the various reasonable models all involve electrophilic tin, and these reactions are included here under that heading.

Electrophilic Tin (R_3Sn^+)

In 1956, van der Kerk and his colleagues showed that triorganotin hydrides will often add to alkenes in the absence of any catalyst in the range 60–100 °C.[82–84] When the alkene carries a strongly electron attracting group (*e.g.* acrylonitrile, alkylidenemalononitriles), the reactions may follow a polar mechanism (equation 4-46). For example, trimethyltin hydride reacts with acrylonitrile at 50–75 °C to give 25% of the α-adduct and 20% of the β-adduct. The amount of α-adduct increases in a polar solvent and results from the polar process in which nucleophilic attack of hydrogen appears to be rate-determining, but in the presence of AIBN as a radical initiator, only the β-adduct is formed, in a radical chain process (equations 4-47 and 4-48).[85, 86]



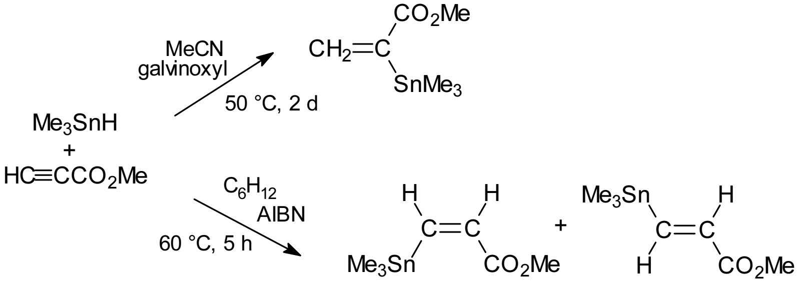
$$R_3Sn{-}H \quad CH_2{=}CHC{\equiv}N \longrightarrow R_3Sn^+ \quad CH_3{-}\bar{C}HC{\equiv}N \longrightarrow CH_3{-}\overset{R_3Sn}{\overset{|}{C}}HC{\equiv}N \qquad (4\text{-}46)$$



$$R_3Sn\cdot \quad CH_2{=}CHC{\equiv}N \longrightarrow R_3Sn{-}CH_2{-}\dot{C}HC{\equiv}N \qquad (4\text{-}47)$$

$$R_3Sn{-}CH_2{-}\dot{C}HC{\equiv}N + R_3SnH \longrightarrow R_3Sn{-}CH_2{-}CH_2C{\equiv}N + R_3Sn\cdot \qquad (4\text{-}48)$$

A clean separation between the homolytic and heterolytic processes can be achieved with trimethyltin hydride and methyl propiolate.[87] In the dark at 50 °C, with acetonitrile as solvent, and galvinoxyl present as a radical inhibitor, only methyl 2-trimethylstannylacrylate is formed, but at 60 °C in cyclohexane, with AIBN as a radical initiator, a 4:1 mixture of methyl *Z*- and *E*-2-trimethylstannylacrylate is obtained (equation 4-49).



(4-49)

The reaction of terminal olefins can be catalysed by a small amount of the corresponding trialkylaluminium compound (or of Bu^i_2AlH which is alkylated by the olefin).[88] The mechanism of these reactions has not been studied in detail, but there appears to be no evidence for the involvement of free radicals, and the steps which are believed to be involved are shown in equations 4-50–4-52 (sn = 1/4Sn, al = 1/3Al).

$$\text{sn}{-}H + \text{al}{-}CH_2{-}CH_2R \longrightarrow \text{sn}{-}CH_2{-}CH_2R + \text{al}{-}H \qquad (4\text{-}50)$$

$$\text{al}{-}H + CH_2{=}CHR \longrightarrow \text{al}{-}CH_2{-}CH_2R \qquad (4\text{-}51)$$

$$\text{sn}{-}H + CH_2{=}CHR \longrightarrow \text{sn}{-}CH_2{-}CH_2R \qquad (4\text{-}52)$$

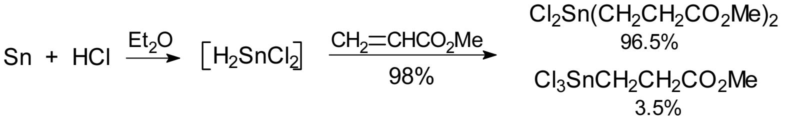
In the presence of $ZrCl_4$ or $HfCl_4$, alkynes react with Bu_3SnH or Bu_2SnH_2 at 0 °C by *anti* addition.[81] Plausible mechanisms involve direct electrophilic hydrostannation via a tin hydride-Lewis acid complex, or initial electrophilic hydrozirconation followed by transmetallation.

Nucleophilic Tin (R_3Sn^-)

Little attention has been paid in recent years to the heterolytic process in which the tin acts as an electrophile, but in 1976 a new route to functionally-substituted organotin compounds was developed by the AKZO company, making use of the chlorotin hydrides Cl_2SnH_2 and Cl_3SnH as intermediates, where the tin acts as a nucleophile. If HCl gas is passed through a suspension of $SnCl_2$ in ether, solvated $HSnCl_3$ is formed, which will add to an α,β-unsaturated carbonyl compound, C=C–CX=O, to give the adduct $Cl_3Sn–C–CH–CX=O$ (e.g. equation 4-53). Acrylic acid, esters, and amides, vinyl ketones (but not acrolein), propiolic acid, and acrylonitrile can be used, and HBr and HI give similar reactions. The $HSnX_3$ can be preformed, or the alkene can be present in the initial reaction mixture, in which case a hydrocarbon solvent can be used.[89–91]

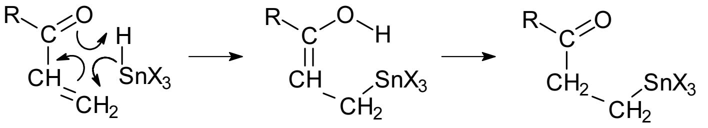
$$SnCl_2 + HCl \xrightarrow{Et_2O} [HSnCl_3] \xrightarrow{CH_2{=}CHCO_2Me} Cl_3SnCH_2CH_2CO_2Me \qquad (4\text{-}53)$$

Similar reactions occur with metallic tin, to give, via Cl_2SnH_2, mainly the adducts $Cl_2Sn(C–CH–CX=O)_2$ (e.g. equation 4-54). The thioglycollates derived from these chlorides, for example $(BuOCOCH_2CH_2)_2Sn(SCH_2CO_2Oct^i)_2$, can be used as stabilisers for PVC.[92] Stabilisers that contain the group $ROCOCH_2CH_2Sn$ are referred to as *ester-tins*.



$$Sn + HCl \xrightarrow{Et_2O} [H_2SnCl_2] \xrightarrow[98\%]{CH_2{=}CHCO_2Me} \begin{array}{c} Cl_2Sn(CH_2CH_2CO_2Me)_2 \\ 96.5\% \\ Cl_3SnCH_2CH_2CO_2Me \\ 3.5\% \end{array} \qquad (4\text{-}54)$$

The tin always is introduced at the β-position, and thus is playing the part of a nucleophile rather than an electrophile. No reaction occurs with isophorone, which is a cyclohexenone, and hence the reaction is suggested to involve a cyclic mechanism (equation 4-55).

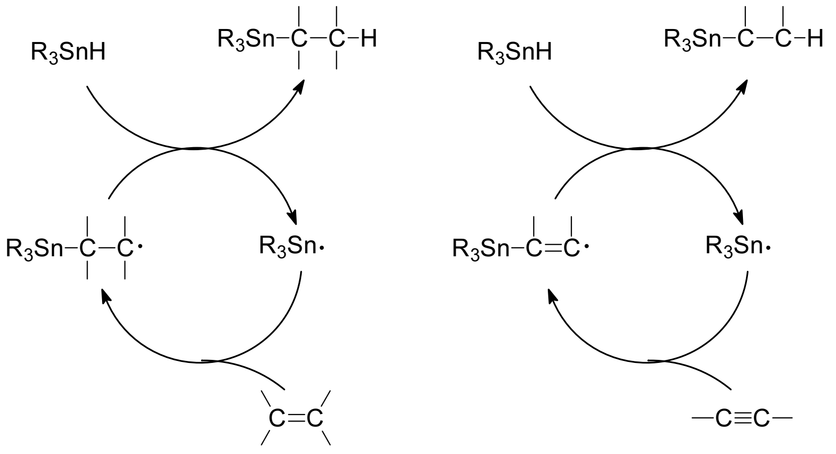


(4-55)

Homolytic Tin ($R_3Sn^\bullet$)

Hydrostannation reactions of alkenes and alkynes which involve stannyl radicals have received much wider attention. They are often tolerant of a functional group, and can be used for preparing functionally-substituted organotin compounds.[84]

The general mechanism is illustrated in Scheme 4-3.[86, 93] Triorganotin hydrides will often react slowly with alkenes at room temperature, but usually the reactions are carried out at 80–110 °C with AIBN as a radical initiator. Under these conditions, even monomers like styrene show no evidence of polymerisation because the carbon-centred radicals react more rapidly with the tin hydride than with the monomer. Medial olefins, however, often give low yields because the addition of the stannyl radicals is reversible, and the β-stannylalkyl radicals revert to their progenitors rather than abstract hydrogen. This problem can be avoided by initiating the reactions by irradiation with UV light at room temperature or below; this can be done through Pyrex glass, as the tail of the hydride absorption extends to longer wavelengths.[94]

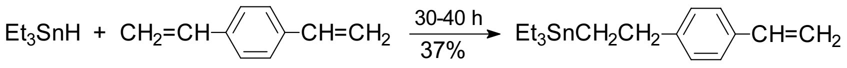


Scheme 4-3 Mechanism of homolytic hydrostannation of alkenes and alkynes.

The reactions of alkenes (and of alkynes) can also be carried out at room temperature or below, using a trialkylborane as catalyst.[95–97] The initiation depends on the presence of an adventitious trace of oxygen which reacts with the borane to generate alkyl and alkylperoxyl radicals and thence organoperoxyboranes.[98]

Some examples which illustrate the scope and conditions of the homolytic hydrostannation reactions of alkenes are shown in equations 4-56 to 4-59,[99] 4-60,[100] 4-61,[94] 4-62,[101] 4.63,[88] and 4-64.[102] The stannane can be formed *in situ* from the reduction of Bu_3SnCl with Et_3SiH in the presence of a Lewis acid catalyst (equation 4-65).[103] In the hydrostannation of an enone, the tin enolate which is formed can be reduced by $PhSiH_3$ to regenerate the tin hydride (equation 4-66), and only a catalytic amount of the tin hydride is required.[104]

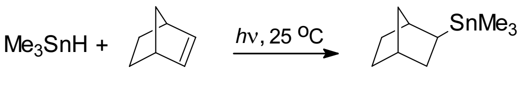
$$Et_3SnH + CH_2{=}CH(CH_2)_7CH_3 \xrightarrow[50\text{-}60\ h.\ 68\%]{AIBN,\ 70\text{-}80\ ^{o}C} Et_3Sn(CH_2)_9CH_3 \qquad (4\text{-}56)$$



(4-57)

$$Bu^i{}_3SnH + CH_2{=}CHOCOMe \xrightarrow[22\ h.\ 92\%]{AIBN,\ 70\ ^{o}C} Bu^i{}_3SnCH_2CH_2OCOMe \qquad (4\text{-}58)$$

$$Et_2SnH_2 + CH_2{=}CMeCO_2Me \xrightarrow[9\ h.\ 95\%]{AIBN,\ 40\text{-}50\ ^{o}C} Et_2Sn(CH_2CHMeCO_2Me)_2 \qquad (4\text{-}59)$$



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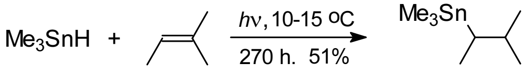
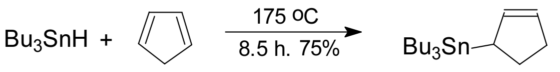
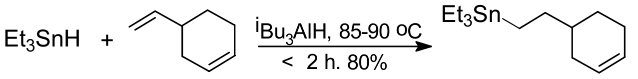


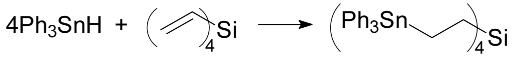
(4-61)



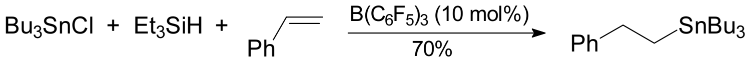
(4-62)



(4-63)



(4-64)



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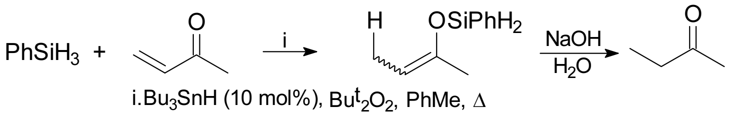
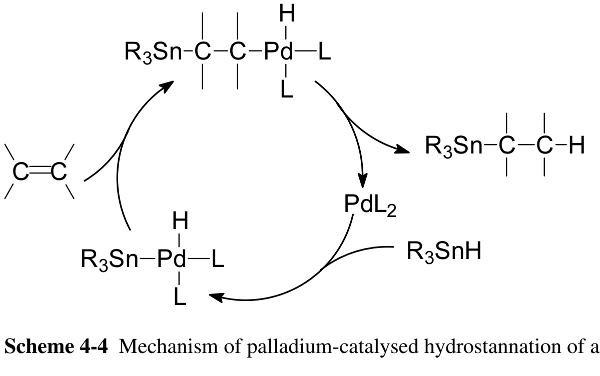


(4-66)

The hydrostannation of alkynes to give vinylstannanes is considered in Chapter 8.

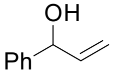
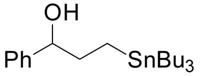
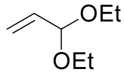
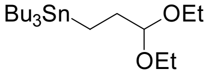
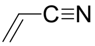
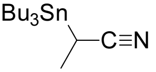
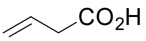
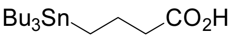
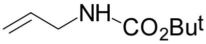
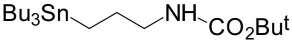
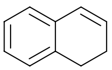
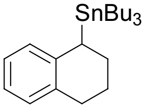
Metal-Bonded tin (R_3SnMH)

There are a few reports of the catalysis of the hydrostannation of active alkenes by soluble palladium catalysts,[105, 106] but, with less active alkenes, the major product is the hexaalkyldistannane. Good yields of hydrostannation products, however, can be obtained with heterogeneous catalysts, and Table 4-2 shows examples of the hydrostannation of alkenes in the presence of a $Pd(OH)_2/C$ catalyst.[107] A recent, thorough, survey in *Chemical Reviews* is available.[108] The mechanism of the palladium-catalysed hydrostannation is not known in detail, but presumably it involves oxidative addition and insertion of the alkene by stannylmetallation (or hydrometallation) as shown, followed by reductive elimination (Scheme 4-4).



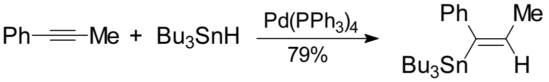
Scheme 4-4 Mechanism of palladium-catalysed hydrostannation of alkenes.

Table 4-2 Palladium-catalysed hydrostannation of alkenes.

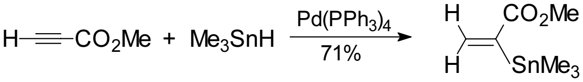
Alkene	Product	Yield (%)
		96
		85
		84
		78
		89
		90

Conditions: 1.5 Equiv. Bu_3SnH, 10 mol% $Pd(OH)_2/C$, THF, rt, 1 h.

Alkynes, on the other hand, readily undergo palladium-catalysed hydrostannation with a homogeneous catalyst. Examples are given in equations 4-67[109] and 4-68,[110] and further details are given in the section on the preparation of vinylstannanes (Section 8.1.1).



(4-67)



(4-68)

4.5 Metallostannation of Alkenes and Alkynes

Metals often act as hydrogen equivalents (Section 3.1), and metallostannations involving stannylmetallic reagents R_3SnM, equivalent to hydrostannations with the hydrides R_3SnH, might be expected (equation 4-69). A number of such reactions are indeed known where the metal M is Sn, Mg, Zn, B, or Cu.[111, 112] Transition metal catalysts, M′, particularly Pd and Cu, are often involved, and the reactions may proceed through the transmetallated intermediates R_3SnM'. Most of these reactions, however, have been carried out with alkynes and allenes. The former reactions are covered in Section 8.1.1 as a route to vinylstannanes and in Section 9.1.1 as a route to allylstannanes. No examples appear yet to have been reported of the metallostannation of simple alkenes, though SnLi,[113] SnZn,[113] and SnCu[54, 114, 115] compounds have been used in Michael-type additions to unsaturated carbonyl compounds.

$$R_3SnM + C\equiv C \longrightarrow R_3SnC{=}CM \qquad (4\text{-}69)$$

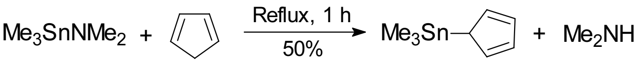
4.6 The Reaction of Acidic Hydrocarbons with Sn–O and Sn–N Bonded Compounds

If A is derived from a weak acid HA, and HC is a "strong" hydrocarbon acid, the SnC bond can be formed by the acidolysis reaction:

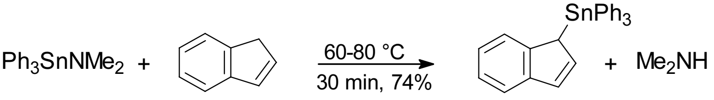
$$R_3SnA + HC \longrightarrow R_3SnC + HA \tag{4-70}$$

HA Is usually a volatile amine which can readily be removed to drive an equilibrium reaction to completion. Reactions of this type are useful for preparing cyclopentadienyl-, alkynyl-, trihalogenomethyl-, and diazoalkyl-tin compounds.

Some examples are given in equations 4-71–4-75, and more are to be found in the sections dealing with the respective specific classes of organotin compounds which are formed. Cyclopentadiene can be both mono- and di-stannylated, and triphenylindenyltin has been obtained from indene (Section 9.3.1).[116] Acetylene can be both mono-and di-stannylated,[116, 117] and the reaction of a diaminotin compound with acetylene gives a linear polymer.[116, 118] The acidity of sulphonylalkynes is sufficient to allow the reaction to be carried out with a tin alkoxide rather than a tin amide,[119] and acetylenes can be stannylated with tributyltin oxide in benzene by dehydration with calcium hydride, or azeotropically.[120]



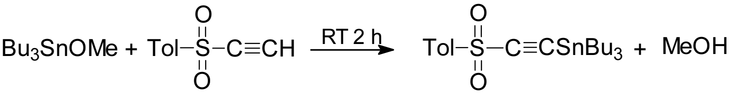
(4-71)



(4-72)

$$Me_3SnNMe_2 + HC{\equiv}CPh \xrightarrow[92\%]{} Me_3SnC{\equiv}CPh + Me_2NH \tag{4-73}$$

$$Bu_2Sn(NMe_2)_2 + HC{\equiv}CH \xrightarrow[94\%]{\text{RT 1.5 h}} \left[Bu_2SnC{\equiv}C\right]_n + Me_2NH \tag{4-74}$$



$$Bu_3SnOMe + Tol{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}{-}C{\equiv}CH \xrightarrow{\text{RT 2 h}} Tol{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}{-}C{\equiv}CSnBu_3 + MeOH \tag{4-75}$$

Chloroform and bromoform react readily at room temperature to give the trihalogenomethyltin compounds in good yield;[121, 122] trichloroethene reacts similarly,[122] and so does pentafluorobenzene.

$$Me_3SnNEt_2 + HCBr_3 \longrightarrow Me_3SnCBr_3 + Et_2NH \tag{4-76}$$

$$Me_3SnNMe_2 + HCCl{=}CCl_2 \xrightarrow[80\%]{\text{Reflux, 15 min}} Me_3SnCCl{=}CCl_2 + Me_2NH \tag{4-77}$$

Diazomethane, trimethylsilyldiazomethane and ethyldiazoacetate give tin derivatives which are intensely coloured, and sensitive to air and light, but apparently not explosive.

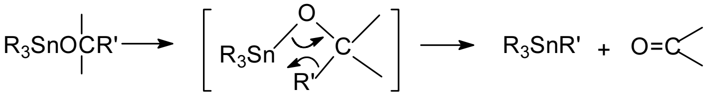
They react with 1,4-dipolarophiles to give organotin derivatives of heterocyclic compounds.[123–126] Nitriles, nitro compounds, and ketones which have a proton in the α- position react to give quantitative displacement of the amine, but the tin-containing products then usually react further under the basic conditions to give a mixture of products.[116] Acetone, for example, gives mesityl oxide,[116] but the products $R_3SnCMe_2NO_2$ have been isolated from 2-nitropropane, and $PhSO_2CH_2SnBu_3$ from methyl phenyl sulfone.[127]

$$\mathrm{Me_3SnNMe_2 + CH_2N_2 \longrightarrow [Me_3SnCHN_2] \longrightarrow (Me_3Sn)_2CN_2} \qquad (4\text{-}78)$$

$$\mathrm{Me_3SnNMe_2 + HCN_2CO_2Et \xrightarrow[\text{ca. 100\%}]{\text{RT, 10 min}} Me_3SnCN_2CO_2Et} \qquad (4\text{-}79)$$

4.7 Carbonyl-forming Eliminations

When the group R′ carries strongly electron-attracting substituents, the Sn–R′ bond can sometimes be generated by a carbonyl-forming elimination as generalised in equation 4-80; the thermal decompostion of trialkyltin formates to give trialkyltin hydrides is formally similar.[128] These reactions show no characteristics of free radical reactions, and it is often assumed that they proceed through a cyclic mechanism as shown in the equation. Similar reactions are known for other heavy metals, particularly mercury;[129] they are sometimes useful for specific compounds where the presence of functional groups renders more usual routes untenable. One limiting factor is the possible disproportionation of the reactants R_3SnX at elevated temperatures.



(4-80)

For example, triphenylpentafluorophenyltin can be prepared from triphenyltin pentafluorobenzoate in refluxing pyridine;[130] the alternative route via pentafluorophenylmagnesium halide gives a relatively poor yield because of the instability of the Grignard reagent.

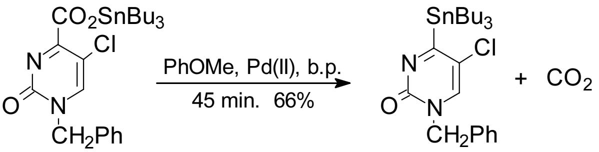
$$\mathrm{Ph_3SnOCOC_6F_5 \xrightarrow[\text{1 h, 65\%}]{\text{Py, b.p.}} Ph_3SnC_6F_5 + CO_2} \qquad (4\text{-}81)$$

Organotin derivatives of propargylic acids and of acetylene dicarboxylic acids usually give good yields of ethynyltin compounds,[131] and cyanoacetates[132] and α-cyanoacrylates at 200 °C[133] give the corresponding cyanomethyl- or α-cyanovinyl-tin compounds. An interesting recent development in this field is the demonstration that some of these decarboxylation reactions can be catalysed by transition metals, particularly palladium, and organotin derivatives of pyrimidines have been prepared by this route.[134]

$$\mathrm{Bu_3SnO_2CC{\equiv}CCO_2SnBu_3 \xrightarrow[\text{92\%}]{\text{m.p.}} Bu_3Sn{-}C{\equiv}C{-}SnBu_3 + 2CO_2} \qquad (4\text{-}82)$$

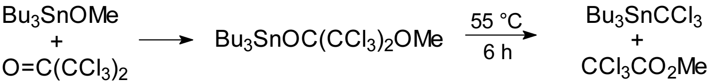
$$\mathrm{Ph_3SnOCOCH_2CN \xrightarrow[\text{25 h}]{140\,^{\circ}\mathrm{C}} Ph_3SnCH_2CN + CO_2} \qquad (4\text{-}83)$$

$$\mathrm{Ph_2C{=}C(CN)CO_2SnMe_3} \xrightarrow{200°\mathrm{C}} \mathrm{Ph_2C{=}C(CN)SnMe_3 + CO_2} \tag{4-84}$$



(4-85)

Analogous carbonyl-forming eliminations occur with the adducts formed between organotin oxides or alkoxides and trihalogenomethyl aldehydes or ketones, and tributyltrichloromethyltin was first prepared by the elimination of methyl trichloroacetate from the adduct of tributyltin methoxide and hexachloroacetone.[135, 136]



$$\begin{matrix}\mathrm{Bu_3SnOMe}\\ +\\ \mathrm{O{=}C(CCl_3)_2}\end{matrix} \longrightarrow \mathrm{Bu_3SnOC(CCl_3)_2OMe} \xrightarrow[6\ \mathrm{h}]{55\ °\mathrm{C}} \begin{matrix}\mathrm{Bu_3SnCCl_3}\\ +\\ \mathrm{CCl_3CO_2Me}\end{matrix} \tag{4-86}$$

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5 Alkylstannanes[1]

5.1 Structures and Properties

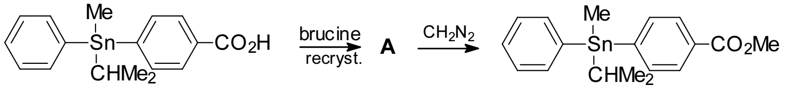
The preparations of tetraalkyltin compounds are described in Chapter 4. They are usually colourless liquids or solids which are stable to air and water; the m.p. or b.p. of some representative examples is given in Table 5-1.

Table 5-1 Tetraalkyltin compounds.

R_4Sn	m.p./°C or b.p./°C(mmHg)	R_4Sn	m.p./°C or b.p./°C(mmHg)
Me_4Sn	77(760)	Me_3SnEt	105(760)
Et_4Sn	63–65(12)	Me_3SnBu	150
Pr_4Sn	112(10)	Me_3Sn(–)-menthyl	75(1.4)
Pr^i_4Sn	103–104(10)	Me_3Sn-1-adamantyl	65–67
Bu_4Sn	145(10)		
Bu^i_4Sn	128–129(8)	Me_2SnBu_2	70(44)
Bu^s_4Sn	148–150(10)	$MeSnBu_3$	122–124(11)
Oct_4Sn	268(10)		
$[Me(CH_2)_{17}]_4Sn$	47	Et_3SnOct	142(10)
(cyclo-$C_3H_5)_4$	68–68(3)	Et_2SnBu_2	205–208(760)
(cyclo-$C_5H_9)_4$	155–160(0.4)		
(cyclo-$C_6H_{11})_4$	263		
$(Me_3SiCH_2)_4Sn$	94(0.2)		

A number of tetraorganotin (though not yet tetraalkyltin) compounds in which the chirality is centred on the tetrahedral tin centre have been optically resolved by either (a) recrystallisation of the diastereoisomers which are formed with an optically active reagent (e.g. equation 5-1 and 5-2), or (b) by an asymmetric synthesis (e.g. equation 5-3), or (c) by chromatography on microcrystalline cellulose acetate (e.g. equation 5-4).[2] These compounds are listed in Table 5-2, where the group which is involved in an asymmetric synthesis is printed in italics. In only a few cases is the optical purity known.

These tetraorganotin compounds are optically stable and sometimes have been distilled without racemisation; in contrast, the derivatives $R^1R^2R^3SnX$ (X = OR, Cl etc.) are usually optically unstable.

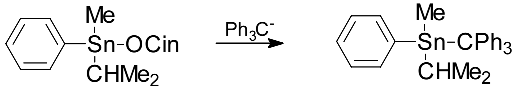


(5-1)

A

$[\alpha]^{22}_D$ -0.5° and +0.35°

-0.1° and +0.1°



(5-2)

(CinOH = cinchonine)

$[\alpha]^{25}_D$ - 22.9° (22% optically pure)

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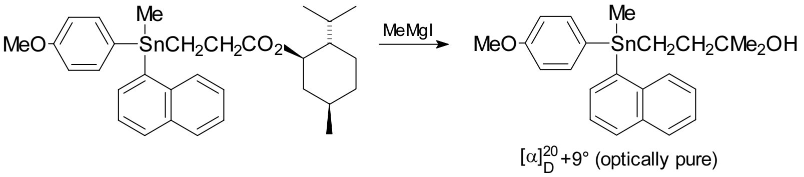
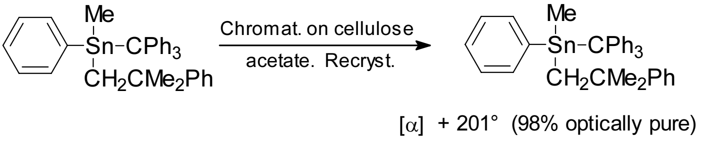


(5-3)



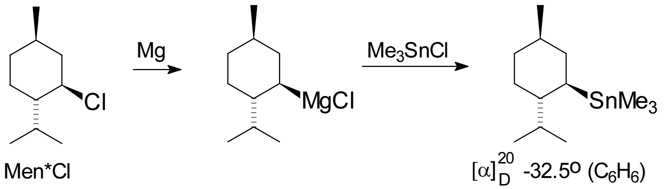
(5-4)

Table 5-2 Optically active tetraorganotin compounds, $R^1R^2R^3R^4Sn$.

R^1	R^2	R^3	R^4	[α]	Method[a]	Ref.
Me	*$CH_2CH_2CMe_2OH$*	5-$MeOC_6H_4$	1-Np	+9	AsSyn	3
Me	$CHMe_2$	Ph	5-$HO_2CC_6H_4$	–0.5	Cryst	4
Me	Ph	*4 $MeCOC_6H_4$*	1-Np	+0.25	AsSyn	5
Me	$CHMe_2$	Ph	*CH_2Ph*	+5.6	AsSyn	5
Me	*$CHMe_2$*	CH_2CMe_2Ph	CPh_3	+5.1	AsSyn	6
Me	Ph	CH_2CMe_2Ph	*Fl_2* [b]	+0.8	AsSyn	6
Me	Ph	CH_2CMe_2Ph	CMe_3	–1.5	AsSyn	7
Me	Ph	CH_2CMe_2Ph	CPh_3	60	Chro	8
Me	Ph	CH_2Ph	CPh_3	32	Chro	8
Me	$CHMe_2$	CH_2CMe_2Ph	CPh_3	5.5	Chro	8
Me	$CHMe_2$	Ph	CH_2Ph	5.0	Chro	8
Me	$CHMe_2$	Ph	*CH_2Ph*	+2.1	AsSyn	9
Me	$CHMe_2$	Ph	*CH_2Ph*	–3.0	AsSyn	10
Me	$CHMe_2$	*Bu*	Ph	–0.8	AsSyn	10
Me	$CHMe_2$	Ph	*1-Np*	+0.6	AsSyn	10
Me	*$CH_2CH{=}CH_2$*	$CHMe_2$	Ph	–0.3	AsSyn	10
Me	*$CHMe_2$*	CMe_3	Ph	+2.1	AsSyn	10
Me	CMe_3	Ph	*CH_2Ph*	–9.6	AsSyn	10
Me	*Bu*	CMe_3	Ph	–2.1	AsSyn	10
Me	$CHMe_2$	CMe_3	Ph	+0.4	AsSyn	10
Me	$CHMe_2$	Ph	*CPh_3*	–22.9[c]	AsSyn	11
Me	Ph	$CHCMe_2Ph$	CPh_3	+201[d]	Chro	12

[a] AsSyn = asymmetric synthesis. Chro = chromatography. Crys = recrystallisation of diastereoisomers. [b] Addition of R_3SnH to difluorenylidine. [c] ca. 22% optically pure. [d] 98% optically pure.

Many organotin compounds have been synthesised in which the tin centre itself is achiral, but one of the alkyl ligands about the tin is chiral. Frequently this ligand is the (1*R*,2*S*,5*R*)-menthyl group (Men*), and compounds such as Men^*SnR_3 [R_3 = Me_3, Me_2Bu^t,[13] $Me_2(PhCMe_2CH_2CH_2)$, $Me(PhCMe_2CH_2CH_2)_2$,[14] Bu_3, or Ph_3[15]], $Men^*_2SnR_2$ (R_2 = Me_2[16] or Ph_2[15]), and $Men^*_3SnCH_2CH{=}CH_2$[17] have been prepared, usually by reaction of the Grignard reagent from (–)-menthyl chloride, with the appropriate halide, for example:



(5-5)

The reaction of Me_3SnLi with (–)-menthyl chloride gives 8% of (–)-Men*$SnMe_3$ and 20% of (+)-neomenthyl$SnMe_3$.

If epimerisation occurs at the 1-position during the Grignard reaction, it can be detected by the ^{119}Sn NMR chemical shift of the diastereoisomeric products, and prevented by adding a Lewis base such as Ph_3P, which may suppress a competing electron-transfer reaction. For example, (1*R*,2*S*,5*R*)-menthylmagnesium chloride reacts with Ph_3SnCl in THF to give (1*R*,2*S*,5*R*)-menthyltriphenyltin (δSn –111.2) and (1*S*,2*S*,5*R*)-menthyltriphenyltin (δSn –108.1) in the ratio of 3:2, but in the presence of 0.15 molar equivalents of Ph_3P, only the (1*R*,2*S*,5*R*)-isomer is formed.

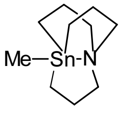
The purpose of preparing the menthyltin compounds is often to convert them into a menthyltin hydride (Section 15.1.5), which may then be used in an asymmetric synthesis.

Simple tetraalkyltin compounds are tetrahedrally 4-coordinate in the solid, liquid, and gaseous states, and show zero quadrupole splitting in the Mössbauer spectra. Electron diffraction shows that gaseous Me_4Sn has *r*Sn–C 215.4(3) pm, with essentially free rotation of the methyl groups.[18, 19] Single crystal X-ray diffraction at 158 K shows a molecule with C_{3v} symmetry with a short bond of 210.8 pm and three longer bonds of 215.6 pm (average 213.7 pm),[20] and neutron diffraction gave rotational activation energies of the methyl groups of 3.4 and 1.9 kJ mol^{-1}, respectively.[21] This deviation in the solid state from pure tetrahedral geometry is suggested to be due to crystal forces.

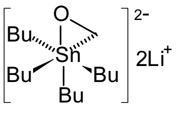
In $(Me_3Sn)_4C$, the average length of the central SnC bonds is 216.2 pm.[22]

Similarly, the Raman and infrared spectra of $(CF_3)_4Sn$ show that the molecule has T_d symmetry, and electron diffraction gives an Sn–C bond length of 220.1(5) pm.[23]

Exceptions occur to this simple tetrahedral 4-coordination when one or more of the four alkyl groups carries a functional substituent which can act as a fifth ligand at the tin centre. The classic case is the triptych stannane **5-1**, which single crystal X-ray diffraction shows to be trigonal bipyramidal, with an elongated apical Sn–Me bond (221.4 pm), and an Sn–N distance of 262.4 pm which is within the van der Waals distance.[24]



(**5-1**)



(**5-2**)

The tetraalkyltins show little tendency to increase their coordination with an external ligand. The exception is the organic nucleophile from organolithium compounds which gives, reversibly, the 5-coordinate tin anion which can be observed by NMR spectroscopy, and which leads to the exchange of alkyl groups (equation 5-6). These reactions are discussed in Sections 5.3.5 and 22.1. An NMR study of the product from treating tributyl(hydroxymethyl)tin with butyllithium implied that it had the 6-coordinate structure **5-2**.[25]

$$R'Li + R_4Sn \rightleftharpoons R'R_4Sn^- Li^+ \rightleftharpoons RLi + R'R_3Sn \qquad (5\text{-}6)$$

5.2 Mechanisms of Cleavage

Tin-carbon bonds can be broken by reaction with electrophiles (e.g. protic acids, Lewis acids, halogens), nucleophiles (e.g. RLi), or free radicals (e.g. succimidyl, t-butoxyl), or with certain transition metal (particularly palladium) compounds. Fragmentation can also be induced through the radical cations which are formed by electron transfer.

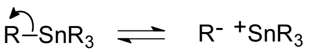
The substitution reactions of organometallic compounds, in which heterolytic attack at the carbon is usually by electrophiles, are not susceptible to the simple mechanistic classification (S_N1, S_N2, and S_Ni) which is so useful in discussing nucleophilic reactions of organo-nonmetallic compounds. The situation is complicated by the propensity of the metal to increase its coordination number, and a spectrum of mechanisms has to be considered in which electrophilic attack at carbon is accompanied by or preceded by nucleophilic attack at the metal.

The principal mechanisms which can lead to the cleavage of the alkyl-tin bond are given below in equations 5-7 to 5-20. It should be emphasised that these are a minimum set of basic types, which are convenient for discussing the reactions, and that various modifications of these simple models must be considered. For example, a continuous gradation of cyclic [S_E2(closed)/S_N2(closed)] mechanisms can be envisaged between the extremes of what are labelled here S_E2(C)(open) and S_N2(Sn)(open), in which there is increasing participation by the nucleophile, and decreasing participation by the electrophile. Again, the S_E2 mechanisms may shade into the S_E1 mechanism through mechanisms involving ion pairs.

Further, these basic models must be modified to include the effect of catalysts. Other mechanisms may be involved when the organic group has a special structure (e.g. aryl, vinyl, benzyl, and allyl).

Evidence for these mechanisms comes mainly from kinetic measurements including steric, solvent, and salt effects, and from some studies of the stereochemistry at the carbon centre which is difficult to obtain because the products R_3SnX are configurationally unstable when X is an electronegative group. Pope and Peachy described the optical resolution of methylethylpropyltin iodide in 1903 by crystallisation of the (+)-camphorsulfonate from water in the presence of KI,[26] and reported the iodide to be optically stable, but this has since been discounted.[27]

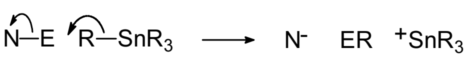
S_E1



$$R{-}SnR_3 \rightleftharpoons R^- \; {}^+SnR_3 \qquad (5\text{-}7)$$

$$R^- \; {}^+SnR_3 + EN \longrightarrow RE + NSnR_3 \qquad (5\text{-}8)$$

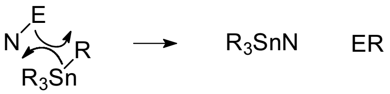
S_E2(C)(open)



$$N{-}E \;\; R{-}SnR_3 \longrightarrow N^- \;\; ER \;\; {}^+SnR_3 \qquad (5\text{-}9)$$

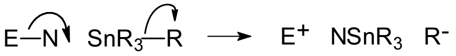
$$R_3Sn^+ \;\; N^- \longrightarrow R_3SnN \qquad (5\text{-}10)$$

S$_E$2(C)(closed)/S$_N$2(Sn)(closed)



$$R_3SnN \quad ER \qquad (5\text{-}11)$$

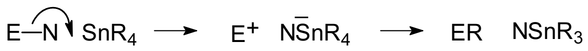
S$_E$2(Sn)(open)



$$E{-}N \quad SnR_3{-}R \longrightarrow E^+ \quad NSnR_3 \quad R^- \qquad (5\text{-}12)$$

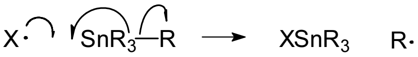
$$E^+ \quad R^- \longrightarrow ER \qquad (5\text{-}13)$$

S$_E$2(Sn)(coord)



$$E{-}N \quad SnR_4 \longrightarrow E^+ \quad N\bar{S}nR_4 \longrightarrow ER \quad NSnR_3 \qquad (5\text{-}14)$$

S$_H$2(Sn)



$$X\cdot \quad SnR_3{-}R \longrightarrow XSnR_3 \quad R\cdot \qquad (5\text{-}15)$$

Transition metals

$$R_4Sn + R'M^{n+2}X \longrightarrow R_3SnX + R'M^{n+2}R \qquad (5\text{-}16)$$

$$R'M^{n+2}R \longrightarrow R'R + M^n \qquad (5\text{-}17)$$

S$_H$1

$$R{-}SnR_3 \longrightarrow R\cdot \quad \cdot SnR_3 \longrightarrow \text{products} \qquad (5\text{-}18)$$

ET

$$R_4Sn \quad EN \longrightarrow R_4Sn^{\cdot+} \quad EN^{\cdot-} \qquad (5\text{-}19)$$

$$R_4Sn^{\cdot+} \quad EN \longrightarrow R\cdot \quad R_3Sn^+ \quad EN^{\cdot-} \longrightarrow \text{products} \qquad (5\text{-}20)$$

These mechanisms are discussed, together with the reactions, below. By most of these mechanisms, the alkyl-tin bond is less reactive than the aryl-, alkenyl-, alkynyl-, allyl-, or benzyl-tin bond, and when two types of group are bonded to tin, reactions are selective for this second class of group.

5.3 Reactions

5.3.1 With Protic Acids

The reactivity of the alkyl-tin bond towards protic acids is rather low, and allyl-, vinyl-, or phenyl-tin bonds are cleaved preferentially. Towards both hydrogen halides and carboxylic acids, the reactivity drops as the size of the alkyl groups increases, and the removal of subsequent alkyl groups becomes successively more difficult. Some examples are shown in equations 5-21–5-24.

$$\mathrm{Pr_4Sn + ClCH_2CO_2H \longrightarrow Pr_3SnOCOCH_2Cl + PrH} \tag{5-21}$$

$$\mathrm{(C_{14}H_{29})_4Sn + HCl \xrightarrow[85\%]{Et_2O} (C_{14}H_{29})_3SnCl + C_{14}H_{30}} \tag{5-22}$$

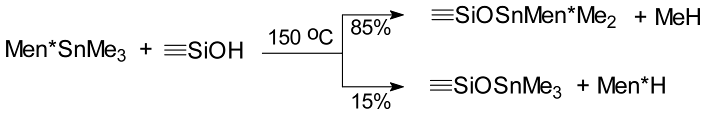
$$\mathrm{Me_4Sn + HF \xrightarrow{25\ ^\circ C} Me_3SnF + CH_4} \tag{5-23}$$

$$\mathrm{Me_4Sn + MeSO_3H \xrightarrow{15\ ^\circ C} Me_3SnOSO_2Me + CH_4} \tag{5-24}$$

Organotin residues from a reaction can be degraded with $\mathrm{HNO_3/HCl}$ to give non-toxic inorganic residues for disposal.[28]

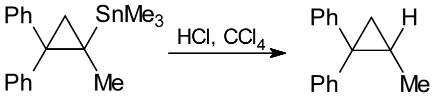
$$\mathrm{R_{\mathit{n}}SnX_{4-\mathit{n}} \xrightarrow[1\ h,\ 85\ ^oC]{HNO_3/HCl} H[SnX_5(H_2O)] \xrightarrow{NaOH} Na_2[Sn(OH)_6]} \tag{5-25}$$

(–)-Menthyltrimethyltin reacts with silica at 150 °C to give, by what is assumed to be an S_E2 mechanism, methane and menthane in a ratio that implies that the Me–Sn bond is 1.9 times more reactive than the Men*Sn bond.[29]

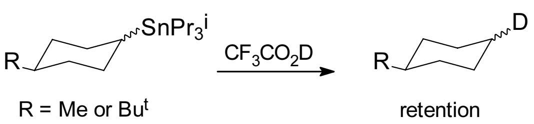


$$\mathrm{Men^*SnMe_3 + {\equiv}SiOH \xrightarrow{150\ ^oC} \begin{cases} \xrightarrow{85\%} {\equiv}SiOSnMen^*Me_2 + MeH \\ \xrightarrow[15\%]{} {\equiv}SiOSnMe_3 + Men^*H \end{cases}} \tag{5-26}$$

Rather little work has been carried out on the mechanisms of these protiodealkylation reactions. The reaction with HCl in methanol or methanol/benzene is second order. Stereochemical studies are restricted by the fact that, though tetraalkyltin compounds with chirality centred on tin are optically stable, the reaction products $\mathrm{R_3SnX}$ are not, and compounds with chirality centred on the α-carbon atom in R would have to have the structure RR′R″CSn or RR′CDSn for the product to be configurationally stable. The only examples appear to be that the reaction of trimethyl(1-methyl-2,2-diphenylcyclopropyl)tin with HCl or HBr,[30] and of *cis*- and *trans*-5-methyl- or -5-t-butylcyclohexyltriisopropyltin with deuteriotrifluoroacetic acid[31] proceed with complete retention (equations 5-27 and 5-28), which would be compatible with either an S_E2(open) or S_E2(cyclic) mechanism.



(5-27)



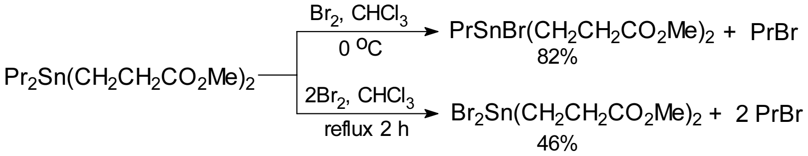
(5-28)

5.3.2 With Halogens

The alkyl-tin bond (R−Sn) is readily cleaved by halogens (X_2), the reactivity usually following the sequences $X_2 = Cl_2 > Br_2 > I_2$, and R = Ph > $PhCH_2$ > CH_2=CH > Me > Et > Pr > Pr^i > Bu > Pe etc. The four alkyl groups in R_4Sn are removed progressively, and the reaction can be taken to the stage of R_3SnX, R_2SnX_2, $RSnX_3$, or SnX_4 depending on the conditions. Compounds R_3SnX can be prepared with iodine in ether, carbon tetrachloride, or chloroform at room temperature. The second stage of dealkylation can be brought about by bromine at 0 °C. One example is given in equation 4-9[32] and more are given in equations 5-29–5-31.[33]

$$\mathrm{Pr_3SnCH_2CO_2Et + Br_2 \xrightarrow{HCCl_3,\ 0\ ^{o}C} \underset{75\%}{Pr_3SnBr} + \underset{71\%}{BrCH_2CO_2Et}} \tag{5-29}$$

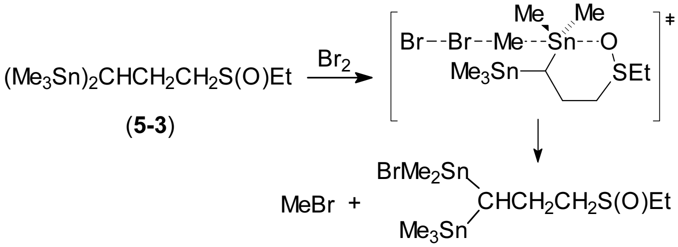
$$\mathrm{Bu_3SnCH_2CH_2CO_2Me + Br_2 \xrightarrow[90\%]{HCCl_3,\ 0\ ^{o}C} BuBr + Bu_2SnBrCH_2CH_2CO_2Me} \tag{5-30}$$



(5-31)

There appears to be no single preferred stereochemistry for the S_E2 cleavage of alkyl–tin bonds by halogen, and there is a delicate balance between retention and inversion pathways. In the cleavage of the Sn-Bu^s bond in various optically active compounds, R_3SnBu^s, bromination in a non-polar solvent (e.g. CCl_4) involves a high degree of retention in the s-butyl group, but in a polar solvent (e.g. MeCN or MeOH), more inversion is involved, suggesting a change from a closed to a more open transition state.[34-36] Bromination of *exo*-2-triorganostannylnorbornanes gives mainly inversion, but the *endo* isomer gives mainly retention.[37] However, inversion is favoured (in MeOH) for the equatorial isomer of the cyclohexyltin compounds shown in equation 5-28, and retention for the axial isomer.[31]

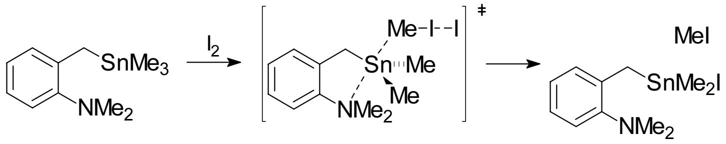
The electrophilic cleavage of an alkyl-tin bond can be assisted by a suitably positioned intramolecular ligating group. Thus in **5-3**, the ease of the cleavage of the methyl-tin bond is ascribed to nucleophilic assistance by the sulphoxide group.[38]



(**5-3**)

(5-32)

Similarly in **5-4**, the cleavage by iodine of the methyl-tin bond rather than the benzyl-tin bond is suggested to be due to stabilisation of the S_E2 transition state by ligation by the nitrogen.[39]



(**5-4**)

(5-33)

An S_E1 mechanism appears to hold in the reaction of iodine with Me_3SnCN and $Et_3SnCH_2COCH_3$ in DMSO or DMSO/CCl_4, where the displaced anion is particularly stable.[40]

5.3.3 With Lewis Acids

Reactions of organotin compounds with Lewis acids by have been carried out particularly with mercury(II) salts in mechanistic studies, with $SnCl_4$ (the Kocheshkov reaction) for the preparation of alkyltin chlorides, and with lead tetraacetate.

In reactions of mercury(II) salts, the reactivity follows the sequence $Hg(OAc)_2 > HgCl_2 > HgI_2$ and electron-attracting groups in the mercury carboxylates accelerate the reaction.[41, 42] The reactivity follows a steric sequence with respect to the group R being transferred ($Me > Et > Pr > Bu^i > Pe^{neo} > Pr^i$), and solvent and salt effects suggest an S_E2(C)(open) mechanism.

$$R_4Sn + HgX_2 \longrightarrow R_3SnX + RHgX \qquad (5\text{-}34)$$

Radioactive $Bu_3{}^{113}SnCl$ for environmental tracer studies has been prepared by this type of reaction.[43]

$$^{113}SnCl_4 \xrightarrow{BuMgCl} Bu_4{}^{113}Sn \xrightarrow{HgCl_2} Bu_3{}^{113}SnCl + BuHgCl \qquad (5\text{-}35)$$

The reaction of lead tetraacetate is similar.[44, 45]

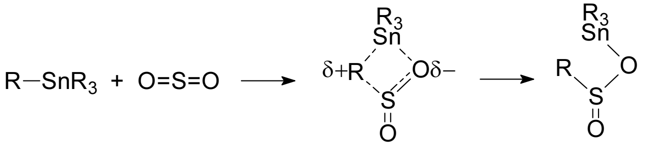
$$Me_4Sn + Pb(OAc)_4 \longrightarrow Me_3SnOAc + MeOAc + Pb(OAc)_2 \qquad (5\text{-}36)$$

The Kocheshkov reactions are discussed in Section 11.1.2 on organotin halides.

5.3.4 With Sulfur Dioxide

Sulfur dioxide inserts into alkyltin bonds to give stannylsulfinates, $R_3SnO\text{-}S(O)R$,[46] but the reactivity falls off in the sequence R = allyl ~ allenyl ~ propargyl > phenyl > benzyl > methyl. Insertion into a vinyl-tin bond occurs with retention of configuration. The reaction with aryl and benzyl compounds is cleanly first order in each of the two reactants, and is rather insensitive to the nature of any substituents in the benzyl ring.

The mechanism is probably best represented as a closed $S_E2(C)/S_N2(Sn)$ process, with the development of some charge in the transition state.



(5-37)

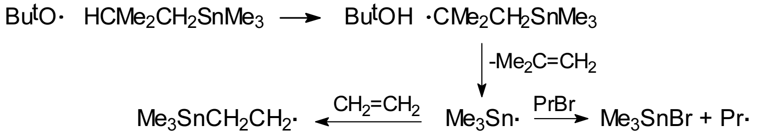
5.3.5 Tin/LithiumTransmetallation[47]

Displacement of an alkyl group from a tetraalkyltin compound with a reagent E–N occurs only when N is a strong nucleophile for tin and E is a weak electrophile for carbon. The simple $S_N2(Sn)$(open) mechanism needs a good alkyl leaving group, and it may be involved in the base-catalysed reaction of benzyltrialkyltin compounds, where the departure of the benzyl anion may be assisted by some degree of nucleophilic assistance by the solvent.[48, 49]

The $S_N2(Sn)$(coord) mechanism, however, is familiar in the synthetically important Sn/Li transmetallation reaction that occurs between tetraalkyltin compounds and alkyl lithiums. This process is discussed in Section 19.1.1, and its applications in synthesis in Section 22.1.

5.3.6 With Free Radicals

Free radical reagents usually react with tetraalkyltin compounds at a hydrogen centre in one of the alkyl ligands to give a stannylalkyl radical. β-Stannylalkyl radicals prepared in this way can then undergo β-scission to break the Sn–C bond. Thus the photolysis of di-t-butyl peroxide in the presence of trimethylisobutyltin and ethylene or an alkyl bromide, gives rise to the ESR spectrum of the β-stannylethyl radical or of the alkyl radical respectively, which are formed by the sequence of reactions shown in equations 5-38.[50]



$$\begin{tikzcd}
\mathrm{Bu^tO\cdot\ \ HCMe_2CH_2SnMe_3} \arrow[r] & \mathrm{Bu^tOH\ \ \cdot CMe_2CH_2SnMe_3} \arrow[d, "-\mathrm{Me_2C{=}CH_2}"] & \\
\mathrm{Me_3SnCH_2CH_2\cdot} & \mathrm{Me_3Sn\cdot} \arrow[l, "\mathrm{CH_2{=}CH_2}"'] \arrow[r, "\mathrm{PrBr}"] & \mathrm{Me_3SnBr + Pr\cdot}
\end{tikzcd}$$

(5-38)

The S_H2 reaction at the tin centre with direct cleavage of the SnC bond in acyclic tetraalkyltins is clearly recognisable only in the reaction of halogens under free radical conditions and in the reaction of the succinimidyl radical from *N*-halogenosuccinimides.

The incursion of a free radical mechanism (equations 5-39 and 5-40) has long been recognised to complicate the study of electrophilic halogenation, and a quinol is often added to suppress the radical chain reaction. The homolytic reaction is promoted by light, and under these conditions the compounds Me_3SnR show for various groups R the reactivities $Pr > Pr^i > Bu = Pr < Et > PhCH_2 > Me$.[51]

$$Br\cdot + SnR_4 \longrightarrow BrSnR_3 + R\cdot \tag{5-39}$$

$$R\cdot + Br_2 \longrightarrow RBr + Br\cdot \tag{5-40}$$

The reaction between *N*-halogenosuccinimides and tetraalkylstannanes in acetone can be inhibited with galvinoxyl, or induced with di-t-butyl hyponitrite, and shows appropriate kinetics for a radical chain reaction, giving the alkyl halide and trialkylstannyl succinimide in >90% yield.[52] The reactivity of compounds R_4Sn follows the sequence R = Me > Et > Pr > Bu > Bu^s, suggesting a steric control of reactivity. Bu_3SnCH_2Ph Is more reactive than Bu_4Sn, and gives benzyl halide; in none of the compounds could a second alkyl group be cleaved. The reactivity of the various *N*-halogenosuccinimides, NXS, followed the sequence NCS < NBS < NIS. The reaction, therefore, is believed to follow a radical chain mechanism, with the propagation steps as shown in equations 5-41 and 5-42.

$$(CH_2CO)_2N\cdot + SnR_4 \longrightarrow (CH_2CO)_2NSnR_3 + R\cdot \tag{5-41}$$

$$R\cdot + (CH_2CO)_2NX \longrightarrow RX + (CH_2CO)_2N\cdot \tag{5-42}$$

An S_H2 reaction apparently occurs at the tin centre in the reaction of tetramethyltin with oxygen, photoinitiated by electron transfer from a flavin analogue in the presence of Mg^{2+}, where the chain process shown in equations 5-43 and 5-44 is thought to be involved.[53]

$$Me\cdot + O_2 \longrightarrow MeOO\cdot \tag{5-43}$$

$$MeOO\cdot + SnMe_4 \longrightarrow MeOOSnMe_3 + Me\cdot \tag{5-44}$$

Cleavage of an alkyl-tin bond by an S_H2 process at the tin centre occurs much more commonly in the compounds R_nSnX_{4-n}, ($n = 1-3$), where X is an electronegative group such as halide or carboxylate.[54, 55] This diversion of the centre of attack from hydrogen in a ligand in R_4Sn to the tin centre in R_nSnX_{4-n} may be associated with greater availability of the 5d orbitals for forming a 5-coordinate transition state or intermediate. S_H2 Reactions involving organotin halides are discussed in Section 11.4.

The behaviour of the stannacyclopentanes is anomalous in that, even in the absence of an electronegative ligand on the tin, the S_H2 reaction of a variety of radicals occurs at the tin centre rather than at hydrogen.[56] These systems are discussed in Section 10.1.

5.3.7 By Electron Transfer

Cleavage of an alkyltin bond via a radical cation occurs in the gas phase in mass spectroscopy (see Section 2.1.3), and can be induced by γ-irradiation, or electrolytically, or by electron transfer from an oxidising agent.

The study by ESR spectroscopy of organotin radical cations generated by γ-irradiation of a dilute solution of the organotin parent in a frozen Freon matrix is discussed in Section 20.3. If the sample is allowed to warm, fragmentation occurs to give a tin cation and an alkyl radical.

$$R_4Sn \xrightarrow[-e]{\text{Freon, }\gamma} R_4Sn^{\cdot+} \longrightarrow R_3Sn^+ + R\cdot \tag{5-45}$$

Similar reactions are involved with the organotin stablilisers in PVC wrapping film when food is sterilised by γ-irradiation.[57]

The induced cleavage of the C–Sn bond also can be followed by ESR when an organotin compound reacts with a quinone in fluid solution (equation 5-49 below).[58]

Studies by cyclic voltammetry of anodic oxidation of organotin compounds at a platinum electrode in acetonitrile show that the primary irreversible process is the outer sphere oxidation of R_4Sn to the radical cation, followed by rapid fragmentation into R_3Sn^+ and $R^\bullet$ which is then rapidly oxidised further to R^+. The rate constants of the reactions correlate with those for the oxidation by Fe(III) complexes. Values for the oxidation potentials and the ionisation energies are given in Table 5-3.

Table 5-3 Oxidation potentials (v. S.H.E.) and ionisation energies for tetraalkylstannanes.[59, 60]

Compound	E_p/V	I_D/eV	Compound	E_p/V	I_D/eV
Me_4Sn	1.90	9.69	Et_4Sn	1.46	8.93
Me_3SnEt		9.10	Bu_4Sn	1.38	8.76
$neoPe_4Sn$	1.57	8.67	$Pr^i{}_4Sn$	1.22	8.46
$Bu^i{}_4Sn$	1.34	8.68	$Bu^s{}_4Sn$	1.21	8.45
			$Me_2SnBu^t{}_2$	1.08	8.22

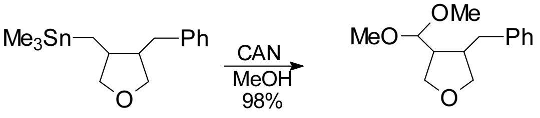
Electron transfer from an oxidising agent has been investigated in detail by Kochi.[59, 60] A series of substituted tris(phenanthroline)iron(III) reagents reacted with R_4Sn by second order kinetics with rate constants related to the reduction potential of the Fe(III) compound and the ionisation potential of R_4Sn. There was no steric effect on the rates, even with $Pe^{neo}{}_4Sn$, and the reaction was identified as an outer sphere process. On the other hand, oxidation by the hexachloroiridate(IV) dianion showed no such correlation, and was sensitive to steric effects, and followed an inner sphere mechanism. Fragmentation of the organotin radical cation was examined for the Et/Me selectivity in reaction 5-46.

$$\mathrm{EtMeSnR_2} \xrightarrow{\text{i}} \mathrm{EtMeSnR_2^{\bullet +}} \longrightarrow \mathrm{Et^\bullet + Me\overset{+}{S}nR_2} \text{ or } \mathrm{Me^\bullet + Et\overset{+}{S}nR_2} \qquad (5\text{-}46)$$

i. Fe(III) or Ir(IV)

For Fe(III), the value of Et/Me was 27 ± 2 and for Ir(IV) it was 11 ± 2. For mass spectrometric fragmentation in the gas phase, the value is 810.

A similar reaction with cerium(IV) ammonium nitrate (CAN) can be used preparatively for cleaving the C–Sn bond (e.g. equation 5-47).



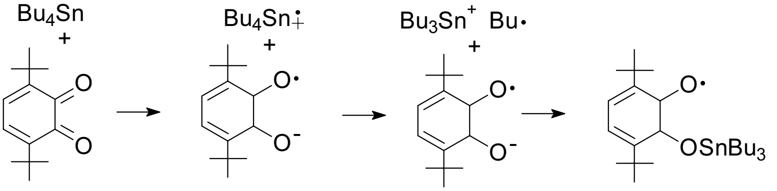
(5-47)

Kochi has interpreted the electrophilic cleavage of organotin and other organometallic compounds in terms of electron transfer mechanisms. The electrophile and organotin compound first form a charge transfer complex, within which electron transfer occurs, and the final products are formed by reaction within the solvent cage of the fragments from the organotin radical cation.

$$\begin{tikzcd}
\mathrm{R_4Sn + EN} \arrow[r, shift left] & \mathrm{[R_4Sn,EN]} \arrow[l, shift left] \arrow[r] & \mathrm{[R_4Sn^{\bullet +}\ EN^{\bullet -}]} \arrow[d] \\
 & \mathrm{RE + R_3SnN} & \mathrm{[R^\bullet\ R_3Sn^+\ EN^{\bullet -}]} \arrow[l]
\end{tikzcd} \qquad (5\text{-}48)$$

This approach has been applied to the reaction involving Fe(III),[59, 60] Ir(IV),[61] Hg(II), Br_2 and I_2.[61] A comparison between this approach and the more conventional one of a heterolytic process is given in reference [42].

Electron transfer to an organic acceptor occurs when an organotin compound reacts with a quinone (equation 5-49), when the resulting semiquinone radical can be observed by ESR spectroscopy.[58]

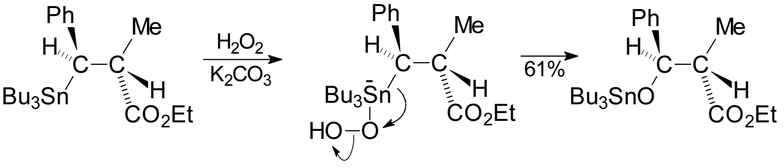


(5-49)

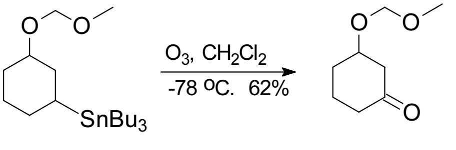
Tetraalkylstannanes also quench, by electron transfer, the fluorescence of singlet excited organic electron acceptors such as anthracene, 9,10-dichloro- or 9,10-dicyano-anthracene, Rose Bengal, Methylene Blue,[62] and analogues of flavin,[53] to give the radical cations, which then fragment. The alkyl radical can be trapped with oxygen, or can induce the polymerisation of alkenes, and these reactions have potential application in photoimaging processes.[62]

5.3.8 With Peroxides

The Sn–C bond can be cleaved with hydrogen peroxide[44, 63] or peroxyacids.[64] The reactions take place with retention of configuration, and presumably involve a nucleophilic rearrangement, for example equation 5-50.[44] Ozonolysis has been used on a few occasions (e.g. equation 5-51),[65] and also oxygen in the presence of a transition metal catalyst.[66]



(5-50)



(5-51)

5.4 Fluorous Alkylstannanes[67, 68]

The term “fluorous” is used to indicate than an alkyl group, or a domain in an alkyl group, contains CF rather than CH bonds. We follow the convention that that a wholly fluorinated alkyl group is given the symbol R^f.

A lot of attention has been paid recently, particularly by D.P. Curran’s group,[69] to the use of fluorous organotin compounds in organic synthesis, with the aim of simplifying the problem of separating the fluorous organotin byproduct from the required non-fluorous product, and minimising the toxicity problem associated with organotin residues. The method relies on the principle that heavily fluorous solvents are immiscible with non-fluorous solvents, and that fluorous and non-fluorous compounds can be cleanly partitioned between the two. Alternatively, the products can be separated by chromatography on a fluorous reversed phase, such as silica gel treated with $C_6F_{13}CH_2CH_2SiMe_2Cl$.[70].

Alkyl bromides, phenyl selenides, nitroalkanes, and dithiocarbonates can be reduced with $(C_6F_{13}CH_2CH_2)_3SnH$. Other reactions that have been carried out include Stille reactions of $(R^fCH_2CH_2)_3SnAr$,[71] ene reactions with aldehydes,[70] radical carbonylations with $(R^fCH_2CH_2)_3SnAllyl$,[72] and transesterifications catalysed by $[(R^fCH_2CH_2)_4Sn_2Cl_2O]_2$.[73] The reactions can be carried out in supercritical CO_2 as solvent,[74] and can microwave-promoted.[75]

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6 Functionally-substituted Alkylstannanes[1]

The terminology used in this section is illustrated in the following examples.

α-Substituted compounds: Me_3SnCH_2Cl, $Ph_3SnC(=O)Ph$, Me_3SnCN_2.

β-Substituted compounds: $Bu_3SnCH_2CH_2OH$, $Bu_3SnCH_2C{\equiv}N$. The compounds containing the entity SnCC=O are dealt with in part here, but also in the section dealing with Sn-O bonded compounds, as they are in equilibrium with the enolates C=C−OSn.

γ-Substituted compounds: $Me_3SnCH_2CH_2CH_2Cl$, $Cl_3SnCH_2CHMeC(=O)OMe$.

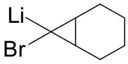
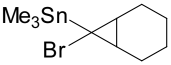
The CF bonds in fluorous tin compounds such as $(C_6F_{13}CH_2CH_2)_3SnH$ have a low reactivity, and can hardly be called functional, and these compounds are covered in Section 5.4.

6.1 α-Halogenoalkylstannanes

α-Halogenoalkyltin compounds are important as intermediates for preparing other alkyltin compounds; in organic synthesis, they provide, by tin/lithium transmetallation, a source of the reagents LiCHRX, and they also serve as halogenocarbene precursors.

The most general route to the α-halogenoalkyltin compounds is the treatment of an organotin halide with the appropriate organometallic reagent $MCH_xR_yX_z$ ($x + y + z = 3$), where X is a halogen. The metal M can be lithium or magnesium, but the group CH_2Br or CH_2I is probably best introduced with the Simmons-Smith reagents, $BrCH_2ZnBr$ or ICH_2ZnI. Some examples of these reactions are given in Table 6-1.

Table 6-1 Preparation of α-halogenoalkyltin compounds

Tin(IV) halide	Reagent	Conditions	Product	Ref.
Me_3SnCl	$IZnCH_2I$	THF, 40 °C 90–95% yield	Me_3SnCH_2I	2, 3
Me_3SnCl	$LiCCl_3$	THF, –100 °C	Me_3SnCCl_3	4
Me_3SnCl		THF, –90 °C		5
Bu_3SnCl	$LiCHBr_2$	LiI, $CrCl_2$, DMF THF, 25 °C	$Bu_3SnCHBr_2$	6
Bu^tMe_2SnCl	$IZnCH_2I$	THF, 40 °C 85% yield	$Bu^tMe_2SnCH_2I$	3

Nucleophilic displacement of the halide in the halogenoalkyltin compounds with reagents such as RS^-, RO^-, or R_2N^-, then gives other α-functionally-substituted compounds, and, particularly, reaction of $Bu_3SnCHBr_2$ with NaI in acetone gives Bu_3SnCHI_2 in quantitative yield, which is useful in synthesis.[7] The compounds R_3SnCH_2MgI (from R_3SnCH_2I and magnesium), and R_3SnCH_2Li, (from R_3SnCH_2I and R′Li)[8, 9] are versatile reagents for introducing a functional group at various positions in the alkyltin chain.

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Halogenoalkyltin compounds have also been prepared by insertion of an alkylene unit from a diazoalkane into $SnCl_4$ (e.g. equation 6-1),[10] and $Bu_3SnCHCl_2$, $Ph_3SnCHCl_2$, and $Bu_3SnCHBr_2$ can be prepared by insertion of a dihalogenocarbene from NaOH/CHX_3 into the SnH bond, under phase-transfer conditions (equation 6-2).[11, 12]

$$\mathrm{SnCl_4} \xrightarrow[0\ ^\circ\mathrm{C},\ 10\ \mathrm{h}]{\mathrm{CH_2N_2,\ PhMe}} \mathrm{(ClCH_2)}_n\mathrm{SnCl}_{4\text{-}n} \quad (n = 1\text{-}4) \tag{6-1}$$

$$\mathrm{Bu_3SnH + CHCl_3} \xrightarrow[\mathrm{CHCl_3,\ RT.\ 51\%}]{\mathrm{NaOH,\ 18\text{-}crown\text{-}6}} \mathrm{Bu_3SnCHCl_2} \tag{6-2}$$

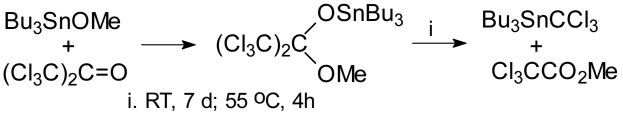
By reactions of these types, the compounds $(XCH_2)_nSnX_{4-n}$ (n = 1–4, X = Cl or Br), $(MeCHCl)_nSnX_{4-n}$ (n = 1–4), and $(PrCHCl)_2SnCl_2$ have been prepared from SnX_4, and $(XCH_2)Me_2SnX$ (X = Cl, Br, I), $(ClCH_2)Bu_2SnCl$, and $Ph_2(BrCH_2)SnF$ from the appropriate dialkyltin dihalide. Anionic exchange then gives compounds such as Me_3SnCH_2SCN, $(RSCH_2)_4Sn$, and $(RSCH_2)_2Sn(SR)_2$.[13] Methylation of Cl_3SnCH_2X with a Grignard reagent gives the compounds Me_3SnCH_2X (X = Cl, Br, or I), which themselves give Grignard reagents which can be used in further transformations.

The trihalogenomethyltin compounds can be prepared by acidolysis of a tin amide R_3SnNEt_2 (R = Me, Bu, or Ph) with the haloform HCX_3 (X = Cl, Br, or I), and the CX_3 group can then be reduced to CHX_2 and CH_2X with lithium aluminium hydride.[14]

$$\mathrm{Bu_3SnNEt_2} \xrightarrow[\mathrm{RT,\ 15\ min}]{\mathrm{CHCl_3}} \mathrm{Bu_3SnCCl_3} \xrightarrow{\mathrm{i}} \mathrm{Bu_3SnCHCl_2} \xrightarrow{\mathrm{i}} \mathrm{Bu_3SnCH_2Cl} \tag{6-3}$$

$$\text{i. LiAlH}_4$$

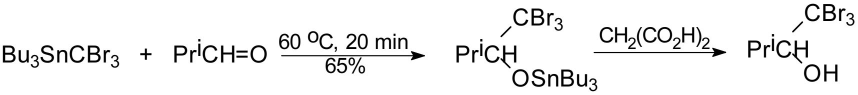
Tributyl(trichloromethyl)tin can also be made by elimination from the adduct of tributyltin methoxide and hexachloroacetone.[15]



$$\mathrm{Bu_3SnOMe + (Cl_3C)_2C{=}O \longrightarrow (Cl_3C)_2C(OSnBu_3)(OMe) \xrightarrow{i} Bu_3SnCCl_3 + Cl_3CCO_2Me} \tag{6-4}$$

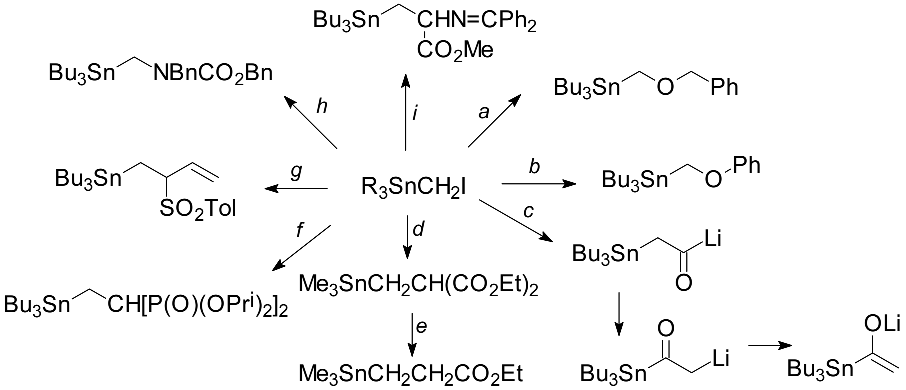
i. RT, 7 d; 55 °C, 4h

The reactivity of the $Sn-CX_nH_{3-n}$ bond increases as n increases, and the trihalogenomethyltin compounds are hydrolysed in air to give the haloforms and trialkyltin hydroxide or oxide, and are cleaved by halogens to give the carbon tetrahalides, YCX_3.[14] The carbonyl-forming elimination which is shown in equation 4-6 is reversible, and tributyltrichloromethyl- and tributyltribromomethyl-tin will add to an aldehyde to give, after hydrolysis, a 1,1,1-trihalogeno-2-hydroxyalkane (e.g. equation 6-5[16]).



$$\mathrm{Bu_3SnCBr_3 + Pr^iCH{=}O \xrightarrow[65\%]{60\ ^\circ C,\ 20\ min} Pr^iCH(CBr_3)(OSnBu_3) \xrightarrow{CH_2(CO_2H)_2} Pr^iCH(CBr_3)(OH)} \tag{6-5}$$

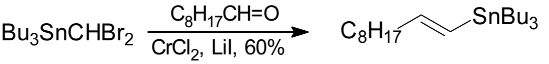
Typical reactions of R_3SnCH_2I are shown in Scheme 6-1. These reactions which change the functionality or shift it to a more remote site, are discussed in more detail in the following Sections.



Reagents and references: *a*. $PhCH_2OH$, NaOH.[17] *b*. PhOH, K_2CO_3.[18] *c*. (i) Bu^tLi, (ii) CO.[9] *d*. $NaCH(CO_2Et)_2$. *e*. KOH.[3] *f*. $NaCH(PO_3Pr^i{}_2)_2$.[3] *g*. $CH_2=CHCH_2SO_2Tol$, BuLi.[19] *h*. BnOCONHBn, BuLi.[19] *i*. $Ph_2C=NCH_2CO_2Me$, NaH.[20]

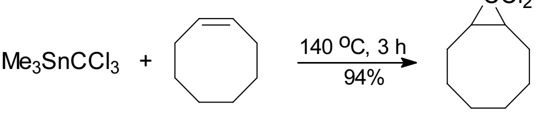
Scheme 6-1 Reactions of R_3SnCH_2I.

Dibromomethyltributyltin reacts with aldehydes in the presence of $CrCl_2$ and LiI, via Bu_3SnCHI_2 and perhaps $Bu_3SnCH(Cr^{III})_2$, to give *E*-alkenylstannanes (e.g equation 6-6).[6, 21, 22] Reactions of this type have been used in constructing the 1,3-diene units in the total synthesis of (-)-Macrolactin A and related compounds.[23, 24]



(6-6)

The trihalogenomethyltin compounds act as carbene-transfer reagents towards alkenes, often giving good yields of the dihalogenocyclopropanes (e.g. equation 6-7),[25] but rather little use has been made of these reactions in organic synthesis.



(6-7)

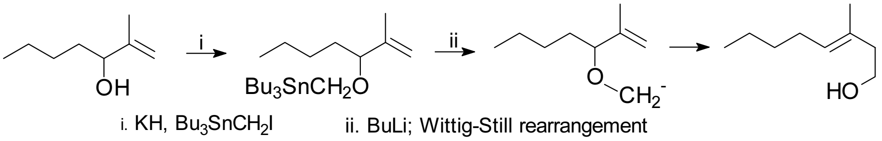
6.2 Other α-Substituted Alkylstannanes

The α-iodoalkyltin compounds described above react readily with a variety of nucleophiles (alcohols, phenols, thiols, amides etc.) to give further types of α-functionally-substituted compounds $R'_3SnCHRX$ (Scheme 6-1).[17, 26] These will then react with butyllithium to give the reagents LiCHRX (Section 22.1) which will react in turn with carbon electrophiles to extend the carbon chain, and this methodology has been exploited extensively in organic synthesis.

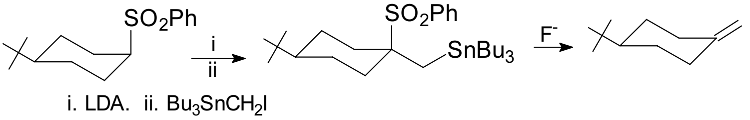
Alternatively, the α-alkoxyalkyltin compounds can be formed from an R_3SnLi or R_3SnMgX reagent and an alkoxyalkyl halide. A convenient one-pot process is shown in equation 6-8.[27]

$$Bu_3SnH \xrightarrow[0\ ^{o}C]{LDA,\ THF} Bu_3SnLi \xrightarrow[-78\ ^{o}C \rightarrow RT]{ClCH_2OBu} \underset{96\ \%}{Bu_3SnCH_2OBu} \qquad (6\text{-}8)$$

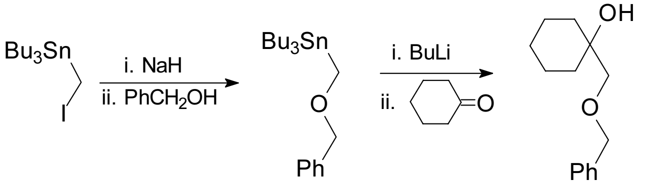
In organic synthesis, iodomethyltributyltin has been used for preparing allyl tributylstannylmethyl ethers which, on transmetallation with BuLi (Section 22.1), undergo a Wittig-Still [2,3]-sigmatropic rearrangement to give *Z*-trisubstituted olefins with high stereoselectivity[17, 28–31] (e.g. equation 6-9). It also provides a method for preparing alkenes from sulfides, sulfones, and nitriles (e.g. equation 6-10),[32] and a source of a carbinyl carbanion equivalent (e.g. equation 6-11).[17]



(6-9)

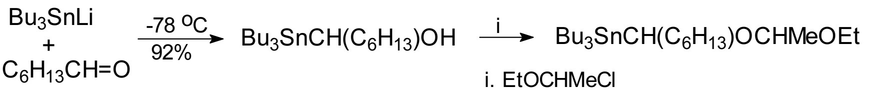


(6-10)



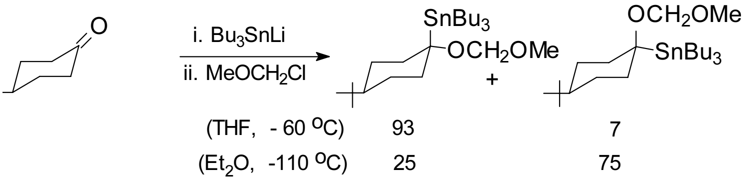
(6-11)

Tributyltinlithium[17] and tributyltinmagnesium chloride[33] react with aldehydes and ketones at low temperature to give α-hydroxyalkyltin compounds[34] which are rather unstable, but which can be stabilised with an alkoxyalkyl protecting group (equation 6-12); reaction with butyllithium then gives configurationally stable α-alkoxyalkyllithium compounds.[34, 35] 4-t-Butylcyclohexanone reacts with tributyltinlithium to give principally the equatorial stannyl compound under conditions of kinetic control, but the axial stannyl compound under conditions of thermodynamic control (equation 6-13).[36] The adduct with crotonaldehyde gives *threo*-selective ene reactions with aliphatic aldehydes and ketones, and with a menthoxymethyl protecting group, the reaction gives optically active products (equation 6-14).[37, 38]

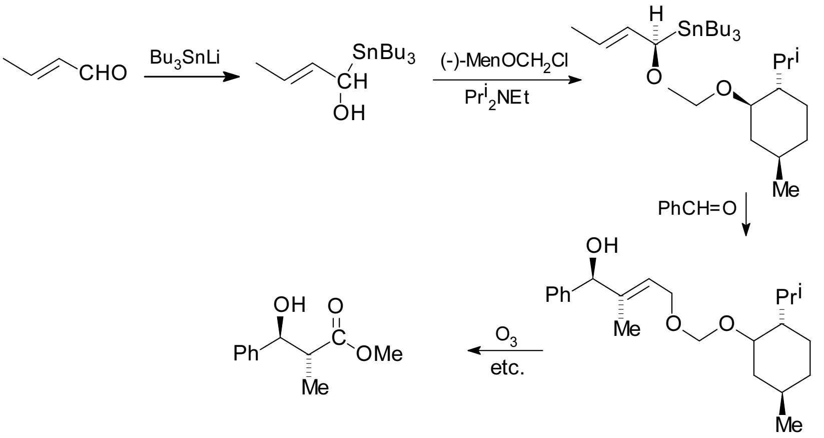


$$\mathrm{Bu_3SnLi} + \mathrm{C_6H_{13}CH{=}O} \xrightarrow[92\%]{-78\,^{\circ}\mathrm{C}} \mathrm{Bu_3SnCH(C_6H_{13})OH} \xrightarrow[\text{i. EtOCHMeCl}]{\text{i}} \mathrm{Bu_3SnCH(C_6H_{13})OCHMeOEt}$$

(6-12)

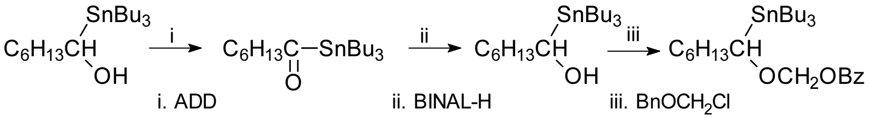


(6-13)



(6-14)

Oxidation of an α-hydroxyalkyltin compound with azodicarbonyldipiperide (ADD) gives the corresponding acyltin compound, which can then be reduced back with an optically active reducing agent (BINAL-H) to give the hydroxyalkyltin compound in high enantiomeric excess.[39] An alternative route to optically asymmetric α-alkoxyalkylstannanes is given below.

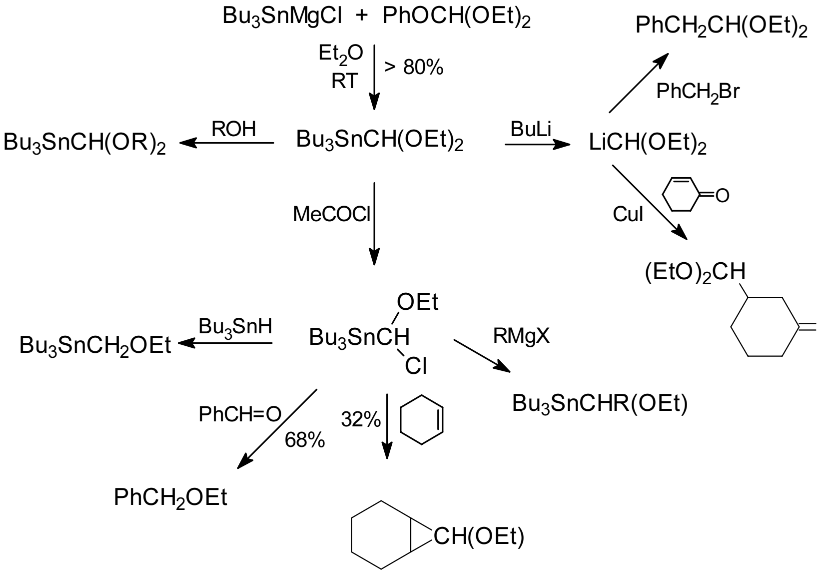


$$\mathrm{C_6H_{13}CH(SnBu_3)OH} \xrightarrow{\text{i}} \mathrm{C_6H_{13}C({=}O){-}SnBu_3} \xrightarrow{\text{ii}} \mathrm{C_6H_{13}CH(SnBu_3)OH} \xrightarrow{\text{iii}} \mathrm{C_6H_{13}CH(SnBu_3)OCH_2OBz}$$

i. ADD ii. BINAL-H iii. $BnOCH_2Cl$

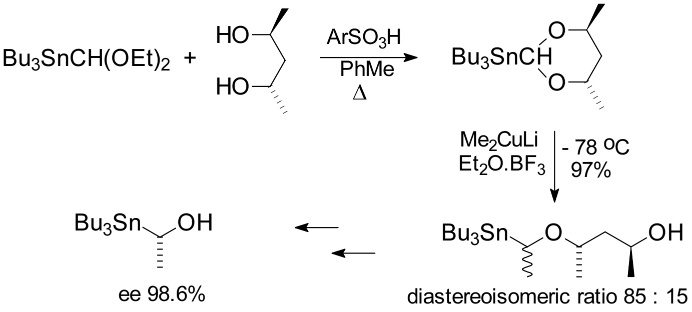
(6-15)

Di-α-ethoxyalkylstannanes (α-stannylacetals) can readily be prepared from a tributyltinmagnesium compound (from tributyltin hydride and isopropylmagnesium chloride) and diethyl phenyl orthoformate,[40] and have a promising potential in organic synthesis as masked aldehyde equivalents. Exchange with other alcohols, which may be optically active, under acid conditions gives other acyclic or cyclic stannylacetals,[41] and reaction with butyllithium gives the lithioacetal which acts a source of the $(EtO)_2CH$- nucleophile.[40] Reaction with acetyl chloride gives the α-chloro-α-alkoxyalkylstannane,[42] which can be reduced to the α-alkoxyalkylstannane, or alkylated with a Grignard reagent; it reacts with aldehydes by reductive etherification to give benzyl ethers, and transfers the (EtO)HC: carbene unit to alkenes. These reactions are illustrated in Scheme 6-2.



Scheme 6-2 Reactions of diethyl tributylstannylacetal.

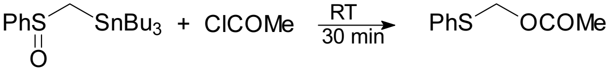
α-Alkoxyalkylstannanes that are optically asymmetric at the α-position can be obtained by the ring-opening of a chiral cyclic α-tributylstannylacetal with an organometallic reagent (equation 6-16). Transmetallation of the α-alkoxyalkylstannanes with butyllithium then gives configurationally stable α-alkoxyalkyllithium compounds.[43]



(6-16)

α-Thioalkoxytin compounds, R_3SnCH_2SR', can be prepared by treating the corresponding iodide with thiols,[2, 44] or a chloromethylthioether with a stannyllithium reagent.[45]

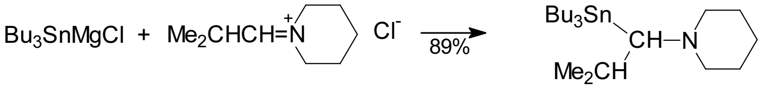
The normal protic Pummerer rearrangement has its metallic equivalent in the stannyl (and silyl) Pummerer reaction,[46–49] for example:[47]



(6-17)

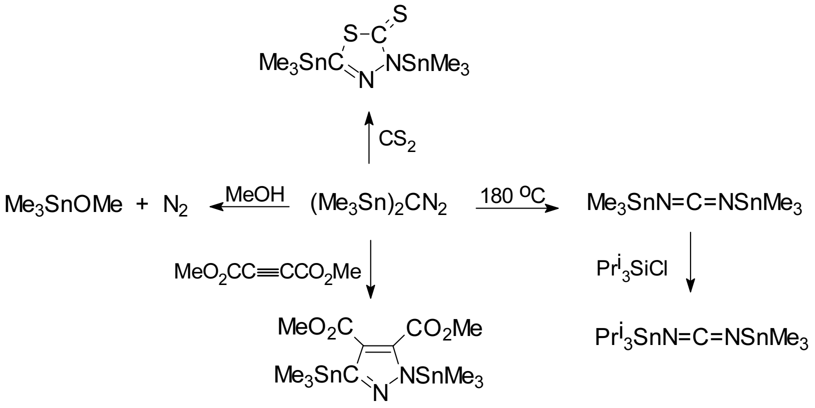
α-Aminoalkyltin compounds, $R_3SnCH_2NR_2'$, can similarly be prepared from the reaction of an amine with a compound R_3SnCH_2I,[50] or via a stannyllithium reagent[51] (e.g. equation 6-18).[50] An alternative method is to treat an immonium salt with R_3SnMgX (equation 6-19).[52] Reaction of these aminomethyltin compounds with butyllithium then gives the aminomethyllithium compounds,[51] which are useful in organic synthesis.

$$\mathrm{Bu_3SnLi + (PhSCH_2)_3N \xrightarrow[70\%]{} (Bu_3SnCH_2)_3N} \qquad (6\text{-}18)$$



(6-19)

The preparation of stannyl diazoalkanes such as $(Me_3Sn)_2CN_2$ and $Me_3SnCN_2CO_2Et$ by acidolysis of the Sn-N bond with a diazoalkane is referred to in Section 4.6. They can also be prepared from the reaction of Me_3SnCl with $LiCHN_2$.[53] At elevated temperatures, the bis(trialkylstannyl)diazomethanes rearrange to distannylcarbodiimides.[54] The Sn-C bond is readily cleaved by protic reagents, and the CN_2 unit reacts with dipolarophiles such as ArN=C=NAr, ArNCS, CS_2, PhNCO, $MeO_2CC{\equiv}CCO_2Me$, $CH_2{=}CHCN$, and $CH_2{=}CMeCO_2Me$ (Scheme 6-3) to give organotin derivatives of heterocycles.[55]

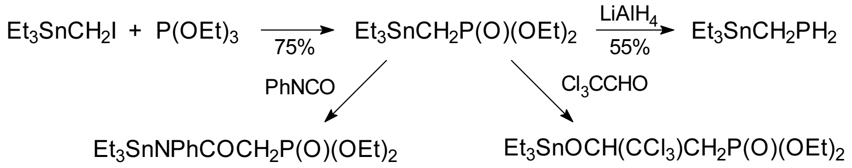


Scheme 6-3 Reactions of bis(trimethylstannyl)diazomethane.

(Trialkylstannylalkyl)phosphonates, $R_3SnCHR'P(O)(OR'')_2$, can be prepared by lithiation of the alkylphosphonate followed by reaction with the alkyltin chloride (equation 6-20),[56] or by an Arbuzov reaction between an iodomethyltin compound and a phosphite (equation 6-21).[57] The activated Sn−C bond will then add to a dipolar double bond, and the phosphonate group can be reduced to CH_2PH_2 with lithium aluminium hydride.

$$\mathrm{(RO)_2P(O)CH_2R' \xrightarrow{i} (RO)_2P(O)CHR'Li \xrightarrow{ii} (RO)_2P(O)CHR'SnR'''_3} \qquad (6\text{-}20)$$

$$\text{i. 2LDA, -60 °C} \qquad \text{ii. } \mathrm{R'''_3SnCl}\text{, -60 to -10 °C}$$



(6-21)

Acylstannanes, R_3SnCOR', have been prepared by a variety of methods, but none appears to be completely general. The acyltriphenylstannanes can be made from the reaction of triphenyltinlithium with an acyl chloride (equation 6-22).[58] Trimethyltrifluoroacetyl tin can be prepared in the same way,[59] but with other trialkyltin reagents the yield is low because the primary adducts undergo further addition. This can be minimised by using instead a thioester, or an ester in the presence of $BF_3.OEt_2$ (equation 6-23).[60] Tributylacylstannanes can conveniently be prepared by heating tributyltinmagnesium chloride with two molar equivalents of an aldehyde under reflux in ether; presumably addition occurs to give an α-stannyl alcohol, which is then oxidised by the aldehyde.[42] This reaction can be split into its constituent steps (equation 6-24); the reaction of tributyltinlithium gives the stannyl alcohol which is then oxidised.[39]

The only example of the equivalent of a Corey-Seebach reaction of the lithium derivative of a carbonyl-protected aldehyde involves an acetylenic ketone (equation 6-25).[61]

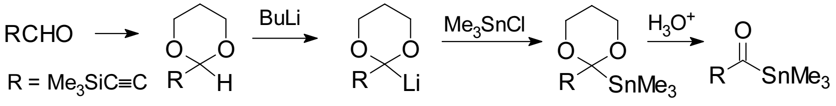
An alternative approach is to treat hexamethylditin with an acyl halide in the presence of a Pd(0) or Pd(II) catalyst, but the reaction is not successful with higher hexaalkyldistannanes.[62]

$$Ph_3SnLi + MeCOCl \xrightarrow[88\%]{THF,\ -70\ ^oC} Ph_3SnCOMe \qquad (6\text{-}22)$$

$$Bu_3SnLi + PrCOSMe \xrightarrow[39\%]{-78\ ^oC,\ 1\ h} Bu_3SnCOPr \qquad (6\text{-}23)$$

$$Bu_3SnLi + C_6H_{13}CHO \longrightarrow Bu_3SnCH(OH)C_6H_{13} \xrightarrow{i} Bu_3SnCOC_6H_{13} \qquad (6\text{-}24)$$

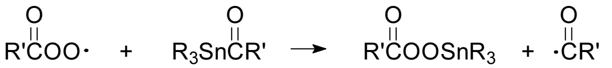
i. Azodicarbonyl dipiperidide



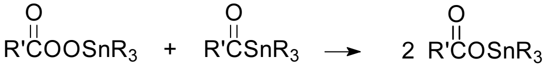
(6-25)

The properties of the acylstannanes (like those of the acylsilanes) belie their representation as simple metallaketones. The acyltrialkylstannanes are usually yellowish-green liquids, which can be distilled under reduced pressure, with ν_{max} ca. 380 nm, and a carbonyl stretching frequency of *ca.* 1640 cm^{-1}. In the NMR spectra, the value of δ ^{119}Sn is at a surprisingly high field (–80 to –90 for Bu_3SnCOR), and δ ^{13}C is at a surprisingly low field (235 to 245 for Bu_3SnCOR).[60, 62]

The acyltrialkylstannanes are readily hydrolysed to the parent aldehydes, and are oxidised in the air to give the corresponding carboxylates, $R_3SnOCOR'$, [63] in a radical chain reaction which presumably is similar to that of the autoxidation of an aldehyde, and involves as a key step the S_H2 reaction of an acylperoxyl radical at tin rather that at hydrogen (equation 6-26). The trialkylstannyl peroxyester which is formed then reacts with the parent stannyl ketone to give the trialkyltin carboxylate.

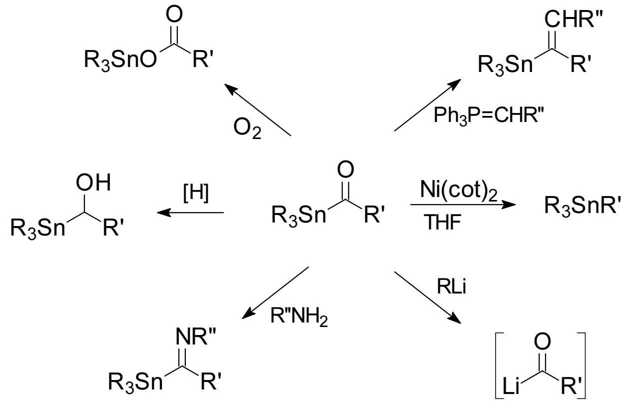


$$R'\overset{O}{\overset{\|}{C}}OO\cdot \; + \; R_3Sn\overset{O}{\overset{\|}{C}}R' \longrightarrow R'\overset{O}{\overset{\|}{C}}OOSnR_3 \; + \; \cdot\overset{O}{\overset{\|}{C}}R' \qquad (6\text{-}26)$$



$$R'\overset{O}{\overset{\|}{C}}OOSnR_3 \; + \; R'\overset{O}{\overset{\|}{C}}SnR_3 \longrightarrow 2\; R'\overset{O}{\overset{\|}{C}}OSnR_3 \qquad (6\text{-}27)$$

The reactions of the acylstannanes are illustrated in Scheme 6-4. They are reduced by aluminium hydrides to the corresponding alcohols,[39, 58] and react with various phosphorus ylids to give vinylstannanes.[64]



Scheme 6-4 Reactions of acylstannanes.

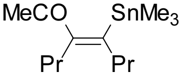
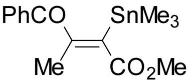
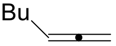
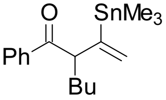
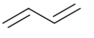
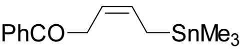
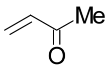
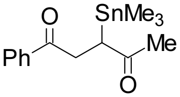
With a Ni(cot)$_2$ catalyst in a polar solvent, carbon monoxide is evolved and the stannane R$_3$SnR′ is formed, presumably by oxidative addition to give R$_3$SnNi^{II}COR′ then elimination of CO followed by reductive elimination, and they react with acyl halides in the presence of a palladium(II) catalyst to give the corresponding α-diketones.[65] Reactions of potential synthetic use have been developed, in which oxidative addition is followed by insertion of an electron-rich[66] or electron-poor alkyne,[67] or of a 1,2-[68] or 1,3-diene,[69] or of an enone.[67] Typical reactions and reaction conditions are shown in Table 6-2.

Cleavage of the acyl-tin bond with an organolithium compound might be expected to give an acyllithium compound which would act as an umpolung reagent for carrying out nucleophilic acylations. Attempts to do this have met with little success,[70] and because of this, and the instability of the parent acylstannanes, these compounds have as yet found limited use in organic synthesis.

Similar attention has therefore been directed towards the imidoylstannanes, R$_3$SnC(=NR′)R″ (often called stannylimines), which are formed by reaction of the acylstannanes with amines,[71] and which might give lithium reagents which would act as masked acyl anion equivalents.

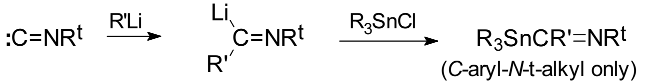
The condensation of an acylstannane with an amine to give an imidoylstannane can be carried out by removing the water azeotropically or with molecular sieves, and appears to be general for alkyl or acyl groups on N or C.[71] The other preparative methods

Table 6-2 Insertion reactions involving acylstannanes

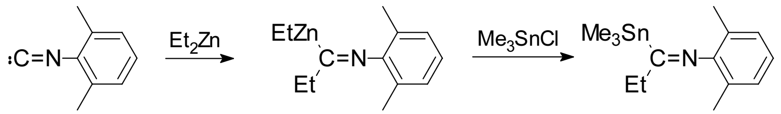
Acylstannane	Co-reactant	Conditions and yield	Product
$MeCOSnMe_3$	$Pr-C\equiv C-Pr$	5 mol% Ni(cod)$_2$, PhMe, 100 °C, 1.5 h. 61%	
$PhCOSnMe_3$	$Me-C\equiv C-CO_2Me$	5 mol% Ni(cod)$_2$, PhMe, 30 °C, 1.5 h. 56%	
$PhCOSnMe_3$		5 mol% Ni(cod)$_2$, PhMe, 50 °C, 1.5 h. 79%	
$PhCOSnMe_3$		5 mol% Ni(cod)$_2$, PhMe, 50 °C, 0.2 h. 73%	
$PhCOSnBu_3$		2.5 mol% Pd(dba)$_3$, THF, 50 °C, 2 h. 71%	

which are available are more restricted, as indicated in equations 6-28,[72–75] 6-29,[76] 6-30, and 6-31.[77, 78]

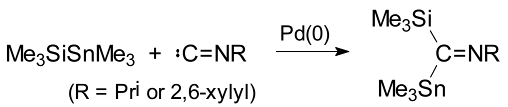
$$Me_3SnLi + ArCCl{=}NAr \longrightarrow \underset{(C\text{-aryl-}N\text{-aryl only})}{Me_3SnCAr{=}NAr} \qquad (6\text{-}28)$$



$$:C{=}NR^t \xrightarrow{R'Li} \begin{matrix}Li\\ \quad C{=}NR^t\\ R'\end{matrix} \xrightarrow{R_3SnCl} \underset{(C\text{-aryl-}N\text{-t-alkyl only})}{R_3SnCR'{=}NR^t} \qquad (6\text{-}29)$$



(6-30)



$$Me_3SiSnMe_3 + :C{=}NR \xrightarrow{Pd(0)} \begin{matrix}Me_3Si\\ \quad C{=}NR\\ Me_3Sn\end{matrix} \qquad (6\text{-}31)$$

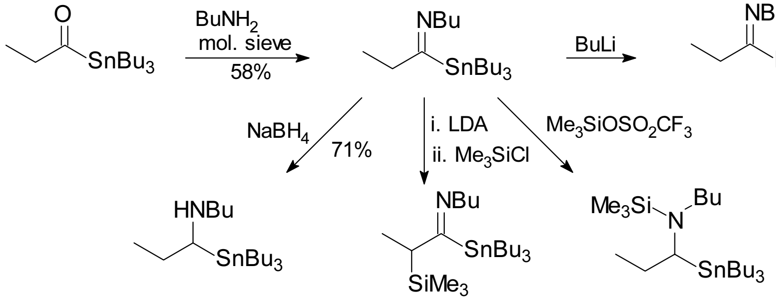
(R = Pr^i or 2,6-xylyl)

Trimethyl(*N*-phenylbenzimidoyl)stannane reacts with halides such as benzyl or allyl bromide, benzoyl chloride, or methyl iodide in the presence of KF and 18-crown-6 to give the corresponding ketimine; presumably attack of the fluoride ion at tin gives an imidoyl anion equivalent.[73]

$$Ph(Me_3Sn)C{=}NPh + PhCH_2Br \xrightarrow[\text{18-crown-6}]{KF} Ph(PhCH_2)C{=}NPh \qquad (6\text{-}32)$$

40%

Further typical reactions of imidoylstannanes are shown in Scheme 6-5.[71] Butyllithium reacts to form the imidoyllithium, which reacts with electrophiles such as alkyl halides, silyl chlorides, aldehydes, or chloroformates,[75] and the Stille reaction with an acyl halide gives an α-carbonylimide which can be hydrolysed to an α-dicarbonyl compound.[75]

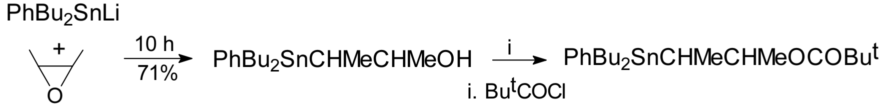


Scheme 6-5 Reactions of imidoylstannanes.

6.3 β-Functional Alkylstannanes

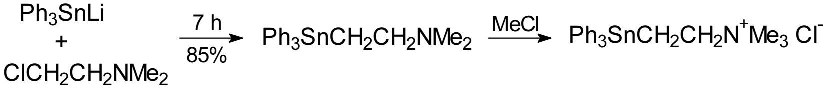
The β-functional alkyl-tin bond can be generated from organotin compounds containing nucleophilic tin ($R_3Sn^{\delta-}$ $M^{\delta+}$) or electrophilic tin ($R_3Sn^{\delta+}X^{\delta-}$), or by reactions which involve radicals or carbenes. The functional group can also be introduced by manipulation of an alkyl chain which is already present. β-Ketoalkyltin compounds, which are in metallotropic equilibrium with the corresponding tin enolates, are considered in Section 14.3 which deals with Sn–O bonded compounds.

β-Hydroxyalkyltin compounds can be prepared by the reaction of a tin-metal bonded compound $R_3Sn^{\delta-}$ $M^{\delta+}$ (M = Li,[79] Na,[80] or MgBr,[81]) with an epoxide, for example equation 6-33.[79]



$$\begin{array}{c}\mathrm{PhBu_2SnLi}\\+\\\text{epoxide}\end{array}\xrightarrow[71\%]{10\ h}\mathrm{PhBu_2SnCHMeCHMeOH}\xrightarrow[\text{i. Bu}^t\text{COCl}]{\text{i}}\mathrm{PhBu_2SnCHMeCHMeOCOBu^t}\qquad(6\text{-}33)$$

A similar reaction with a 2-chloroalkylamine gives β-aminotin compounds:[82]

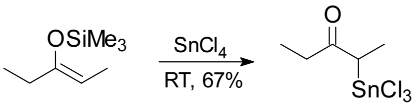


$$\begin{array}{c}\mathrm{Ph_3SnLi}\\+\\\mathrm{ClCH_2CH_2NMe_2}\end{array}\xrightarrow[85\%]{7\ h}\mathrm{Ph_3SnCH_2CH_2NMe_2}\xrightarrow{\mathrm{MeCl}}\mathrm{Ph_3SnCH_2CH_2N^+Me_3\ Cl^-}\qquad(6\text{-}34)$$

The opposite polarity in the organotin reagent $R_3Sn^{\delta+}X^{\delta-}$ can be exploited in, for example, the reaction of a tin alkoxide with an vinyl ester,[83] the addition of an alkoxy- or amino-tin compound to a ketene,[84] the reaction of a silyl enolate with a tin chloride,[85] or the addition of an alkyltin hydride under non-radical conditions to an α,β-unsaturated carbonyl compound.[86]

$$\mathrm{Et_3SnOMe} + \mathrm{MeC(O)OC(CH_3){=}CH_2}\xrightarrow[95\%]{30\ \text{min},\ 50\ ^\circ\text{C}}\mathrm{Et_3SnCH_2C({=}O)CH_3}\qquad(6\text{-}35)$$

$$Me_3SnOMe + CH_2{=}C{=}O \longrightarrow Me_3SnCH_2CO_2Me \qquad (6\text{-}36)$$

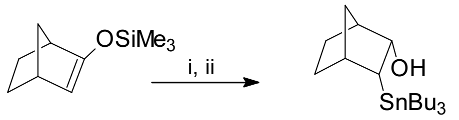


(6-37)

$$Me_3SnH + HC{\equiv}CHCO_2Me \xrightarrow{\text{galvinoxyl}} CH_2{=}C(SnMe_3)CO_2Me \qquad (6\text{-}38)$$

The alkyltin bond can also be formed by the homolytic hydrostannation of a vinyl compound C=C–X, provided the group X is itself not subject to attack.[87]

$$Et_3SnH + CH_2{=}CHOEt \xrightarrow[\text{2 h, 65\%}]{\text{AIBN, 30-40 }^{o}\text{C}} Et_3SnCH_2CH_2OEt \qquad (6\text{-}39)$$



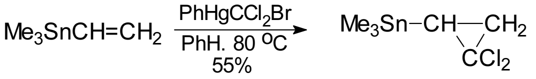
(6-40)

i. Bu_3SnH, AIBN, 110 °C, 48 h. ii. Bu_3SnF

An alternative approach involves the insertion of a carbene unit from a diazoaliphatic compound, N_2CHX (X = CN, CO_2Et, COMe, *etc.*), into an SnH bond to generate the group $SnCH_2X$, for example:[88]

$$Pr_3SnH + N_2CHCO_2Et \longrightarrow Pr_3SnCH_2CO_2Et \qquad (6\text{-}41)$$

An example of the introduction of the functional group by manipulation of an organic group is shown in equation 6-42.[89, 90]

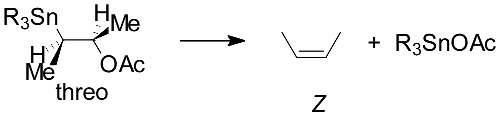


$$Me_3SnCH{=}CH_2 \xrightarrow[\substack{\text{PhH. 80 }^{o}\text{C} \\ 55\%}]{PhHgCCl_2Br} Me_3Sn{-}\underset{\diagdown\ \diagup}{CH{-}CH_2}\atop CCl_2 \qquad (6\text{-}42)$$

Two particular reactions are characteristic of the β-functional alkyltin compounds. First, conjugative electron attraction by the functional group makes $^{-}C{-}C{=}X$ a good leaving group, and the Sn–C bond has an enhanced reactivity in substitution (e.g. hydrolysis) and addition; where C=X is a nitrile, ketone, ester, or amino group, the compounds add across the N=C bond in isocyanates, and undergo Reformatsky-type reactions with carbonyl compounds.[91, 92]

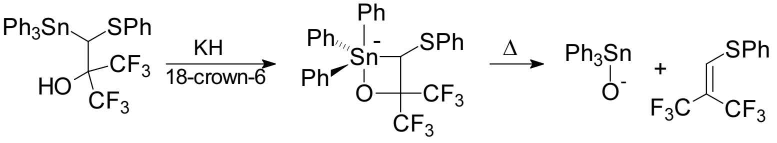
$$\begin{matrix} Bu_3SnCH_2C{\equiv}N \\ + \\ C_6F_5CH{=}O \end{matrix} \longrightarrow Bu_3SnOCH(C_6F_5)CH_2C{\equiv}N \xrightarrow{H^+} HOCH(C_6F_5)CH_2C{\equiv}N \qquad (6\text{-}43)$$

Second, if the functional group is singly bonded (Sn–C–C–X, X = $^{+}NR_3$,[82] OH,[80] or OAc[93]) β-elimination occurs to give R_3SnX and the alkene C=C. Highly stereospecific *anti*-eliminations usually occur (*e.g.* equation 6-44)[93] and the compounds $R_2Sn(CH_2CHR'OCOR'')_2$ have been proposed as latent catalysts which release the dicarboxylates $R_2Sn(OCOR'')_2$ at high temperature, which can then induce the room temperature vulcanisation of silicone polymers or the formation of polyurethanes.[94]



(6-44)

The compound $Bu_3SnCHMeCHMeOH$ shows *anti*-elimination up to 100 °C, but *syn*-elimination above 100 °C, when the reaction occurs through the compound $Bu_3SnCHMeCHMeOSnBu_3$ which is formed by reaction with the bis-tributyltin oxide which is eliminated.[95] The intermediate **6-1** in the base-induced tin-Peterson elimination of a β-hydroxyalkyltin compound has been isolated as a stable compound. X-Ray crystallography shows that the configuration at the tin is closer to a square pyramid than a trigonal bipyramid.[96, 97]



(**6-1**)

(6-45)

6.4 γ-Functional Alkylstannanes

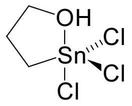
ω-Bromoalkylstannanes, $R_3Sn(CH_2)_nBr$, where $n \geq 3$, can be prepared by the oxidative addition of an α,ω-dibromoalkane to stannous bromide. Conversion of the bromide to the Grignard reagent then makes it possible to introduce a variety of other functional groups here and further down the chain, as illustrated in equation 6-46.[98]

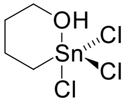
$$\begin{tikzcd}
{} & SnBr_2 + Br(CH_2)_3Br \arrow[r, "Et_3Sb,\ 150\text{-}160\ ^{o}C", "4\text{-}5\ h,\ 74\%"'] & Br_3Sn(CH_2)_3Br \arrow[d, "MeMgBr"] \\
Me_3Sn(CH_2)_3CO_2H & Me_3Sn(CH_2)_3MgBr \arrow[l, "CO_2"'] & Me_3Sn(CH_2)_3Br \arrow[l, "Mg"']
\end{tikzcd} \qquad (6\text{-}46)$$

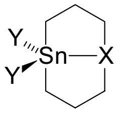
A simple and ingenious route to the γ-hydroxyalkyltin compounds is shown in equation 6-47. The Grignard reagent derived from a γ-bromoalkoxytin compound reacts at the SnO bond to make the new Sn–C bond and transfer the OH group to the end of the chain.[99]

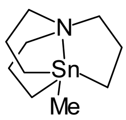
$$\begin{tikzcd}
(Bu_3Sn)_2O + HO(CH_2)_3Br \arrow[r] & Bu_3SnO(CH_2)_3Br \arrow[d, "\text{Mg, ether}"'] \\
Bu_3Sn(CH_2)_3OH & Bu_3SnO(CH_2)_3MgBr \arrow[l, "i.\ \Delta"', "ii.\ H_3O^+"]
\end{tikzcd} \qquad (6\text{-}47)$$

When functional groups are in the γ or more distant position, they may coordinate intramolecularly to the tin. The compounds $Cl_3Sn(CH_2)_nOH$ have the cyclic structures **6-2** and **6-3**, respectively, when $n = 3$ or 4, but exist as linear coordination polymers with Sn–O 235.6(6) pm when $n = 5$.[100]


(6-2)

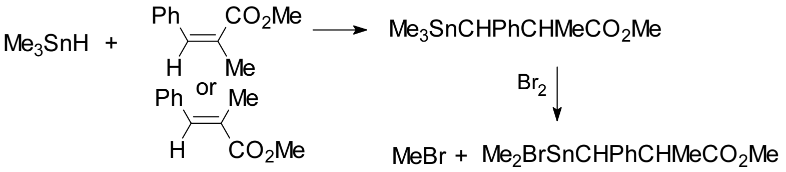

(6-3)


(6-4)


(6-5)

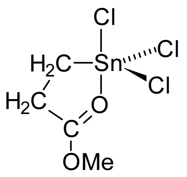
The cyclic compounds $Y_2Sn[(CH_2)_3]_2X$ (X = NMe, NBu, NBu^t, NPr^i, O, S; Y = Cl or Ph_3Si) all have the bicyclic structure **6-4**,[101] and the stannatrane $MeSn[(CH_2)_3]_3N$ has the triptych structure **6-5**.[102]

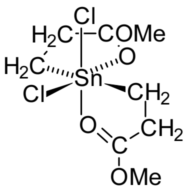
The hydrostannation of α,β-unsaturated nitriles, esters, ketones, amides, etc. under free radical conditions provides another easy entry into γ-functional alkyltin compounds. The method was initially applied to the preparations of compounds such as $R_3SnCH_2CHMeC{\equiv}N$, $R_3SnCH_2CH_2CONH_2$, $R_3SnCH_2CH_2CH_2OH$, $R_3SnCH_2CH_2CO_2Me$, $R_3SnCH_2CH_2CH(OEt)_2$, and $R_3SnCH_2CH_2C{\equiv}N$,[103] and has since been widely exploited. It will be obvious that the functional group can be further manipulated to provide other functionalities, and an example of this is given in equation 5-3. The initial addition of the stannyl radical to the double bond is reversible, and the *E*- and *Z*-isomers of an olefin can give identical products (equation 6-48).[104] Bromine now cleaves the tin-methyl bond, rather than the tin-benzyl bond, in the product, and this is attributed to intramolecular participation of the carbonyl group in the transition state, which places the benzyl group equatorial and a methyl group in the (reactive) apical position.[105]


(6-48)

$$SnCl_2 + HCl \xrightarrow{Et_2O} [HSnCl_3] \xrightarrow{CH_2{=}CHCO_2Me} Cl_3SnCH_2CH_2CO_2Me \qquad (6\text{-}49)$$

Addition of a trialkyltin hydride under polar conditions to an acrylic ester places the tin on C-2, i.e. the tin is acting as an electrophile, $R_3Sn^{\delta+}H^{\delta-}$. In the reagents Cl_3SnH and Cl_2SnH_2, however, the electron-attracting halogen atoms reverse the polarity, and the nucleophilic $H_{3-n}Cl_nSn^{\delta-}$ group adds at C-3 (equation 6-49) to give the "estertin" derivatives which are the precursors of PVC stabilisers (see Sections 4.4 and 23.1).[106–108] The presence of the halogen atoms enhances the Lewis acidity of the tin, and the estertin halides $Cl_3SnCH_2CH_2CO_2Me$ (**6-6**) and $Cl_2Sn(CH_2CH_2CO_2Me)_2$ (**6-7**) are already 5- and 6-coordinate, respectively, in the crystalline state,[109] modelling the interaction which is thought to be involved in the transition state for bromination, which is discussed above.


(6-6)


(6-7)

γ-Hydroxyalkylstannanes can be prepared by the reaction of an SnMg compound with an oxetane,[81] but the oxetanes are not so readily available as the oxiranes, and indeed one useful route to the oxetanes involves the cycloelimination from a 3-chloropropoxystannane.

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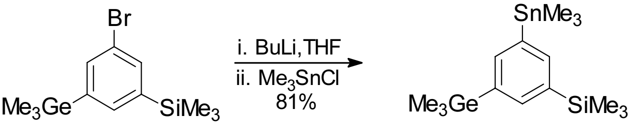
7 Aryl- and Heteroaryl-stannanes[1]

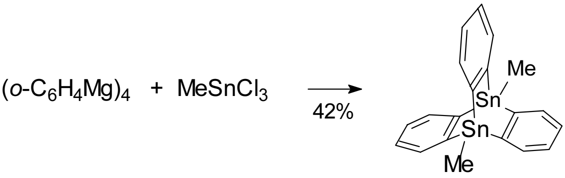
7.1 Arylstannanes

Some examples of the application of the general methods for forming the Ar–Sn bond, which are described in Chapter 3, are given in equations 7-1,[2] 7-2,[3] and 7-3.[4] Lee has described the synthesis of arylstannanes in good yield by the Barbier reaction between aryl halides, magnesium, and bis(tributyltin) oxide, with ultrasonication (equation 7-4).[5]

$$C_6F_5I \xrightarrow[\text{v. high yield}]{\text{Sn, 240 }^oC} (C_6F_5)_4Sn \xleftarrow[60\%]{\text{Sn, 260 }^oC} (C_6F_5)_2Hg \qquad (7\text{-}1)$$



(7-2)



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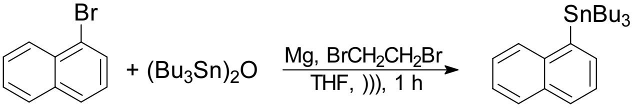
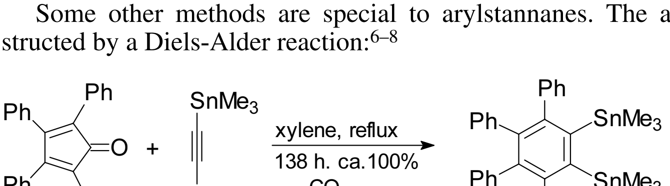


(7-4)

Some other methods are special to arylstannanes. The aromatic ring can be constructed by a Diels-Alder reaction:[6–8]



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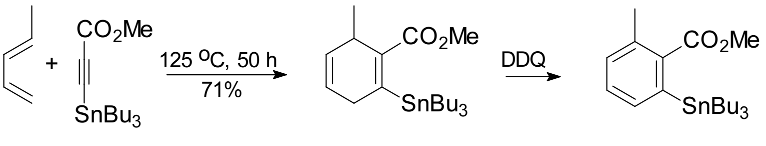

(7-6)

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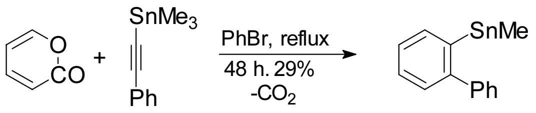
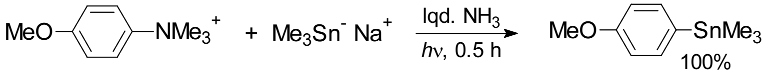


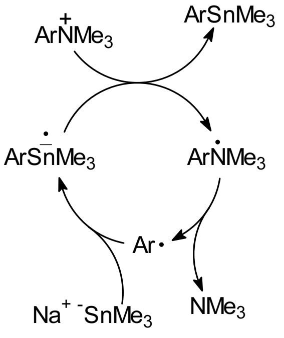
(7-7)

Metallic stannides can react with aryl halides,[9–11] or phenols via the aryl dialkyl phosphates,[12, 13] or aryl ammonium salts,[14] in a photostimulated $S_{RN}1$ reaction, for example:



(7-8)

The likely mechanism is illustrated for the ammonium salt in Scheme 7-1. The reaction is initiated by electron transfer from R_3Sn^- to the arene, and then the radical chain is carried by $ArNMe_3$• and $ArSnMe_3$•-.



Scheme 7-1 $S_{RN}1$ mechanism for the formation of arylstannanes.

Arylstannanes can also be made by the reaction between aryl bromides and hexamethylditin with a palladium catalyst,[15–17] for example reaction 7-9.[17] The mechanism might reasonably be assumed to involve oxidative addition of ArX, followed by transmetallation and reductive elimination (equation 7-10).

$$\text{1-Br,2-NO}_2\text{C}_6\text{H}_4 + \text{Me}_3\text{SnSnMe}_3 \xrightarrow[\text{THF, reflux}]{\text{Pd(PPh}_3)_4} \underset{75\%}{\text{1-Me}_3\text{Sn,2-NO}_2\text{C}_6\text{H}_4} + \text{Me}_3\text{SnBr} \qquad (7\text{-}9)$$

$$\text{L}_4\text{Pd}^{\text{o}} + \text{ArX} \longrightarrow \text{L}_2\text{Pd}^{\text{II}}(\text{Ar})\text{X} \xrightarrow[-\text{R}_3\text{SnX}]{\text{R}_6\text{Sn}_2} \text{L}_2\text{Pd}^{\text{II}}(\text{Ar})\text{SnR}_3 \xrightarrow{2\text{L}} \text{L}_4\text{Pd}^{\text{o}} + \text{ArSnR}_3 \qquad (7\text{-}10)$$

6-Tributylstannylazulenes have been prepared in a similar reaction from 6-bromoazulene and hexabutylditin in the presence of $Pd(PPh_3)_4$, and then used in Stille reactions for making polyazulenylbenzenes.[18]

The aryl-tin bond, like the alkyl-tin bond, is stable to air and moisture, but it is more susceptible to cleavage by electrophiles. Melting points of some aryltin compounds are given in Table 7-1.

Table 7-1 Tetraarylstannanes.

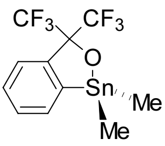
Compound	m.p./°C	Compound	m.p./°C
$(C_6H_5)_4Sn$	226	$(C_6F_5)_4Sn$	220–222
$(2\text{-}MeC_6H_4)_4Sn$	219	$(C_6Cl_5)_4Sn$	447–449
$(3\text{-}MeC_6H_4)_4Sn$	130	$(4\text{-}FC_6H_4)_4Sn$	144–145
$(4\text{-}MeC_6H_4)_4Sn$	236–237	$(4\text{-}ClC_6H_4)_4Sn$	197–199
$(4\text{-}MeOC_6H_4)_4Sn$	135	$(2,4,6\text{-}Me_3C_6H_2)_4Sn$	> 300dec.
$(4\text{-}MeSC_6H_4)_4Sn$	169–170	$(1\text{-}Np)_4Sn$	310–320

Tetraphenyltin is nominally tetrahedral in the crystal and in the gas phase, with rSn–C 213.9(4) pm (X-ray diffraction)[19] or 216.0(7) pm (electron diffraction).[20] Deviations from strict tetrahedral symmetry at tin in the triarylstannanes have been ascribed to π–π repulsion and π–σ(CSn) attraction.[21, 22]

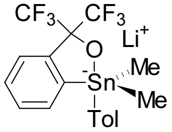
The photoelectron spectrum of Ph_4Sn (and of Ph_4C, Ph_4Si, Ph_4Ge, and Ph_4Pb) resembles that of benzene, with ionisation energies 9.25 and 9.04 eV, respectively, implying that any interaction between the phenyl groups is small.[23] The ESR spectrum of the radical anion $Me_3SnPh^{\bullet-}$ shows that the unpaired electron occupies principally the ψ_S orbital of the benzene ring, indicating that, in at least this situation, the trimethylstannyl substituent withdraws electrons from the benzene ring[24] (as do also the Me_3Si and Me_3Ge groups).[25] Electron-donating groups in the *para* position in compounds Ar_4Sn and Ar_3SnX move the ^{119}Sn NMR chemical shift *downfield*, e.g. Ph_4Sn δ –128.84, $(4\text{-}MeC_6H_4)_4Sn$ δ -122.98, $(4\text{-}MeOC_6H_4)_4Sn$ δ –115.38.[26] In the series of compounds $Ph_{4-n}Sn(p\text{-}Tol)_n$ the ^{13}C-*ipso* chemical shifts show an increase in shielding in the series Si < Ge < Sn << Pb (e.g. Ph_4M: Si 134.3, Ge, 136.2, Sn 138.0, Pb 150.1).[21]

The introduction of *ortho* substituents lengthens the phenyl-tin bond slightly, and the steric hindrance imposed by extensive *ortho* substitution may confer kinetic stability on a stannylium ion Ar_3Sn^+ (Section 7.2), a stannyl radical $Ar_3Sn^\bullet$ (Section 18.2.3), a stannylene Ar_2Sn: (Section 21.1.2), a small oligomer cyclo-$(Ar_2Sn)_n$ (Section 18.4), a stannene $Ar_2Sn{=}X$ (Section 21.4), or a distannene $Ar_2Sn{=}SnAr_2$ (Section 21.2). Some examples are $Ar_2Sn{=}SnAr_2$ (Ar = $2,4,6\text{-}Pr^i{}_3C_6H_2$),[27] *cyclo*$(Ar_2Sn)_3$ (Ar = $2,6\text{-}Et_2C_6H_3$),[28] $Ar_2Sn{=}NMes$ [Ar = $2,4,6\text{-}(CF_3)_3C_6H_2$],[29] Ar_2Sn: [Ar = $2,4,6\text{-}(CF_3)_3C_6H_2$],[30] and $Ar_3Sn^\bullet$ (Ar = $2,4,6\text{-}Pr^i{}_3C_6H_2$),[31] and these compounds are discussed in the appropriate later sections.

Tetraphenyltin, like the tetraalkyltin compounds, has little propensity to accept a further ligand to become 5-coordinate, but it reacts with phenyllithium to form the complex Ph_5Sn^- in solution.[32] When phenyl and methyl groups are mixed, the compounds $Ph_nMe_{5-n}Sn^-$ are all in equilibrium, the relative concentration increasing as n increases, and the phenyl groups apparently preferring to occupy the apical positions in the trigonal bipyramid. 3-Tributylstannaindene similarly reacts with butyllithium to give a deep red ate complex.[33]

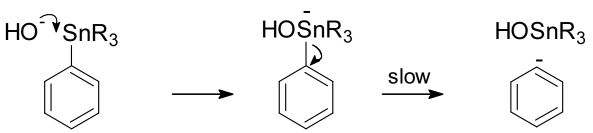


(7-1)



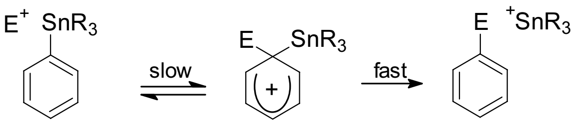
(7-2)

The cyclic alkoxide **7-1** reacts with *p*-tolyllithium to give the diaryldialkylalkoxytin 10-Sn-5 ate complex **7-2**.[34] The Ar-Sn bond in ArSnMe$_3$ is cleaved by hydroxide ion in DMSO/aq. KOH, by nucleophilic attack at the tin. The rate-determining stage is the cleavage of the Sn-Ar bond, and this may derive some electrophilic assistance from the solvent.[35]



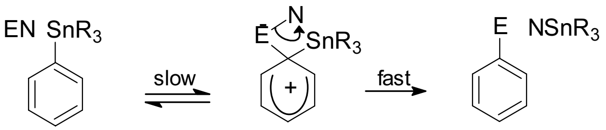
(7-11)

The aryl−Sn bond is cleaved by electrophiles much more readily than the aryl-H bond, and aryl−tin compounds react by *ipso* substitution by the classic mechanism for electrophilic substitution.[36] The part that symmetry-enhanced hyperconjugation plays in determining the reactivity and regioselectivity is discussed in Section 3.1.2.2.[37]



(7-12)

With electrophiles E−N, nucleophilic assistance may be provided:[38]



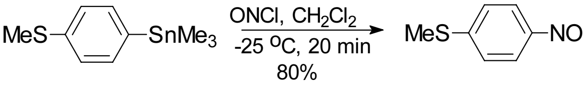
(7-13)

Relative rates of cleavage of the Ph−M bond (by aqueous ethanolic perchloric acid) where M = H, Me$_3$Si, Me$_3$Ge, Me$_3$Sn, and Me$_3$Pb are approximately $2.5 \times 10^{-5} : 1 : 36 : 3.5 \times 10^{5} : 2 \times 10^{8}$.[39] These reactions of arylstannanes, therefore, make it possible to introduce an electrophilic group E under mild conditions, regiospecifically overruling the normal directive effect of substituents.[40] For example, deuterium- or tritium-labels can be introduced regiospecifically into an aromatic ring under mild conditions which do not risk subsequent protium-deuterium or protium-tritium exchange,[41] and a short-lived radioactive fluorine or iodine label can be introduced rapidly and in essentially quantitative yield.[42] The mild conditions under which nitrosyl chloride reacts with aryltin compounds makes this the preferred route to some nitrosoarenes,[43] and the diazo-coupling reaction can be carried out when the parent arene (e.g. toluene) is unreactive, and at a site which is usually inaccessible (e.g. *meta* to a methyl group).[44]

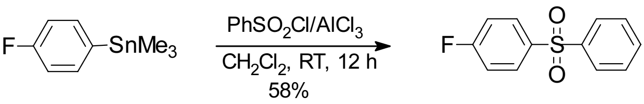
The principal electrophiles which have been used are shown in Table 7-2[38, 45, 46] and some examples of these reactions are shown in equations 7-14,[43] 7-15,[47] 7-16,[42] 7-17,[45] 7-18,[48] 7-19,[49] and 7-20.[50]

Table 7-2 Reaction of aryltin compounds with electrophiles: Ar–SnX$_3$ → ArE.

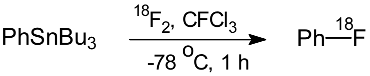
E in ArE	Reagent	Ref.	E in ArE	Reagent	Ref.
H, D	HX, DX	41	NC	NCCl	51
F	F_2	42	R_2NCH_2	$R_2N{=}CH_2^+\ Cl^-$	52
Br	Br_2	53	ArN=N	ArN_2Cl	50
I	ICl	53	PhS	PhSCl	38
O=N	ON-Cl	43	$ArS(O)_2$	$ArSO_2Cl$	47, 54
HgX	HgX_2	55, 56	$H_2NS(O)_2$	$OCNSO_2Cl$	57
BEt_2	Et_2BCl	58	$RNHS(O)_2$	$RNHSO_2Cl$	54
BH_2	BH_3	59, 60	ArNHCO	$ArN{=}C{=}O/AlCl_3$	38
AlMeCl	$AlMe_2Cl$	49	$ArSO_2NHCO$	$ArSO_2N{=}C{=}O/AlCl_3$	38
GaCl	$GaCl_3$	61	EtO_2ONHCS	$EtO_2ON{=}C{=}S/AlCl_3$	38
InCl	$InCl_3$	62	$R_3SnOS(O)$	SO_2	45
$CuNO_3$	$Cu(NO_3)_2$	63	$R_3SnOS(O)_2$	SO_3	45
$Pd^{II}L_2X$	$Pd(0)L_4$	64			
HCO	$PhMeNCHO/POCl_3$	46, 65			
RCO	$RCOCl/AlCl_3$	45			



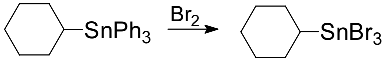
(7-14)



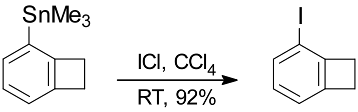
(7-15)



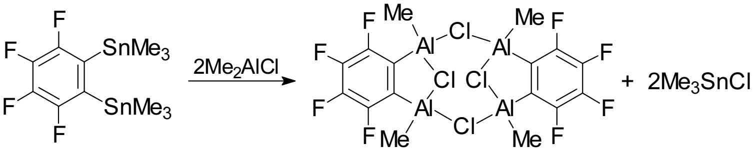
(7-16)



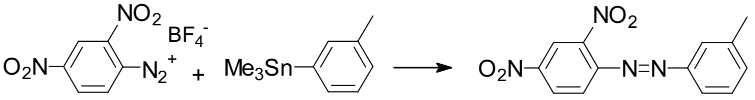
(7-17)



(7-18)

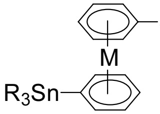


(7-19)



(7-20)

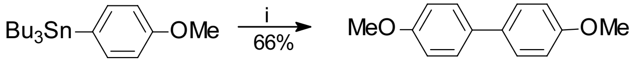
Co-condensation of aryltrialkylstannanes with metal vapour gives rise to the η^6-arene-metal complexes **7-3**.[66]



M: V or Cr
R: Me or Ph

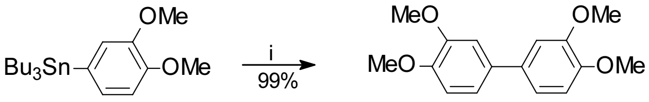
(7-3)

Aryltin compounds react with copper(II) nitrate to give, via the intermediate arylcopper(II) compounds, the corresponding biaryls (equation 7-21).[63] Rather better yields have been obtained with $Pd(OAc)_2$ as the catalyst and $CuCl_2$ which acts as the reoxidant for the catalyst (equation 7-22).[67]



(7-21)

i. $Cu(NO_3)_2$, THF, RT, 10 min.



(7-22)

i. $Pd(OAc)_2$, $CuCl_2$, THF, 23 °C, 30 min.

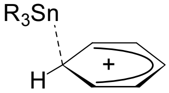
Much of the recent interest in the arylstannanes, particularly the aryltrialkylstannanes, however, derives from their use in the Stille reaction in which an aryl–C bond is generated by reaction with a halide or sulfonate RX, where R = vinyl, allyl, benzyl, or aryl, to give Ar–R under catalysis by palladium[68] or another transition metal.[69-72] The reactions are very tolerant of various functional groups, and are finding wide application in organic synthesis, and are considered in Section 22.2.

7.2 The Stannylium Ion and the Wheland Intermediate

Attempts to generate the stannylium ion, R_3Sn^+, involve also the question of the structure of the Wheland intermediate for the electrophilic exchange of R_3Sn^+ and H^+ at an aromatic ring, as the ion has usually been studied (by NMR) in benzene or toluene solution. Furthermore, the most successful attempts have involved the triarylstannylium ions, Ar_3Sn^+.

Apart from X-ray diffraction, the best criterion for the R_3Sn^+ species is the Sn NMR chemical shift which moves downfield with increasing ionic character of the tin, and is calculated (IGLO) to be > 1,700 for a trialkylstannylium ion, about 1100 for a triaryl stannylium ion, and ca. 400 ppm for the Wheland complex $Ar(H)(SnR_3)^+$.[73, 74]

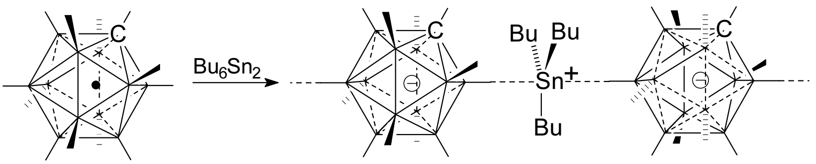
The early attempts to prepare the ion were by conventional routes to the salts R_3Sn^+ X^- of strong acids, namely: Me_3SnOSO_2H,[75] R_3SnClO_4, $R_3SnB(C_6F_5)_3H$,[76] $Bu_3SnB[3,5\text{-}(CF_3)_2C_6H_3]_4$,[77] $Bu_3Sn[C_6F_4\text{-}1,2\text{-}\{B(C_6F_5)\}_2(\mu\text{-}OMe)]$[78], and $Bu_3Sn(PhMe)$ $[B(C_6F_5)_4]$,[78]. None of these compounds was obtained in crystalline condition. The values of δSn that were observed ranged from about 250 to 450 ppm, usually with benzene or toluene as solvent, and presumably relate to a Wheland type adduct (**7-4**) (equation 7-12), in which the R_3Sn^+ cation is loosely bound to ring, and the C–Sn bond is stretched and weakened, and bent towards the ring, by symmetry enhanced hyperconjugation (Section 3.1.2.2); this model owes much to the parallel work that has been carried out on the silylium ion, R_3Si^+.[79, 80]



(7-4)

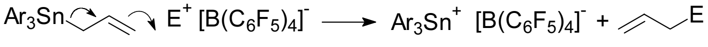
There have been, however, two successful attempts to obtained stannylium salts in crystalline form.

Michl showed that the stable radical $CB_{11}Me_{12}$• reacts with hexabutyldistannane to give Bu_3Sn^+ $CB_{11}Me_{12}^-$ (equation 7-23). X-Ray crystallography shows a planar Bu_3Sn unit with *r* Sn–C 207 pm, shorter than the normal Sn(*sp*^{3}-C) length of 214 pm. Each Bu_3Sn^+ cation interacts with two $CB_{11}Me_{12}^-$ anions to give an infinite column of alternating units. The average Sn–C(Me) separation is 281 pm, much shorter than the sum (417 pm) of the van der Waals radii of a methyl group and tin: the tin appears to coordinate to the methyl group as though it were initiating a backside S_E2 attack at the carbon.[81] The ^{119}Sn chemical shift is little lower in solution than it is in the solid, suggesting that ion aggregation persists in solution.[81]



(7-23)

In Lambert's approach, the triarylstannylium ion is generated by the reaction of an electrophile with an allyltriarylstannane. The bulky aryl groups sterically protect the tin centre in the stannylium ion from attack by nucleophiles, yet the allyl ligand permits unhindered conjugate electrophilic displacement of the tin.



(7-24)

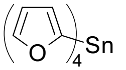
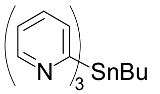
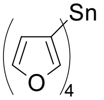
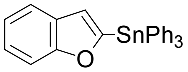
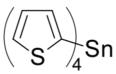
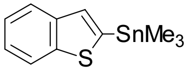
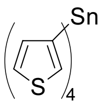
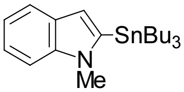
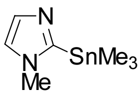
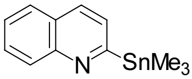
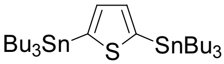
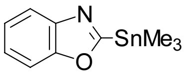
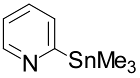
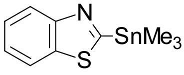
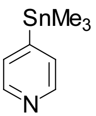
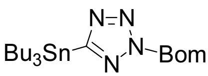
$E^+ = Et_3Si(C_6H_6)^+$ or $Et_3SiCH_2CPh_2^+$

The products Mes_3Sn^+ (Mes = mesityl), $PhTip^2Sn^+$ (Tip = 2,4,6-triisopropylphenyl)[74] and Dur_3Sn^+ (Dur = duryl)[80] were obtained only in solution, presumably in the solvated form **7-4**, when they showed δSn (C_6D_6) 806, 697, and 720 respectively. However, Tip_3Sn^+ $B(C_6F_5)_4^-$ was obtained as a solvent-free crystalline solid, and its structure could be determined by X-ray diffraction, which showed that the $Trip_3Sn^+$ ion is planar about the tin, with the aryl rings twisted, propeller-fashion, by an average of 61.1°, and there is no interaction with the anion or intramolecular agostic interaction.[82] In C_6H_6, the value of δSn is 714, similar to the values for the other Ar_3Sn^+ salts that were obtained previously only in solution.

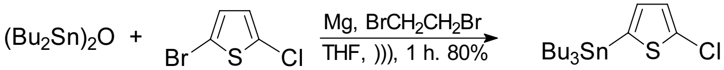
7.3 Heteroarylstannanes[83]

The last thorough review of heteroaryltin compounds appears to have been in 1988, when about 300 examples were listed.[84] Their chemistry is little different from that of the homoaryl compounds. They are usually prepared from the reaction between a heteroaryllithium (from the heteroarene or heteroaryl halide and butyllithium), or a heteroaryl Grignard reagent, and the appropriate tin halide. Some simple examples are given in Table 7-3. The compounds Het_4Sn will then undergo the Kocheshkov reaction to give the chlorides Het_nSnCl_{4-n}.

Table 7-3 Heteroarylstannanes.

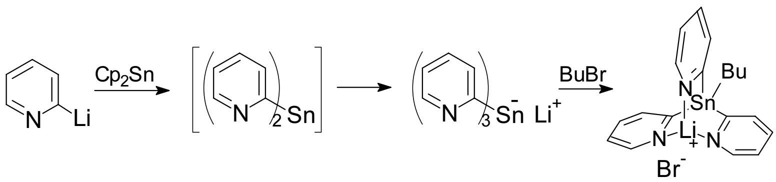
Stannane	m.p./°C or b.p./mm Hg	Ref.	Stannane	m.p./°C or b.p./mm Hg	Ref.
	68–69	85		white powder	86
	104	85		87–88	87
	156	85		96–98/0.8	88
	220–222	85		145–155/ 0.05	89
	109/50	90		74/0.1	90
		91			92
	75/4.0	90		74/0.1	90
	55/0.5	93		oil	94

The reaction involving magnesium can be run under Barbier conditions, using tributyltin oxide with ultrasonication (e.g. equation 7-25).[5]



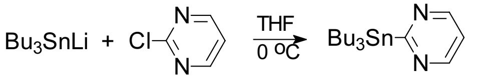
(7-25)

Butyl(tri-2-pyridyl)stannane can be prepared from the reaction of 2-pyridyllithium with stannocene, followed by treatment with butyl bromide.[95] Presumably the reaction involves nucleophilic displacement of the cyclopentadienyl group, followed by oxidative addition. The product, which can also be prepared from 2-pyridyllithium and butyltin trichloride,[86] acts as a tripodal ligand, and the Li^+,[95] $Mo(CO)_3$, and $W(CO)_3$ complexes have been isolated.[86]

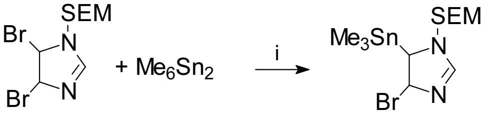


(7-26)

Stannylpyrimidines have been prepared from the reaction of halogenopyrimidines with stannyllithium or stannylsodium reagents (e.g. equation 7-27),[96] and again, by analogy with the homoarylstannanes, the heteroarylstannanes can be made from the heteroaryl halide and a distannane with a palladium catalyst (equation 7-28).[97]



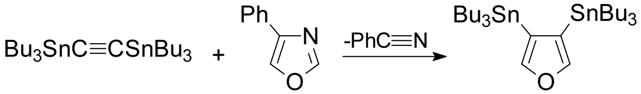
(7-27)



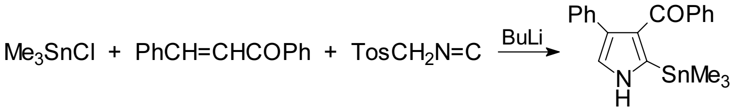
(7-28)

i. $PdCl_2(PPh_3)_2$, xylene, reflux 5.5 h. SEM = $Me_3SiCH_2CH_2OCH_2$

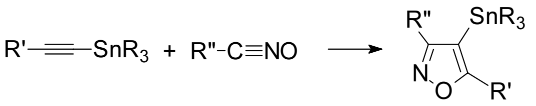
Cycloaddition reactions have a wider scope in building heteroaromatic than homoaromatic rings, and equations 7-29 to 7-33 illustrate this route to stannyl-furans,[98] -pyrroles,[99] -isooxazoles, [100] -tetraazoles, -pyridines,[101–103] and -pyridazines.[104–106] The reaction between organotin azides and organic cyanides gives *N*-stannyltetraazoles,[107–109] and that between organotin cyanides with organic azides gives *C*-stannyltetraazoles.[107]



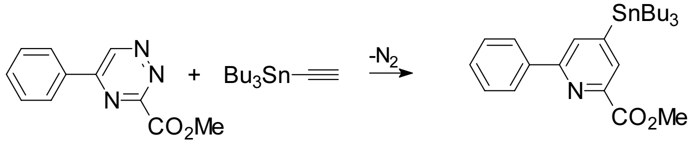
(7-29)



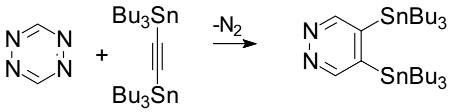
(7-30)



(7-31)



(7-32)

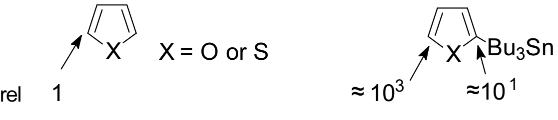


(7-33)

Pyrrole,[110] imidazoles, and 1,2,4-triazoles [111] are readily stannylated on nitrogen, but the products are better considered as stannylamines (Section 16.1) rather than heteroaromatic derivatives. The only route as yet to *C*-stannylpyrroles with an unblocked NH group appears to be by cycloaddition (see above).

The imidazole, benzoxazole, and benzthiazole derivatives in Table 7-3 are rather moisture-sensitive.[92] On the whole, however, the heteroarylstannanes show the same reactions that characterise the homoarylstannanes. With a palladium catalyst, they undergo coupling[112] and cross-coupling reactions[68] and indeed much of the recent interest in the heteroarylstannanes stems from their applications in the Stille reaction (see Section 22.2). One aspect of this is the synthesis of oligomers and polymers or copolymers, for example by the cross-coupling of 2,5-distannylthiophene with a 1,4-diiodoarene.[113, 114]

An interesting difference between the homoaryl and heteroaryl compounds is found in the reaction of 2-(tributylstannyl)-furan and -thiophene towards benzyhydryl cations.[115] Whereas homoarylstannanes appear always to undergo *ipso* attack by electrophiles, the relative reactivities at the 2 (*ipso*) and 5 position in these two heteroarenes are shown in Scheme 7-2: at both positions the reactivity is increased, but the effect is much larger at the 5-position. If C-Sn hyperconjugation is important in stabilising the Wheland intermediate, this unusual regioselectivity might be taken to imply that here there is an early transition state in which such an effect would be less important.



Scheme 7-2 Relative reactivities at the 2- and 5-positions in 2-(tributylstannyl)-furan and -thiophene.

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8 Alkenyl- and Alkynyl-stannanes, and Stannacyclopentadienes

8.1 Alkenylstannanes

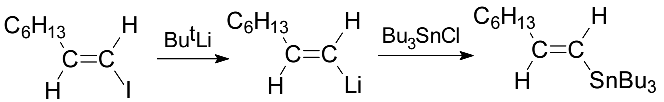
8.1.1 Formation

The most common routes to alkenyltin compounds involve reaction between an alkenylmetallic compound and a tin halide, or the hydrostannation of an alkyne (see Section 4.4). In recent years, the stannylmetallation of alkynes has become increasingly important. Direct hydrogenation of an alkynylstannane to a vinylstannane does not appear to be practicable, presumably because the catalyst is poisoned by the tin compound, but *cis* addition of dihydrogen can be achieved by hydrozirconation followed by hydrolysis,[1] or in some cases, by cyclotitanation followed by hydrolysis[2] (Section 8.2.2 below).

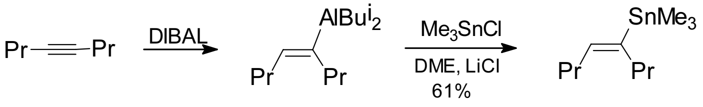
From RM + SnX

Some examples of the first route are shown in equations 8-1,[3] 8-2,[4] 8-3,[5] and 8-4.[6] The formation of vinylstannanes, $RCH{=}CHSnR'_3$, from the reaction between $RCH{=}O$ and $R'_3SnCHBr_2$ in the presence of $CrCl_2$ and LiI (equation 6-6) is thought to involve the initial formation of the $R'_3SnCH(Cr^{III})_2$ derivative which then adds to the carbonyl group, followed by elimination of an $O(Cr^{III})_2$ species.[7]

$$\mathrm{CH_2{=}CHMgBr + SnCl_4.2THF \xrightarrow[\text{reflux 12 h}]{\text{THF}} (CH_2{=}CH)_4Sn} \qquad (8\text{-}1)$$



(8-2)



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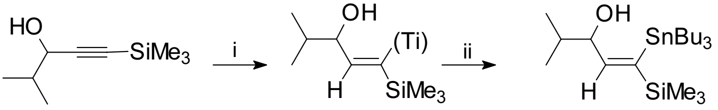

(8-4)

i. Cp_2TiCl_2, Bu^iMgCl, Et_2O, 4.5 h. ii. Bu_3SnCl, THF, 4 h.

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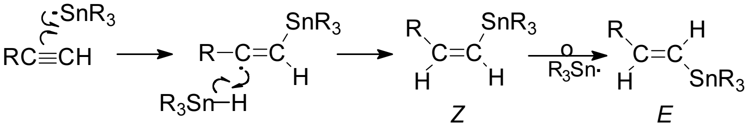
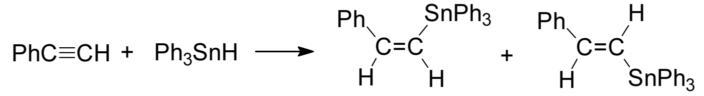
From SnH + C≡C

The general principles of hydrostannation are described in Section 4.4. The most common tin hydride to be used is tributyltin hydride, which is commercially available. Alkynes are more reactive than alkenes. With non-polar alkynes, the reaction follows a radical chain mechanism, and is typically carried out at 60–80 °C, often with AIBN as a radical initiator, but reactions can be carried out at room temperature or below with initiation with UV light or sonication,[8] or with a trialkylborane in the presence of a trace of air.[9]

The *Z*-product is formed initially, probably because the tin hydride donates its hydrogen at the less hindered face of the vinyl radical, but as the reaction progresses, this *Z*-adduct is partially rearranged to the *E*-adduct by reversible addition/elimination of a tin radical, particularly at elevated temperatures or prolonged reaction times (equation 8-5). The variation of product composition with reaction conditions is illustrated in equation 8-6.



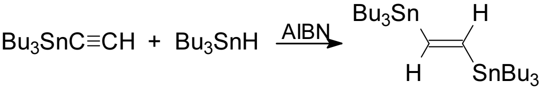
(8-5)



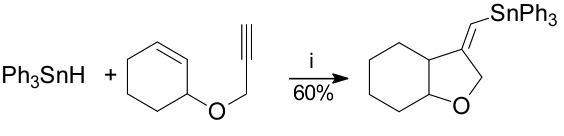
(8-6)

Et_3B,O_2 RT	75% yield	–	100%
Sonication, -8 °C	50% yield	> 92%	–

Some examples of vinylstannanes prepared by homolytic hydrostannation are given in equations 8-7,[10, 11] 8-8,[12] and 8-9.[13]

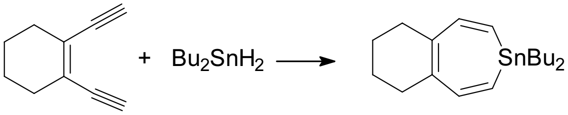


(8-7)



(8-8)

i. PhMe, Et_3B, 25 °C, 3 h

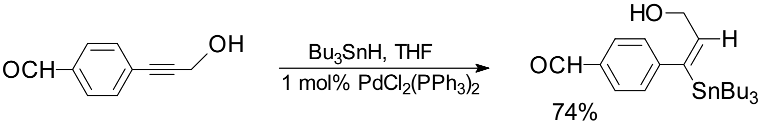


(8-9)

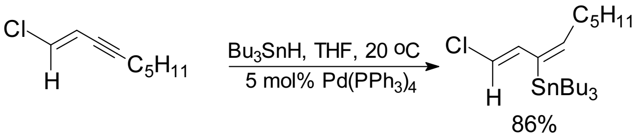
Alkynes and allenes can be converted into the corresponding vinylstannanes by *trans* addition with Bu_3SnH or Bu_2SnH_2 in the presence of $ZrCl_4$ or $HfCl_4$ which are regarded as acting as Lewis acid catalysts, but the detailed mechanism is not known.[14, 15]

From SnH/Pd + C≡C[16, 17]

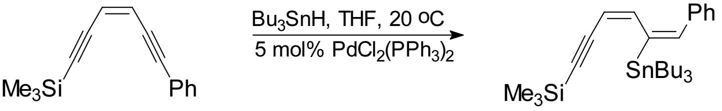
A variety of transition metals have been used as catalysts for hydrostannations,[18] but Pd(0) or Pd(II) compounds are most commonly used. A thorough recent review is available.[17] The mechanism is outlined in Section 4.4. The reactions are characterised by (1) *syn*-addition to the multiple bond, (2) steric effects on the regioselectivity, the large R_3Sn group tending to avoid the larger of the two alkyl groups in R′C≡CR″, and (3) polar effects in the addition to polar triple bonds, resulting from the $Pd^{\delta+}$-$H^{\delta-}$ polarisation. Benzene, toluene, and THF are commonly used as solvents. The reactions take place under mild conditions and are tolerant of a variety of functional groups (NO_2, CHO, Cl, OH, NMe_2 etc). Some examples are given in equations 8-10,[19] 8-11,[20] and 8-12.[21]



(8-10)



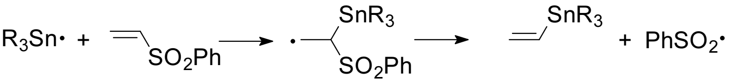
(8-11)



(8-12)

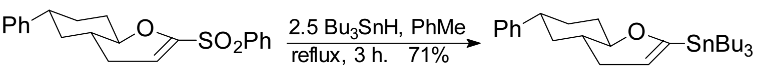
From SnH + C=CX

Vinylsulfones react homolytically with tributyltin hydride to give the corresponding vinylstannanes.[22–24] An addition-elimination sequence seems most likely (equation 8-13), though an electron-transfer mechanism has also been suggested.[22] Examples are given in equation 8-14[22] and 8-15.[23] A similar reaction has been demonstrated for vinyl phenyl sulfides.[25]



(8-13)

$$\mathrm{PhCH{=}CHSO_2Ph} \xrightarrow[140\ ^{\circ}\mathrm{C},\ 7\ \mathrm{h.}\ 75\%]{2\mathrm{Bu_3SnH,\ xylene}} \mathrm{PhCH{=}CHSnBu_3} \qquad (8\text{-}14)$$

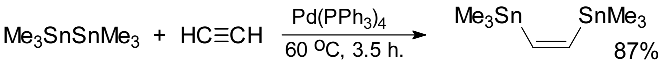


(8-15)

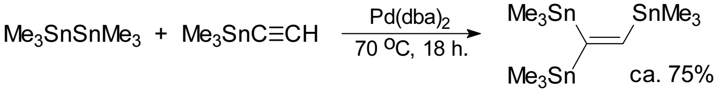
From SnSn/Pd + C≡C or C=C=C[16]

The addition of distannanes to acetylenes or allenes can be catalysed by palladium compounds giving 1,2-distannylalkenes or 1-stannyl-1-(stannylmethyl)alkenes, respectively.[26, 27]

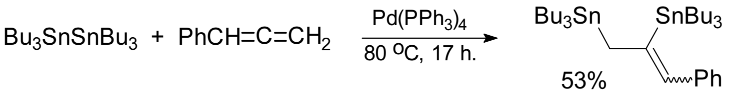
Cis-addition occurs initially, but the product may isomerise. Hexamethylditin adds quantitatively to alkynes, but the addition of hexabutylditin is complete only under high pressure.[26, 28] Allenes undergo 1,2-addition at room temperature, but at high temperatures the product may undergo allylic rearrangement of the Sn-C-C=C moiety.[29] Some examples of these reactions are shown in Equations 8-16–8-18.



(8-16)

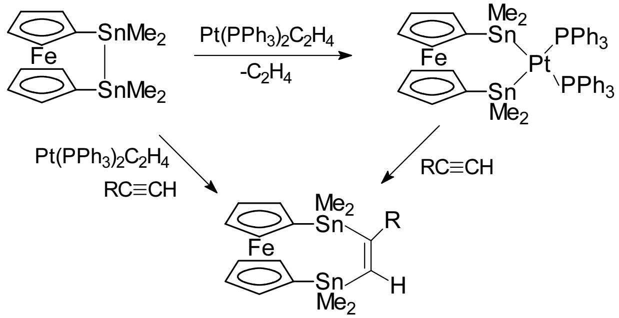


(8-17)



(8-18)

The nature of the intermediate is made clear in the particular case of distannation in the presence of a platinum catalyst, when the Sn-Pt-Sn bonded intermediate can be isolated.[30]



(8-19)

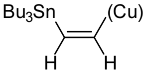
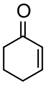
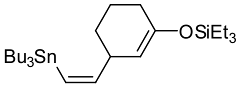
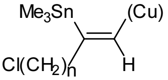
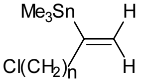
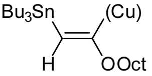
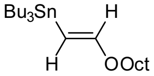
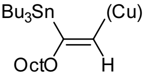
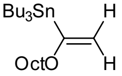
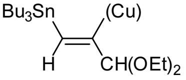
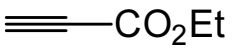
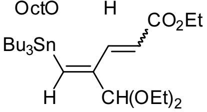
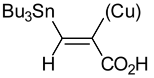
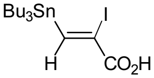
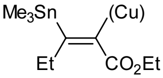
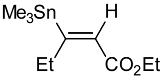
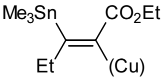
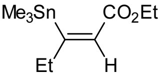
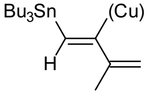
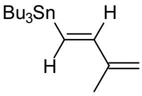
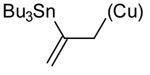
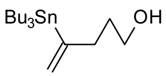
From SnM + C≡C or C=C=C[16]

The behaviour of metals as hydrogen equivalents (Section 3.1.1) suggests that stannylmetallic compounds might show metallostannation reactions similar to the above hydrostannation, and indeed such reactions are well known, not only when M is tin (see above). When M is a transition metal, no catalyst is needed, and many stoichiometric reactions have been established between SnCu-bonded compounds and alkynes or allenes. When M is a Main Group metal, copper or palladium are the favoured catalysts. The reactions occur under mild conditions, can tolerate a wide variety of functional groups, and, by varying the metal, the regio- and stereo-selectivity can be controlled. The dimetallofunctional alkenes that are formed are versatile synthons and are often used in further reactions without being isolated.[16]

Stannylcupration has been studied extensively. The regioselectivity and the stereoselectivity vary with the nature of the reagents and with the solvent, temperature, and time of the reaction, but conditions have been developed under which highly efficient syntheses can be carried out. Some examples are shown in Table 8-1.

Cis-addition occurs across the triple bond to give the *Z*-adduct, but at higher temperatures and prolonged reaction times, this can rearrange to the thermodynamically-controlled *E*-adduct. In entry 7, the product of kinetic control is obtained by *in situ* quenching of the Z-adduct as soon as it is formed, but in entry 8, the thermodynamically controlled product is obtained with delayed quenching. With allene (entry 10), at –100 °C, the tin adds to the terminal carbon and the copper to the medial carbon to give an allylstannane, but this regioselectivity is reversed above –78 °C.

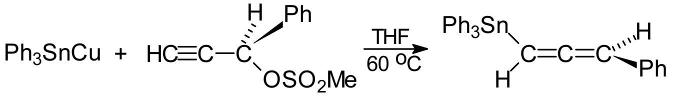
Table 8-1 Stannylcupration of alkynes.

	Reagent	Conditions	Intermediate	Electrophile	Product
1	$HC{\equiv}CH$ Bu_3SnLi, CuCN, LiCl	THF, -45 °C		 Et_3SiCl	
2	$Cl(CH_2)_nC{\equiv}CH$ $Me_3SnCu(SMe_2)$ (n = 2-4)	THF, -63 °C MeOH		MeOH	
3	$HC{\equiv}COOct$ $(Bu_3Sn)_2Cu(CN)Li_2$	THF, -78 °C		MeOH	
4	$HC{\equiv}COOct$ $(Bu_3Sn)_2Cu(CN)Li_2$	HMPA, 0 °C		MeOH	
5	$HC{\equiv}CCH(OEt)_2$ $Bu_3SnCu(Bu)CNLi_2$	THF, -78 °C			
6	$HC{\equiv}CCO_2H$ $Bu_3SnCu(Bu)CNLi_2$	THF, -78 °C		I_2	
7	$EtC{\equiv}CCO_2Et$ $Me_3SnCu(SPh)Li$	THF, -78 °C MeOH		H^+	
8	$EtC{\equiv}CCO_2Et$ $Me_3SnCu(SPh)Li$	THF, -48 °C		MeOH	
9	$HC{\equiv}CCMe{=}CH_2$ $Bu_3SnCu(Bu)CNLi_2$	THF, -40 °C		NH_4Cl	
10	$CH_2{=}C{=}CH_2$ $(Bu_3Sn)_2CuLi$	THF, > -78 °C			

Refs. to Table: 1,[31] 2,[32] 3 and 4,[33] 5,[34, 35] 6,[36] 7 and 8 ,[37] 9,[38] 10.[39]

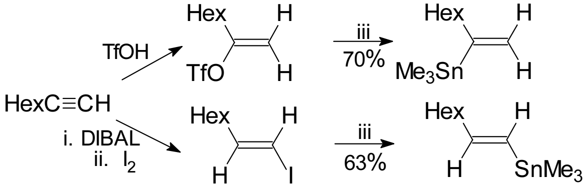
The vinyl-copper bond is reactive towards electrophiles such as protic acids (entries 2, 3, 4, 8, 9), Br_2, I_2, alkyl iodides, allyl and benzyl bromide, acyl halides, benzaldehyde, enones (entry 1), propargylic esters (entry 5), and epoxides (entry 10).

Propargyl derivatives $R^1C{\equiv}CCR^2R^3X$ (X = Br, AcO, $MeSO_2$, $MeSO_3$) react with stannyl cuprates to give allenes in high yield (unless the group R^1 is very bulky), when the propargyl stannane is formed, the group X being eliminated from the *anti*-position (equation 8-20).[40]



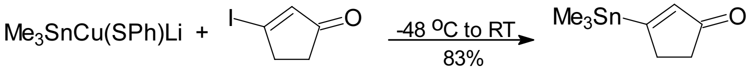
(8-20)

Stannylcuprates will also react with enol triflates (equation 8-21)[41] and with vinyl iodides (equation 8-22)[42] to give vinylstannanes, in a reaction which may be regarded either as a nucleophilic substitution or as stannylcupration followed by elimination of CuX.



iii. $Me_3SnMgMe$, CuCN, THF

(8-21)

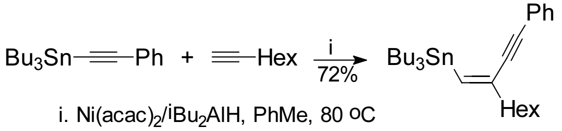


(8-22)

SnMn-Bonded compounds will similarly add stoichiometrically to alkynes,[43] and the following SnM-bonded compounds will add in the presence of a copper or platinum catalyst: SnLi/Cu,[44] SnMg/Cu[34, 41, 45] SnZn/Cu,[41, 45] SnZn/Pd,[41, 45] SnB/Cu,[38, 46–48] SnB/Pd,[48, 49] SnAl/Cu,[34, 38, 41, 45, 50] SnSi/Pd,[26, 34, 51, 52] and SnGe/Pd.[53]

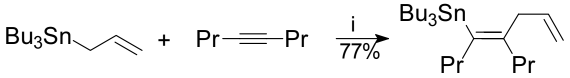
From SnR/Ni + C≡C or C=C=C

In the presence of a nickel catalyst, alkynes can be inserted into bonds between tin and an alkynyl, allyl, or acyl group, to give new vinylstannanes.[54–60] Examples from this rapidly developing field are shown in equations 8-23 to 8-25.[57]



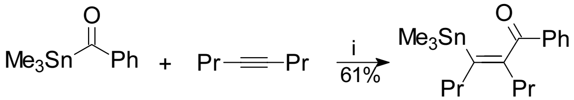
i. $Ni(acac)_2/^iBu_2AlH$, PhMe, 80 °C

(8-23)



i. $Ni(cod)_2$, PhMe, 80 °C

(8-24)

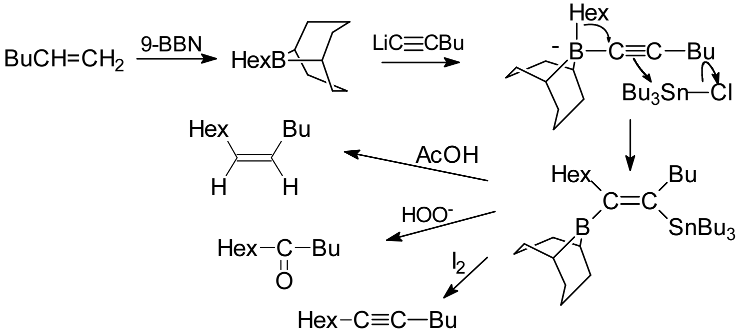


i. $Ni(cod)_2$, PhMe, 100 °C

(8-25)

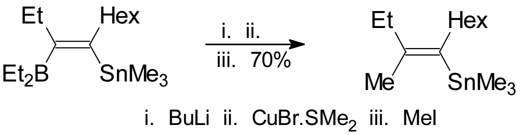
From $R_3BC{\equiv}CR$ + SnCl

A different technique for the stannylation of an alkyne is shown in Scheme 8-1. Electrophiles add to the triple bond of lithium trialkylalkynylborates with migration of one of the alkyl groups to give a vinyl derivative, and when the electrophile is a trialkyltin halide, the migrating group and the tin are situated *trans*.[61] The *cis*-bimetallic alkene can then be demetallated providing a route to *Z*-alkenes, ketones, and alkynes. 9-BBN Can be used as the source of the boron to conserve a valuable alkyl group.[62]



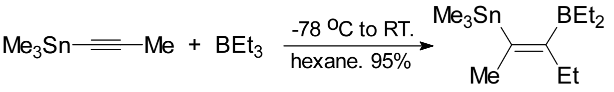
Scheme 8-1 Reaction of an alkylalkynylborates with tributyltin chloride.

The boron can be removed from the vinylstannane to give a stannylvinylcuprate, which will react with an alkyl halide, providing a general method for preparing trisubstituted vinylstannanes with >98% isomeric purity (equation 8-26).[63]

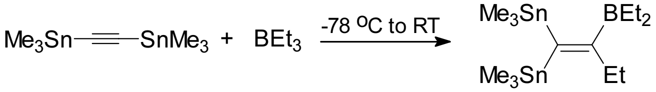


(8-26)

As an alternative to this addition of an organostannane to an alkynylborane, vinylstannanes can also be formed by the complementary process of adding an organoborane to an alkynylstannane.[64] Examples of these reactions are shown in equations 8-27 and 8-28, and a mechanistic rationalisation is included in equation 8-52.



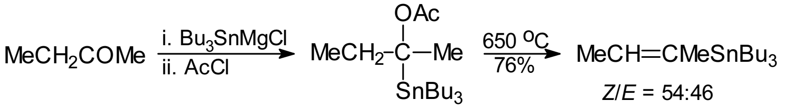
(8-27)



(8-28)

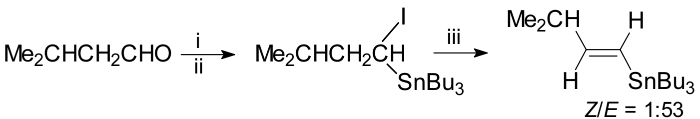
By Elimination

Equations 8-29 and 8-30 illustrate the introduction of a double bond into vinylstannanes by elimination reactions. Flash vacuum pyrolysis at 600–950 °C of the α-acetoxyalkylstannanes or of the corresponding thiocarbonates shows little regioselectivity,[65] but base-induced elimination of HI from the α-iodoalkylstannanes gives principally the *E*-isomer.[66]



$$\mathrm{MeCH_2COMe} \xrightarrow[\text{ii. AcCl}]{\text{i. Bu}_3\text{SnMgCl}} \mathrm{MeCH_2\text{-}\overset{OAc}{\underset{SnBu_3}{C}}\text{-}Me} \xrightarrow[76\%]{650\ ^\circ\mathrm{C}} \mathrm{MeCH{=}CMeSnBu_3} \quad Z/E = 54{:}46$$

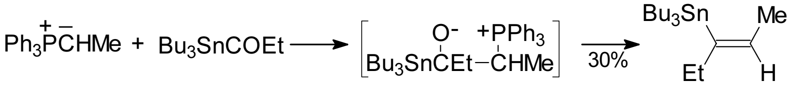
(8-29)



i. Bu_3SnLi ii. Ph_3P, I_2 iii. DBU, THF, 85 °C

(8-30)

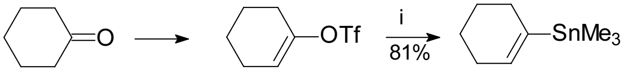
An aldehyde RCH=O will also react with $Bu_3SnCHBr_2$ in the presence of $CrCl_2$ to give the corresponding *E*-vinylstannane (equation 6-6). Acyclic compounds can be prepared by the reaction of acylstannanes with phosphorus ylides, for example reaction 8-31.[67]



(8-31)

By Stille-type Couplings

Vinylstannanes can also be prepared by Stille-type coupling between a vinyl triflate and a hexaalkyldistannane.[68]



i. Me_6Sn_2, LiCl, $Pd(PPh_3)_4$, 60 °C, 3 h.

(8-32)

8.1.2 Reactions

In organic synthesis, the preparation of most vinylstannanes is aimed at tin/lithium transmetallation (equation 8-33), or at Stille coupling reactions (equation 8-34). These reactions are discussed in Sections 22.1 and 22.2, respectively, and the remaining reactions are covered in this section.

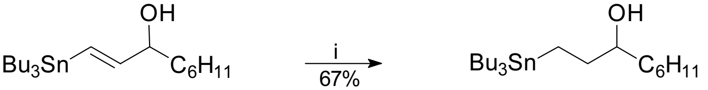
$$\mathrm{C{=}C\text{-}SnR_3 + R'Li \longrightarrow C{=}C\text{-}Li + R_3SnR'} \qquad (8\text{-}33)$$

$$\mathrm{C{=}C\text{-}SnR_3 + R'X \xrightarrow{Pd^0} C{=}C\text{-}R' + R_3SnX} \qquad (8\text{-}34)$$

(R' = vinyl, alkynyl, allyl, aryl, heteroaryl)

At the Double Bond

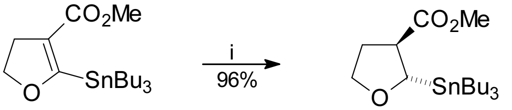
It is difficult to reduce the vinyl group without also cleaving the C−Sn bond. The normal hydrogenation catalysts are apparently poisoned by organotin compounds, but this reduction has been achieved with a rhodium catalyst (equation 8-35),[69] and β-stannylacrylates can be reduced to β-stannylpropionates with triethylsilane in the presence of trifluoroacetic acid (equation 8-36). 1,2-Bis(trimethylstannyl)alkenes and 1-trimethylsilyl-2-trimethylstannylalkenes have been hydrogenated with diimine produced *in situ* from hydrazine hydrate, hydrogen peroxide, and copper sulphate solution (equation 8-37).[70]



(8-35)

i. 5 mol% [(dppb)Rh(nbd)] BF_4^-, H_2, 103 At.

dppb = 1,4-bis-(diphenylphosphinobutane) nbd = norbornadiene



(8-36)

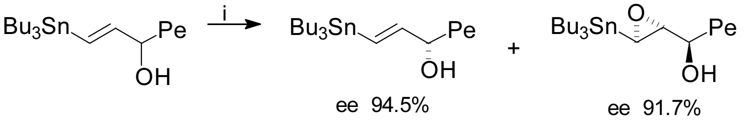
i. CH_2Cl_2, Et_3SiH, TFAH, -78 to 0 °C

$$Z\text{-}Me_3SnCH{=}CHSnMe_3 + H_2NNH_2 + H_2O_2 \xrightarrow[100\%]{i} Me_3SnCH_2CH_2SnMe_3 \quad (8\text{-}37)$$

i. 1% $CuSO_4$

Electrophilic reagents usually cleave the vinyl-tin bond, and additions can be achieved only with mild electrophiles, or by radical or pericyclic mechanisms.

Certain vinylstannanes will undergo cyclopropanation with diiodomethane and samarium amalgam.[69, 71] Epoxidation of the double bond can be carried out with *meta*-chloroperoxybenzoic acid,[71, 72] and the kinetic resolution of a 3-stannylallyl alcohol has been achieved under Sharpless conditions (equation 8-38).[73]

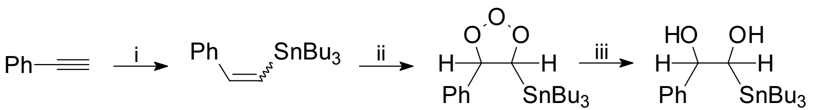


(8-38)

i. Bu^tOOH, D-(-)-diisopropyl tartrate, $Ti(OPr^i)_4$

The cycloaddition between cyclopentadiene and $Bu_3SnC{\equiv}CCHO$ can be catalysed by a chiral Lewis acid to give the norbornadiene with 80% ee, and then reactions at the stannyl group can lead to the synthesis of other chiral bicycloheptadienes.[74]

The primary ozonides derived from vinylstannanes are unusually stable, providing a method for converting alkynes into 1,2-diols.[75]



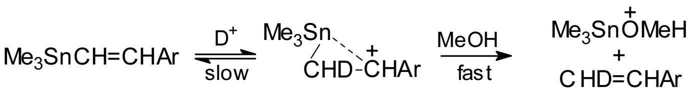
(8-39)

i. Bu_3SnH, Et_3B ii. O_3, -78 °C. 15 min iii. $BH_3.SMe_2$

At the C–Sn Bond

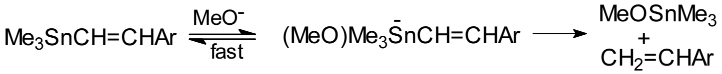
The vinyl-tin bond can be cleaved by electrophiles such as acids, halogens, acyl halides, and metal halides. The *cis*- and *trans*-styrylstannanes $ArCH{=}CHSnMe_3$ react with deuterioacetic acid in MeOD in the presence of aluminium chloride, to give the products

ArCH=CHX with retention of configuration.[76] The reaction probably involves rate-determining protonation at the α-carbon atom of the double bond to give the carbonium ion in which the configuration is held by interaction with the β-trimethylstannyl group;[77, 78] the tin-carbon bond is then cleaved by rapid attack of the nucleophile at tin.



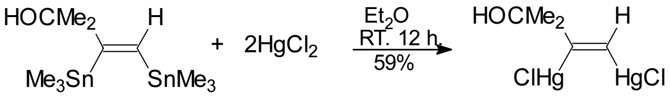
$$\mathrm{Me_3SnCH{=}CHAr} \underset{\text{slow}}{\overset{D^+}{\rightleftharpoons}} \overset{\mathrm{Me_3Sn}\;\;\;+}{\mathrm{CHD{-}CHAr}} \xrightarrow[\text{fast}]{\text{MeOH}} \begin{matrix}\mathrm{Me_3Sn\overset{+}{O}MeH}\\ +\\ \mathrm{CHD{=}CHAr}\end{matrix} \qquad (8\text{-}40)$$

The cleavage can also be catalysed by base; the reaction now probably involves rapid attack of the nucleophile at tin, followed by rate-determining attack of the proton at the α-carbon atom.



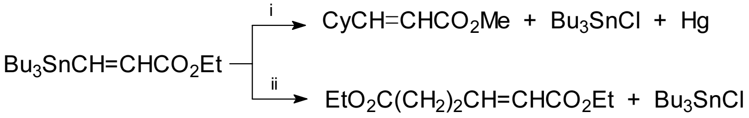
$$\mathrm{Me_3SnCH{=}CHAr} \underset{\text{fast}}{\overset{\mathrm{MeO^-}}{\rightleftharpoons}} \mathrm{(MeO)Me_3\overset{-}{S}nCH{=}CHAr} \longrightarrow \begin{matrix}\mathrm{MeOSnMe_3}\\ +\\ \mathrm{CH_2{=}CHAr}\end{matrix} \qquad (8\text{-}41)$$

The reaction of vinylstannanes with lead tetraacetate to give vinylplumbanes,[79] and with mercury salts (e.g. equation 8-42)[80] to give vinylmercury compounds, similarly proceeds with retention.



(8-42)

If the vinyl group carries an aryl or carboxylate group in the β-position, the vinyl-tin bond can also be cleaved by radicals. Addition of a radical at the α-carbon atom gives a β-stannylalkyl radical, in which there is again some evidence for a configuration-holding interaction with the stannyl group. The stannyl radical is then eliminated, and, in a chain process, regenerates the radical which attacks the double bond.[81, 82]



(8-43)

i. CyHgCl, PhH/Me$_2$SO, *h*ν, 5 h. ii. Br(CH$_2$)$_2$CO$_2$Et, PhMe, AIBN, 86 °C.

8.2 Alkynylstannanes

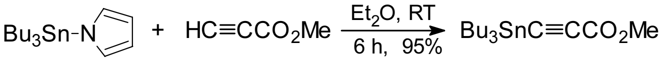
8.2.1 Formation

The high protic acidity of the acetylenic CH bond makes the alkynylstannanes readily accessible either directly from the terminal alkynes or through their metal derivatives. The alkynes react with distannoxanes in boiling benzene, and the water which is eliminated can be removed azeotropically, or with calcium hydride[83] or molecular sieves (e.g. equation 8-44).

$$\mathrm{(Et_3Sn)_2O + 2HC{\equiv}CCH{=}CHOMe \xrightarrow{i} 2Et_3SnC{\equiv}CCH{=}CHOMe} \qquad (8\text{-}44)$$

i. C$_6$H$_6$, CaH$_2$. 82%

If the alkyne carries an electron-attracting group, acidolysis of an alkoxystannane[84] or of an aminostannane will occur at low temperature,[85, 86] and *N*-stannylpyrroles have been recommended for this purpose because of the non-nucleophilic character of the amine which is liberated.[87]



(8-45)

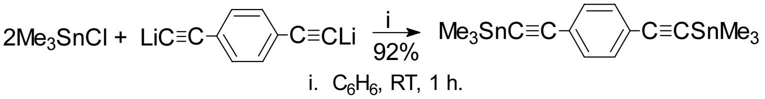
Terminal alkynes react with tin halides in the presence of a tertiary amine, particularly in the presence of cuprous iodide, when the reaction presumably takes place through the cuprous acetylide (equation 8-46).[88] The trichlorostannylalkyne $Cl_3SnC{\equiv}CAr$ is presumably the intermediate when phenols, react with acetylene in the presence of $SnCl_4.NBu_3$ to give the bis(trichlorostannyl)styrenes, $ArCH{=}C(SnCl_3)_2$, which can then be alkylated to give the bis(trialkylstannyl)styrenes, $ArCH{=}C(SnMe_3)_2$.[89]

$$\mathrm{Ph_3SnCl + HC{\equiv}CPh \xrightarrow[25\ ^\circ C,\ 70\%]{Et_3N,\ CuI} Ph_3SnC{\equiv}CPh} \qquad (8\text{-}46)$$

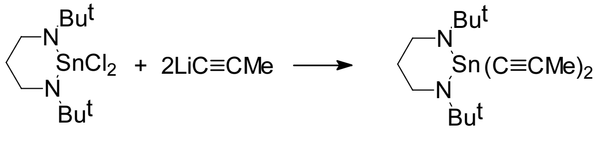
The reaction between the tin halide and calcium carbide assisted by sonication in a cleaning bath provides a convenient route to the distannylalkynes.[90]

$$\mathrm{2Me_3SnCl + CaC_2 \xrightarrow[36\ h,\ 57\%]{DMF,\ )))} Me_3SnC{\equiv}CSnMe_3} \qquad (8\text{-}47)$$

Alternatively, stannylalkynes can be prepared by conventional reactions between the tin halides and alkynyl-lithium or alkynyl Grignard reagents (e.g. reactions 8-48 and 8-49).[3, 91, 92] The synthesis of $Me_3SnC{\equiv}CPh$,[3] $Me_2Sn(C{\equiv}CH)_2$, $Et_2Sn(C{\equiv}CH)_2$,[93] and $R_3SnC{\equiv}CSnR_3$ (R = Me, Et, or Bu)[94] by these methods are given in *Organometallic Synthesis.* Molar solutions of ethynylmagnesium bromide can be prepared by introducing acetylene into a solution of ethylmagnesium bromide in THF at 10 °C. Trialkyltin chlorides then react to give the ethynylstannanes in good yield ($Me_3SnC{\equiv}CH$, 70%; $Bu_3SnC{\equiv}CH$, 85%).[95]



(8-48)



(8-49)

Alkynylsilanes will react with tributyltin oxide in an analogous fashion if tetrabutylammonium fluoride is used as a catalyst.[96] The hexamethyldisiloxane which is formed can readily be removed under reduced pressure, and yields are excellent (equation 8-50).

$$\mathrm{(Bu_3Sn)_2O + 2Me_3SiC{\equiv}CPh \xrightarrow{i} 2Bu_3SnC{\equiv}CPh + (Me_3Si)_2O} \qquad (8\text{-}50)$$

i. Bu_4NF, 60 °C, 2.5 h. 98%

8.2.2 Reactions

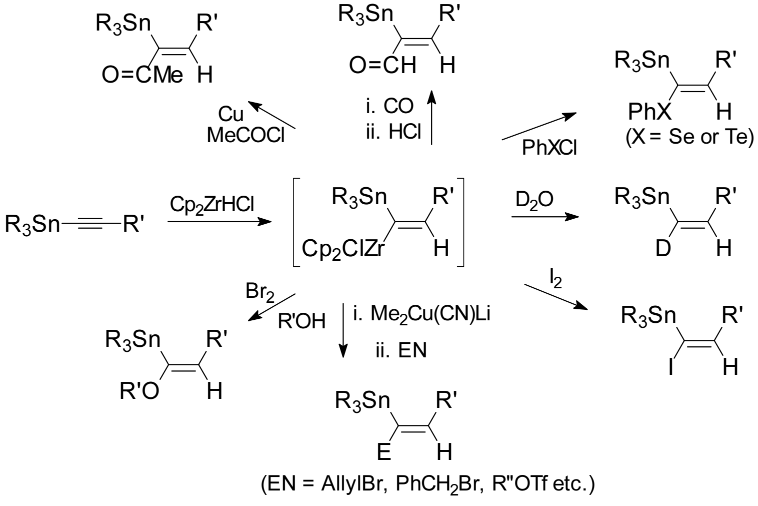
Tetraethynyltin is reported to explode if it is heated rapidly. Furthermore, the ethynyl-tin bond can be hydrolysed by moisture giving ethyne, and it is recommended that the compound should not be stored in sealed vessels as ethyne is explosive under pressure. $Me_3SnC{\equiv}CBr$ Is reported to be hydrolysed instantaneously in air, with spontaneous ignition.[97]

This reactivity towards protic acids can be exploited in synthesis. Hydrolysis of alkyltrihexynylstannanes (from alkyltrichlorostannanes and hex-1-ynyllithium) gives the *closo* clusters $(RSn)_{12}(\mu^3O)_{14}(\mu^2OH)_6(OH)_2$, reaction with primary or secondary alcohols gives the alkyltin trialkoxides, $RSn(OR)_3$,[98] and reaction with carboxylic acids gives the carboxylates $(RSn(O)OCOR')_6$.[99]

Electrophilic reagents such as halogens or halogen acids cleave the alkynyl-tin bond rather than add to the triple bond. Presumably, rapid *ipso* attack is favoured by the stabilising β-effect of the tin (Section 3.1.2.2), then this is followed by cleavage of the Sn–C bond.

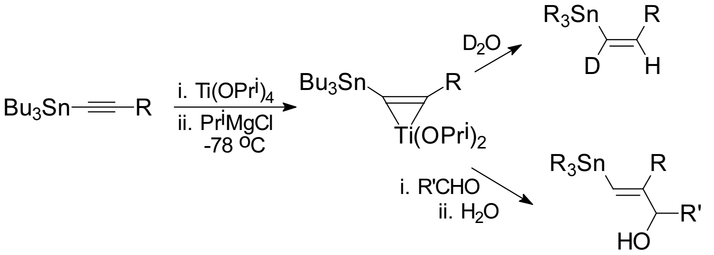
Schwarz's reagent (Cp_2ZrHCl)[100] brings about *syn* hydrozirconation of the triple bond to give a 1-stannyl-1-zirconylalkene in which the C–Zr bond is more reactive than the C–Sn bond.[1] Electrophiles such as water,[1, 101] or iodine,[102] or selenyl or telluryl halides[103] react to give α-substituted stannyl alkenes. At atmospheric pressure, carbon monoxide is inserted into the C–Zr bond, then hydrolysis generates a CH=O group,[104] or treatment with bromine and an alcohol generates an alkoxycarbonyl group.[105] With cuprous iodide and an acyl halide, an acyl group is formed,[106] and a higher order cuprate gives the vinylcopper compound which can be caused to react with a variety of electrophiles EN (Scheme 8-2).[102]

Hydrostannations of the triple bond, catalysed by zirconium(IV) chloride, may be mechanistically similar to these reactions.[14, 15]



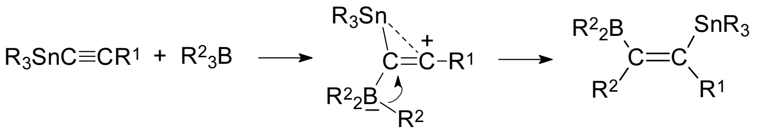
Scheme 8-2 1-Stannyl-1-zirconylalkenes.

Titanation of the triple bond has been investigated as a possible alternative to the expensive hydrozirconation, but it is more limited in that the yields are poor unless there is an alkoxyl group in the alkyne, to coordinate to the titanium.[2]



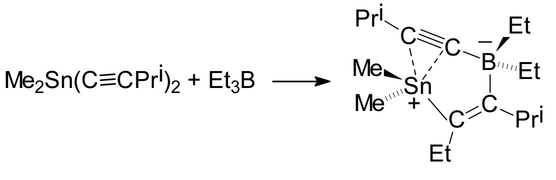
(8-51)

Organoboranes react at the triple bond to give *cis*-1-boryl-2-stannylalkenes (e.g. equations 8-27 and 8-28).[107] The yields are high and the reactions are stereoselective for the product in which the R_2B and R_3Sn groups are *cis*. Similar reactions occur with alkynyl compounds of silicon, germanium, and lead. The reactivity follows the sequence Si < Ge < Sn < Pb, and the reaction of, for example, $Me_3SnC{\equiv}CMe$ and Et_3B starts at –40 °C, and is strongly exothermic at room temperature. A mechanistic rationalisation is given in equation 8-52. The structure of the intermediate can be regarded as a β-stannyl cation, stabilised by a strong β-stannyl effect (Section 3.1.2.2) as in equation 8-52, or as a weak zwitterion complex between the triple bond and an organotin cation as in equation 8-53.



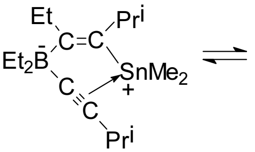
(8-52)

This type of bonding can be observed by X-ray crystallography in the initial products from the reaction of dialkyldialkynyltin compounds with organoboranes (equation 8-53).[64] The ethyne group is unsymmetrically bonded to the tin with C–Sn distances 233.9(4) and 252.3(5) pm, and the other three groups about the tin are close to coplanar, as would be expected for a triorganotin cation.

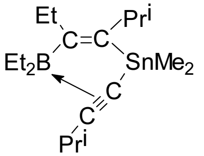


(8-53)

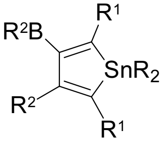
The strong temperature-dependence of the ^{119}Sn NMR chemical shift indicates that the alkynyl group is exchanging between the boron and the tin atoms (**8-1** and **8-2**). Intramolecular reaction between the second alkyne and the organoboron group can then lead to a stannacyclopentadiene (**8-3**; by migration of the vinyl group from boron) or a 1-bora-4-stannacyclohexadiene (**8-4**; by migration of an alkyl group from boron).[107]



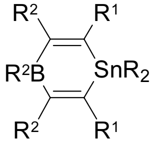
(8-1)



(8-2)



(8-3)



(8-4)

Butyllithium cleaves the Sn–C bond in alkynylstannanes to give the alkynyllithium (Section 22.1), which can then be used for further transformations (e.g. equation 8-54).

$$\mathrm{Me_3SnC{\equiv}C{-}C{\equiv}CSnMe_3 \xrightarrow{i} Me_3SnC{\equiv}C{-}C{\equiv}CLi \xrightarrow{ii} Me_3SnC{\equiv}C{-}C{\equiv}CSiMe_3} \qquad (8\text{-}54)$$

i. BuLi ii. $\mathrm{Me_3SiCl}$

1-Alkynylstannanes react with copper(II) nitrate to give, via the alkynylcopper(II) derivatives, the corresponding 1,3-dialkynes[108] and they show a high reactivity in Stille-type palladium-catalysed coupling reactions (Section 22.2).[109]

$$\mathrm{Bu_3SnC{\equiv}CBu \xrightarrow[60\%]{i} BuC{\equiv}C{-}C{\equiv}CBu} \qquad (8\text{-}55)$$

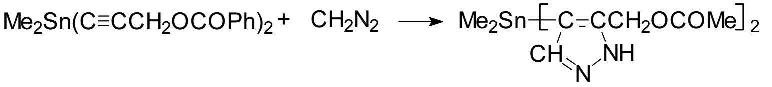
i. $\mathrm{Cu(NO_3)_2}$, THF, 10 min.

$$\mathrm{Bu_3SnC{\equiv}CCO_2Me + PhCOCl \xrightarrow[64\%]{i} PhCOC{\equiv}CCO_2Me} \qquad (8\text{-}56)$$

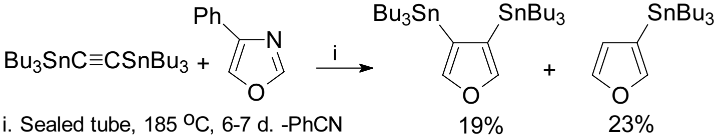
i. $\mathrm{ClCH_2CH_2Cl}$, 1.8 mol% $\mathrm{BzPdCl(PPh_3)_2}$, 84 °C, 2 h.

The trialkylstannyl group has a strong deactivitating effect on the behaviour of an alkyne as a dienophile, but Diels-Alder cycloadditions can be carried out under forcing conditions with dienophiles such as tetracyclone, α-pyrone, and hexachlorocyclopentadiene (e.g. equations 7-5–7-7).[110] With activating substituents X (X = CN, COR, $\mathrm{CO_2Me}$, $\mathrm{SO_2Ar}$, $\mathrm{CONMe_2}$), cycloaddition can be achieved between $\mathrm{R_3SnC{\equiv}CX}$ and less reactive dienes (e.g. butadiene, cyclopentadiene, or cyclohexadienes), providing a route into the 1-stannylcyclohexa-1,4-dienes, and thence, by dehydrogenation, into arylstannanes (e.g. equation 7-6).[111] The cycloaddition between cyclopentadiene and $\mathrm{Bu_3SnC{\equiv}CCHO}$ can be catalysed by a chiral Lewis acid to give the norbornadiene with 80% ee, then reactions at the stannyl group can lead to the synthesis of other chiral bicycloheptadienes.[74]

[2+3]-Cycloadditions can also be achieved with diazomethane giving pyrazoles (equation 8-57),[112] and with 4-phenyloxazole to give 3,4-bis(tributylstannyl)- and 3-tributylstannyl)-furan (equation 8-58), which can be converted into other symmetrically or unsymmetrically 3,4-disubstituted furans by Stille coupling or via monolithiation.[113, 114]



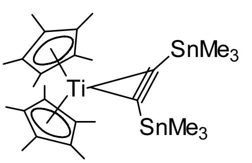
$$\mathrm{Me_2Sn(C{\equiv}CCH_2OCOPh)_2 + CH_2N_2 \longrightarrow Me_2Sn{\left[\underset{CH{=}N{-}NH}{C{=}CCH_2OCOMe}\right]_2}} \qquad (8\text{-}57)$$



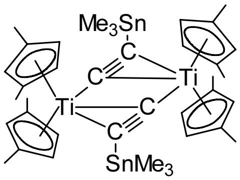
(8-58)

i. Sealed tube, 185 °C, 6-7 d. -PhCN 19% 23%

If dicyclopentadienyltitanium dichlorides $(C_5H_{5-n}Me_n)_2TiCl_2$ (n = 0, 2–5) are reduced with magnesium in the presence of bis(trimethylstannyl)acetylene, π-complexes are formed with structures such as those shown in **8-5** and **8-6**;[115] similar complexes are known for silylacetylenes.



(8-5)

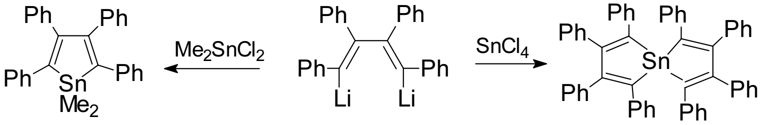


(8-6)

8.3 Stannacyclopentadienes

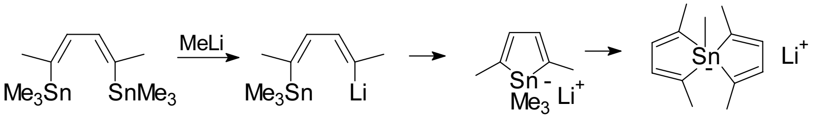
The stannacyclopentadienes (stannoles) can be prepared by a variety of methods, all of which involve some other metal.

The first examples were obtained by the conventional reaction of an organolithium reagent with a tin halide.[116]



(8-59)

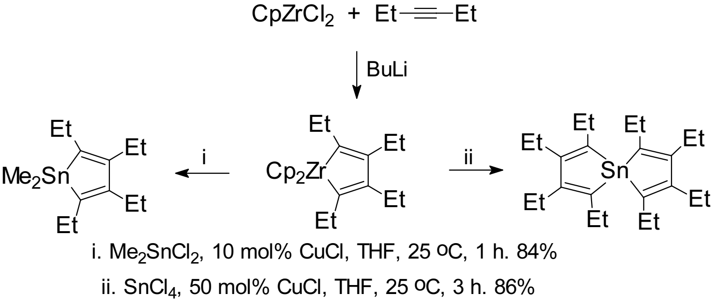
The stannoles, however, are liable to form hypercovalent ate complexes with organolithium compounds.[4]



(8-60)

A second route is provided by Wrackmeyer's alkylboronation of a diyne as shown in equation 8-53 and formula **8-3**.[107]

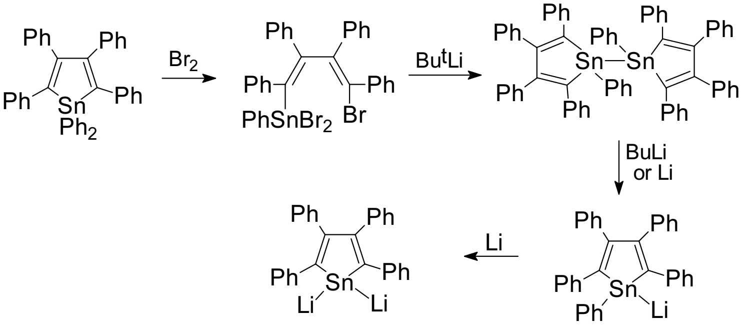
Thirdly, transmetallation of zirconacyclopentadienes[117–119] is catalysed by cuprous chloride, and provides a versatile route to the stannoles.[120]



(8-61)

C-Unsubstituted or 3,4-disubstituted stannoles can be obtained from a [2+2+1] cycloaddition reaction of two alkynes and one stannylene unit in the presence of a Pd° catalyst. The key intermediate in the catalytic cycle is a strained 3,4-pallada(II)stanna(IV)cyclobutene (Scheme 21.8).[121]

Rather little work has been carried out on the properties of the stannoles, but hexaphenylstannole has been used to prepare the first bi(1,1-stannole) (δ^{119}Sn –99.3), and stannole monoanion (**8-7**; δ^{119}Sn –30.3) and di-anion (**8-8**; δ^{119}Sn 186.7).[122]



(8-62)

(**8-8**) (**8-7**)

The bistannole has a centrosymmetric structure with a near-planar ring and a normal Sn-Sn bond length of 278.44(7) pm, and the monoanion and dianion react with methyl iodide to give the 1-methyl-1-phenyl- and 1,1-dimethyl-stannoles, respectively. The remarkable downfield value of δ^{119}Sn for the dianion may imply delocalisation of the negative charges into the ring, leaving the tin with the character of a stannylene.[122]

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9 Allyl-, Allenyl-, Propargyl-, and Cyclopentadienyl-stannanes

9.1 Allylstannanes[1]

9.1.1 Formation[2]

Allyltin compounds can be prepared by the standard methods (Chapter 4) of the reaction of an allylmetallic compound with a tin halide, or of a stannylmetallic compound with an allyl halide, or of tin metal or a tin(II) compound with an allyl halide. There are, further, some special methods that depend on the presence of the double bond.

An example of the first method is the reaction of allylmagnesium bromide with triphenyltin chloride to give $Ph_3SnCH_2CH{=}CH_2$ in 88% yield, and with Ph_2SnCl_2 to give $Ph_2Sn(CH_2CH{=}CH_2)_2$ in 71% yield.[3] Allyltributylstannanes are more conveniently prepared from bis(tributyltin) oxide, which gives $Bu_3SnCH_2CH{=}CH_2$ in 94% yield.[4] In the presence of fluoride ion, trimethylallylsilane is nucleophilic enough to react with bis-tributyltin oxide in THF at 60 °C in 16 h, to give tributylallyltin in 95% yield.[5]

Similar reactions give functionally-substituted allylstannanes, for example:[6]

$$\begin{tikzcd} CH_2{=}CHCH(OMe)_2 \arrow[r, "\text{THF, BuLi}", "-60\ ^{\circ}C"'] & Li^{+}[CH_2{=}CH\bar{C}(OMe)_2] \arrow[d, "Me_3SnCl"] \\ Me_3SnCH_2CH_2CO_2Me & Me_3SnCH_2CH{=}C(OMe)_2 \arrow[l, "H^{+}"'] \end{tikzcd}$$

(9-1)

Various allylic halides have also been cross-coupled with tributyltin chloride or tin tetrachloride under the action of ultrasound in the presence of a metal to give the corresponding allyltributylstannane or tetraallylstannane in excellent yield; this procedure avoids the formation of biallyl which is sometimes a problem in making the Grignard reagent.[7]

$$Bu_3SnCl + Me_2C{=}CHCH_2Cl \xrightarrow[100\%]{i} Bu_3SnCH_2CH{=}CMe_2 \qquad (9\text{-}2)$$

$$SnCl_4 + CH_2{=}CHCH_2Cl \xrightarrow[100\%]{i} (CH_2{=}CHCH_2)_4Sn \qquad (9\text{-}3)$$

i. THF, Mg, 0 °C,))), 45 min.

Optically active allylstannanes, $R_3SnC^*HR'(CH{=}CHR'')$, are formed from active secondary propargyl phosphates from the sequence of reactions shown in equation 9-4, [8] using the $Ti(OPr^i)_4/Pr^iMgBr$ reagent.[9] Presumably the titanium/tin transmetallation involves an S_N2' process.

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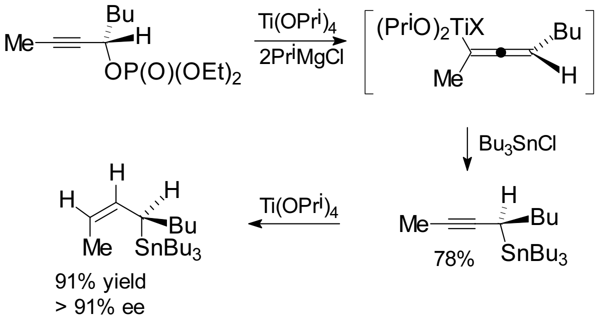
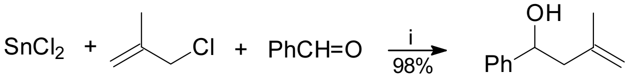


(9-4)

The allylation of an aldehyde can be carried out by the direct reaction of tin with an allyl bromide in aqueous ethanol or in water,[10] or in the absence of any solvent.[11] Allylation can also be achieved by generating the allylstannane reagent *in situ* from tin(II) chloride and the appropriate allyl bromide.[12, 13] The reaction can be carried out with the more accessible but less reactive allyl chloride if sodium iodide is added, which converts the chloride into the iodide.[14]

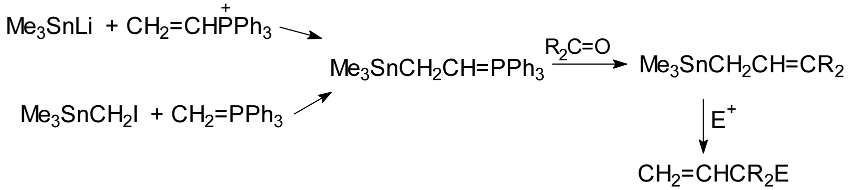


i. DMF, NaI, RT, 20 h

(9-5)

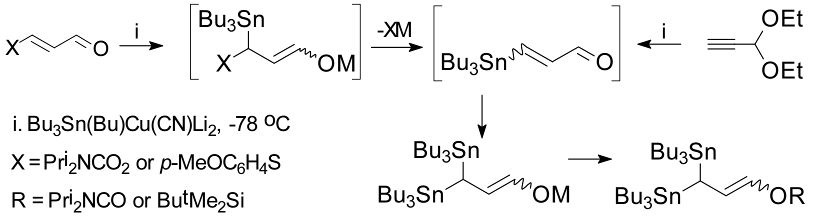
Monoallylstannanes, $\text{AllylSnX[N(SiMe}_3)]_2$, are formed when the stannylene, $:\text{Sn[N(SiMe}_3)]_2$, reacts with allyl bromide,[15–17] and the reaction of allyl bromide with the tin(II) catecholate complex of a dialkyl tartrate,[18] or with the oxathiastannolane complex of (R)-binaphthol[19] gives chiral allyltin reagents.

Allylstannanes can also be prepared by the reaction of triorganostannyllithium compounds with vinylphosphonium salts, which gives a β-stannylylide, that can be methylenated.[20]



(9-6)

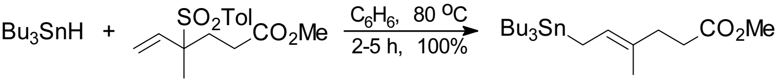
3,3-Bis(tributylstannyl)propenes are available from the double stannylcupration of an enone or the acetal of propargyl aldehyde.[21]



i. $\text{Bu}_3\text{Sn(Bu)Cu(CN)Li}_2$, -78 °C
$\text{X} = \text{Pr}^i{}_2\text{NCO}_2$ or $p\text{-MeOC}_6\text{H}_4\text{S}$
$\text{R} = \text{Pr}^i{}_2\text{NCO}$ or $\text{Bu}^t\text{Me}_2\text{Si}$

(9-7)

Allylstannanes carrying functional substituents (e.g. CN, CO_2Me, or SO_2Ar) can be obtained by the radical-chain hydrostannation of the corresponding allyl sulfones in refluxing benzene,[22] and 1,3-bis(trimethylstannyl)-2-methylenepropane is formed in a similar reaction with the corresponding allylic sulfide.[23]



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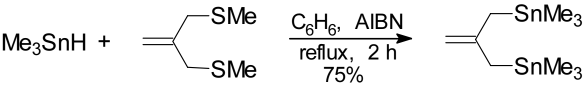
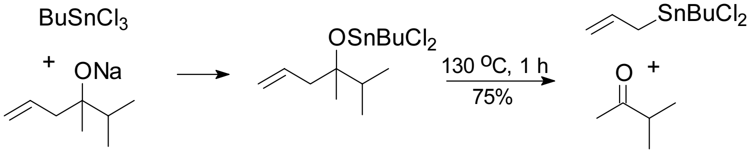


(9-9)

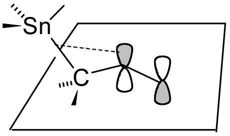
Allyltin halides are formed by the Kocheshkov reaction, and have also been obtained by the retro-ene elimination of a ketone from a homoallyloxystannane.[24]



(9-10)

9.1.2 Properties

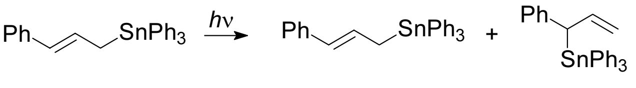
The crystal structures of allyl-,[25] cyclopent-2-enyl-,[26] cyclohex-2-enyl-, and cyclohept-2-enyl-triphenyl-tin[27] show that the Sn−allyl bond is oriented orthogonally to the plane of the C=C group with a Sn−C−C=C dihedral angle of 100 ± 10°, and this is ascribed to $\sigma-\pi^*$ conjugation (carbon-metal hyperconjugation) (**9-1**) between the σ-Sn−C bond and the π^*-C=C orbitals. This is supported by the photoelectron spectra, and by linear combination of bond orbitals calculations (see Section 3.1.2.3).[28]



(**9-1**)

There appear to be no direct measurements of the Allyl−SnR_3 bond dissociation energy; a value of about 217 kJ mol^{-1} has been suggested, about 40 kJ mol^{-1} less than that of a simple Alkyl−Sn bond.[29]

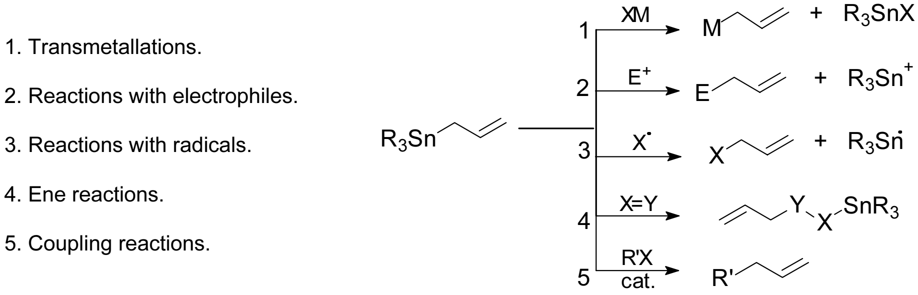
Allylstannanes are stable towards allylic rearrangements up to ca. 100 °C in non-polar solvents, or at rather lower temperature in polar solvents.[30, 31] Photolytic sigmatropic rearrangement occurs in competition with homolysis, and, in the presence of oxygen as a radical trap, cinnamyltriphenylstannane gives a 1 : 9 mixture with the α-stannyl isomer.[32]



(9-11)

9.1.3 Reactions

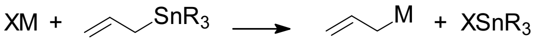
The allylstannanes are stable to air, and easy to handle, and find extensive use in organic and organometallic synthesis[33, 34] as a source of allyl groups, based on five principal reactions as shown in Scheme 9-1.



Scheme 9-1 Principal reactions of the allylstannanes

The detailed discussion of transmetallation reactions with organolithium compounds (1, XM = RLi), and coupling reactions (5) in the presence of transition metal catalysts (particularly the Stille reactions) is deferred until Sections 22.1 and 22.2.

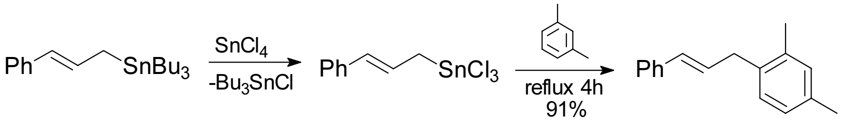
9.1.3.1 Transmetallations



(9-12)

Seyferth showed in 1959 that allyllithium, which is not available from allyl halides because of competing substitution reactions, can be prepared from the reaction of allylstannanes with organolithium reagents (XM = R′Li; Section 22.1). These reactions involve nucleophilic attack of R′ upon tin to form a pentacoordinate intermediate. Lewis acids, MX, on the other hand, react by electrophilic attack at the γ-position.

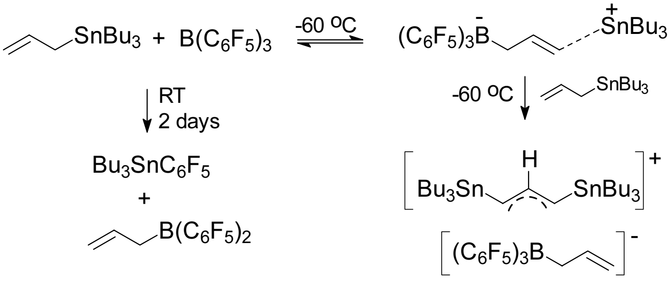
Allylstannanes rapidly undergo the Kocheshkov comproportionation reaction with $SnCl_4$, even at –50 °C. The initial product is apparently formed with allylic inversion, but further transmetallation may give other allylic isomers.[35] The $SnCl_3$ group which is formed enhances the electrophilic power of the allyl group. This has been exploited in aromatic allylation (equation 9-13),[36] and transmetallations of this type provide the basis for some, but not all, of the examples of the catalysis of the allylation of carbonyl compounds by allylstannanes in the presence of Lewis acids[37, 38] (Section 9.1.3.4).



(9-13)

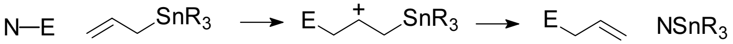
Transmetallation reactions between allyltin compounds and other Lewis acid metal halides (e.g. Bu_2SnCl_2, BCl_3, BBr_3, $AlCl_3$, or $TiCl_4$) are similarly very fast,[39] and the reaction between allyltriphenyltin and BCl_3 (though not $BF_3{\cdot}OEt_2$) is complete within one second.[40] Reactions of this type have been used for preparing allylic derivatives of boron,[41, 42] indium,[10, 38] copper,[43] phosphorus, arsenic, antimony,[44] and other metals.

Tris(pentafluorophenyl)borane catalyses nucleophilic allylations by allylstannanes, and the intermediates shown in equation 9-14 have been identified by NMR spectroscopy.[45]



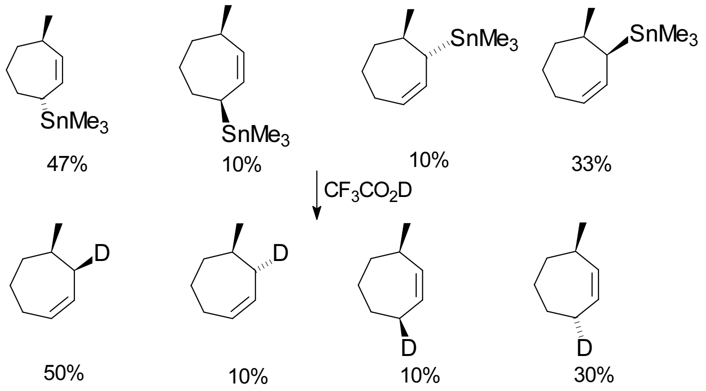
(9-14)

9.1.3.2 Reactions with Electrophiles

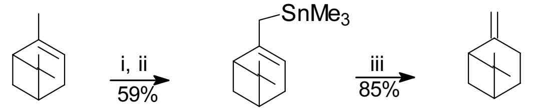


(9-15)

Allyltin compounds are useful in organic synthesis as a non-basic source of a weakly nucleophilic allyl group. Electrophiles usually react in a γ-*anti* (S_E2') sense, which involves allylic rearrangement. (Some multiply-bonded electrophiles such as SO_2 and aldehydes are exceptional in that they react with *syn*-stereochemistry, but these reactions are perhaps better regarded as ene-reactions, and are considered as such in Section 9.1.3.4). Thus the acidolysis of a mixture of methylcyclohepten-2-ylstannanes proceeds as shown in equation 9-16.[46] Reactions of this type can be used for the allylic isomerisation of terpene hydrocarbons, for example of (+)-α-pinene into (+)-β-pinene (equation 9-17).[47]



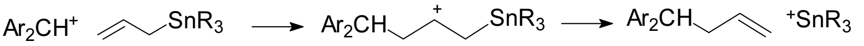
(9-16)



(9-17)

i. BuLi, TMEDA ii. Me_3SnCl iii. HCl/MeOH, 4% H_2O

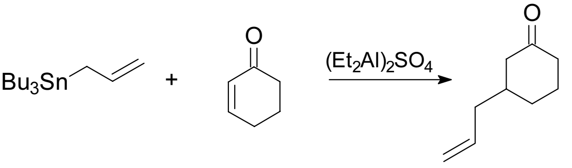
The reactions of diarylcarbenium ions, Ar_2CH^+, with allylstannanes are kinetically first order in each reagent and involve irreversible addition to give the cation which is stabilised by the β-stannyl substituent, followed by loss of R_3Sn^+ (or sometimes attack of a nucleophile at C2).[40]



(9-18)

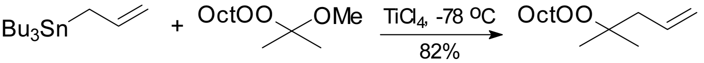
The relative reactivity in the series $CH_2{=}CHCH_2MPh_3$ (M = Si, Ge, and Sn) is 1:5.6:1600, and in the series $CH_2{=}CHCH_2M$ (M = H, $SiBu_3$, and $SnBu_3$) it is $1:5\times10^5:3\times10^9$. Inductively-withdrawing ligands on the tin reduce the reactivity; in contrast, such ligands usually appear to accelerate the ene reactions, which are considered below.

In the presence of a Lewis acid, allylstannanes couple with various electrophiles such as aldehydes (see Section 9.1.3.4), acetals, α,β-unsaturated ketones and nitro compounds (e.g. equation 9-19), and bis(diethylaluminium) sulfate is reported to be a better catalyst than boron trifluoride.[48]



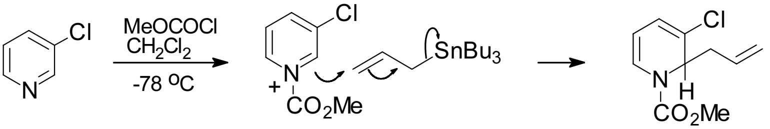
(9-19)

Homoallylic peroxides can be prepared from monoperoxyketals via the peroxycarbenium ions which are formed with $TiCl_4$.[49]



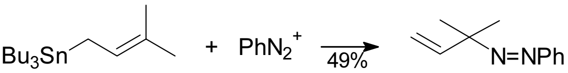
(9-20)

Pyridines, quinolines,[50] isoquinolines,[51] and imidazoles[52] react with allylstannanes in the presence of acyl halides, via the corresponding *N*-acyl salts, to give the 1-acyl-2-allyl derivatives of the 1,2-dihydro compounds.



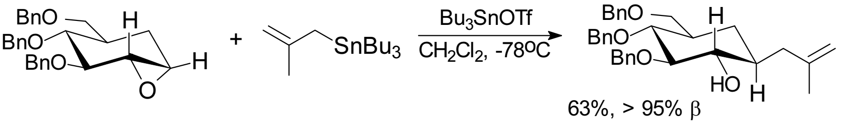
(9-21)

Allylstannanes react with benzenediazonium tetrafluoroborate to give the allylazo compounds (whereas the allylsilanes react only with the more strongly electrophilic mono- or di-nitrobenzenediazonium salts).[53]



(9-22)

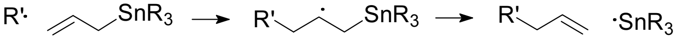
β-*C*-Allyl glycosides have been prepared by the ring-opening of epoxides by allylstannanes in the presence of a Lewis acid.[54]



63%, > 95% β

(9-23)

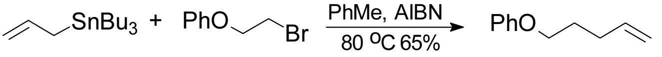
9.1.3.3 Reactions with Radicals[55]



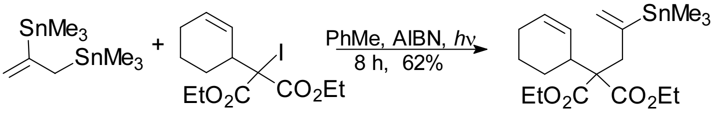
(9-24)

Radicals react with allylstannanes in the same way as electrophiles, through attack at the γ-position to give a radical intermediate which again obtains some stabilisation by interaction with the β-stannyl substituent (Section 3.1.2). The rate constant for the addition of a simple alkyl radical to an allylstannane is about 10^4–10^5 M^{-1} s^{-1} at 50–80 °C;[56] quantitative comparisons are difficult to make, but this must be faster than additions to a simple alkene, as the reaction product is an alkene, and the reactions are reasonably clean. The attacking radical $R'^{\bullet}$ is usually an organic radical derived from R′X where X is Cl, Br, I, SPh, SePh, OC(S)SMe, OC(S)imidazole, or HgCl, so that the displaced stannyl radical abstracts X from R′X to regenerate $R'^{\bullet}$ and propagate the chain. The reactions can be initiated with AIBN at 80 to 100 °C, or at or below room temperature by photolysis or with a trialkylborane in the presence of a trace of oxygen. Zinc chloride etherate has been reported sometimes to act as a co-catalyst.[57]

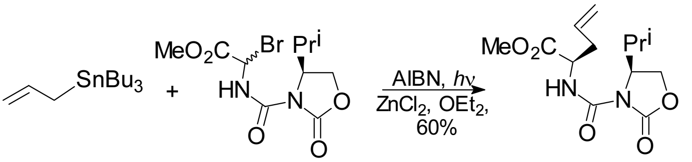
Some examples of these reactions are shown in equations 9-25,[58] 9-26,[59] and 9-27.[57]



(9-25)

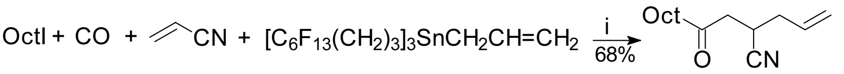


(9-26)



(9-27)

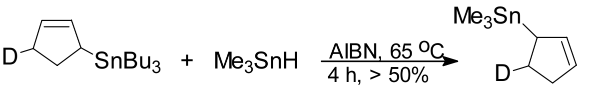
Cascade reactions can be designed that depend on the relative electrophilicities of the intermediate organic radicals, and carbon monoxide can provide one of the components (equation 9-28).[60]



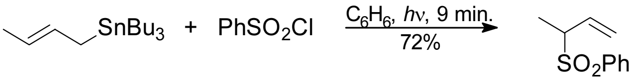
(9-28)

i. $PhCF_3$, 1,1'-azobis-(cyclohexane-1-carbonitrile), 80-100 atm, 100 °C

Similar reactions can occur where $R'^{\bullet}$ is a heteroatomic-centred radical such as $Me_3Sn^{\bullet}$ (from Me_3SnH), $PhS^{\bullet}$ (from PhSSPh), $PhSe^{\bullet}$ (from PhSeSePh), $PhTe^{\bullet}$ (from PhTeTePh), or $PhSO_2^{\bullet}$ (from $PhSO_2Cl$). In the reactions of PhSSPh, PhSeSePh, and PhTeTePh with allyltrialkyl-silanes, -germanes, -stannanes, and -plumbanes, the reactivity decreases in the sequences S > Se > Te and Pb > Sn > Ge > Si.[61] Two examples are given in equations 9-29[62] and 9-30.[63]



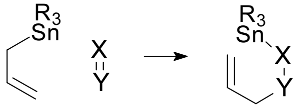
(9-29)



(9-30)

Allyltriethyltin has been shown to react with $(Me_3Si)_2NBr$ under UV irradiation to give allene as a major product. On the basis partly of CIDNP evidence, the reaction is suggested to involve attack of a bromine radical on the β- rather than the γ-carbon centre of the allyl group, with ultimate elimination of Et_3SnBr from $Et_3SnCH_2CBr{=}CH_2$, but the reason for this unusual regioselectivity is not clear.[64]

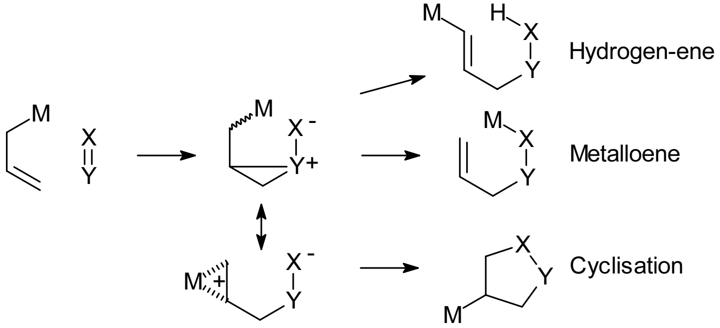
9.1.3.4 Ene Reactions[65]



(9-31)

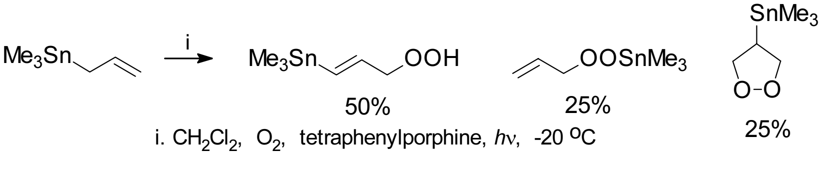
Ene reactions of allylstannanes which involve intramolecular transfer of the organotin group (equation 9-31) are known where the reagent X=Y is $O{=}CR_2$, $RC{\equiv}CR$, $R_2C{=}CR_2$, O=O, RN=NR, O=NR, or SO_2. These are the metallic equivalents of the more familiar hydrogen-ene reactions in which hydrogen is transferred (Section 3.1.1), and are sometimes referred to as metalloene reactions. The reactions involving carbonyl compounds as the enophiles were established by Neumann in 1967,[66] and are used extensively in organic synthesis. The reactions with the other enophiles are of more recent recognition, and as yet, only the reactions involving singlet oxygen are important in synthesis. The reactions with singlet oxygen and with azo compounds, where the enophile is homonuclear (X = Y), are in some ways simpler, and are considered first.

The kinetic hydrogen isotope effects which have been observed in the hydrogen-ene reactions of deuterium-labelled alkenes with singlet oxygen, *N*-phenyltriazolinedione, nitrosopentafluorobenzene, formaldehyde, methyl chloroacrylate, and ethyl propiolate as the enophiles, and the stereoselectivity of the reactions, imply the initial formation of a complex between the alkene group and the enophile. The various products which have been identified in the metalloene reactions can be rationalised on the basis of a similar mechanism (Scheme 9-2).[67]

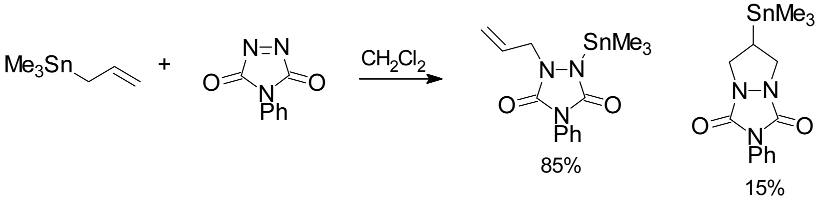


Scheme 9-2 Mechanism of metalloene and related reactions.

Allyltrialkylstannanes react with singlet oxygen in non-polar solvents to give all three types of product (hydrogen-ene, metalloene, and cyclisation; equation 9-32; see Section 14.5),[68–70] but with one or more electronegative ligands on the tin, only the metalloene reaction is involved;[71] tetraallylstannane similarly cleanly gives tetra(allylperoxy)tin. Polar solvents also favour the metalloene process, and the reactions are accelerated by high concentrations of lithium perchlorate.[72, 73] The formation of the 4-stannyl-1,2-dioxolane is presumably another manifestation of the interaction of a β-stannyl substituent with the positively charged carbon (see Scheme 9-2). With *N*-phenyltriazolinedione as the enophile, allyltrialkylstannanes show the metalloene and cyclisation reactions (equation 9-33),[74] and little or no hydrogen shift, and again with an electronegative ligand on the tin, only the metalloene reaction is observed.[71]



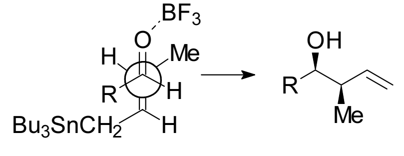
(9-32)



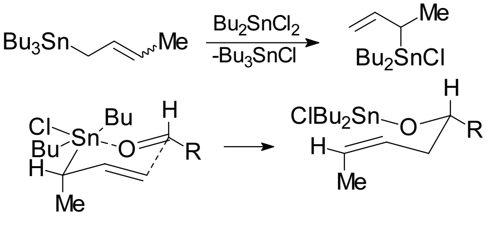
(9-33)

The reaction of allylstannanes with aldehydes, in the presence of a Lewis acid catalyst, to give homoallylic alcohols can be regarded as a special group of ene reactions, which have mechanistic features different from those shown in Scheme 9-2. These reactions are important in organic synthesis and have an extensive literature;[75] a number of reviews are available.[2, 37, 76–81]

A wide variety of Lewis acids have been used, including $BF_3.OEt_2$, $AlCl_3$, $InCl_3$, $MeSiCl_3$, $SnCl_2$, $SnCl_4$, $BuSnCl_3$, Bu_2SnCl_2, $MgBr_2$, $ZnCl_2$, $TiCl_4$, $Sc(OTf)_3$, and $PdCl_2(PPh_3)_2$,[82] and can lead to different products. For example, in the presence of $BF_3.OEt_2$, *cis*- and *trans*-crotyltributyltin react with aldehydes with allylic inversion, to give the homoallylic alcohol with, principally, a *syn* disposition of the groups Me and OH[83] but, in the presence of Bu_2SnCl_2, the reaction takes place with allylic retention.[84] In the former reaction, it appears that the BF_3-coordinated carbonyl group is too weak a Lewis base to interact with the Bu_3Sn group, and there is an open transition state in which steric repulsion between these groups is important (Scheme 9-3). In the latter reaction, the carbonyl addition is preceded by a transmetallation; the free carbonyl group then coordinates to the Bu_2SnCl group, which is a stronger Lewis acid than Bu_3Sn, and the reaction takes place through a cyclic transition state, the allylic retention resulting from two inversions (Scheme 9.4).

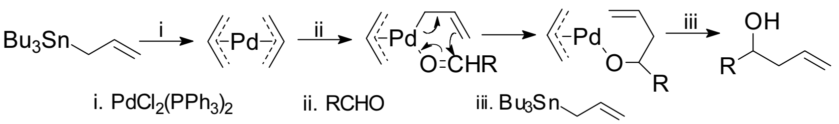


Scheme 9-3 Catalysis by $BF_3.OEt_2$.



Scheme 9-4 Catalysis by Bu_2SnCl_2.

Two molar equivalents of BF_3 have to be used, as one mole is deactivated by being coordinated by the product, but there is no such problem when Bu_2SnCl_2 or similar catalysts are used. The reactions can alternatively be carried out with a few mol% of $Sc(OTf)_3$, which is not deactivated by the product, and which can be used in aqueous solvents.[85] Reactions with $PdCl_2(PPh_3)_2$ take place through the formation of the bis-π-allyl complex.[86]

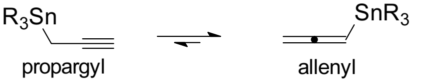


(9-34)

Chiral alkoxyallyltin chlorides, prepared *in situ* with $BuSnCl_3$ or $SnCl_4$ as catalyst, add to aldehydes with high degrees of 1,5-, 1,6-, or 1,7-asymmetric induction, which is ascribed to intramolecular interaction between the alkoxyl group and the tin which imposes a highly organised transition state.[87]

9.2 Allenyl- and Propargyl-stannanes[2, 37]

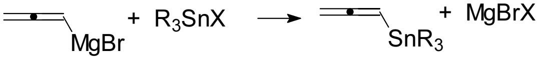
Propargylstannanes are unstable with respect to the allenylstannanes, and isomerise under the action of heat, or acids or bases, the position of the equilibrium depending on steric factors.



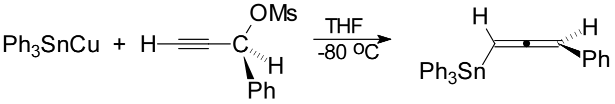
(9-35)

9.2.1 Preparation

Allenylstannanes can be prepared by the reaction of allenyl Grignard reagents with tin halides (equation 9-36), or of stannylmetallic reagents (e.g. R_3SnLi, R_3SnCu) with propargyl halides or sulfonates (equation 9-37);[88, 89] reactions of this latter type occur with complete inversion of structure.

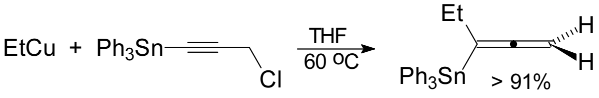


(9-36)



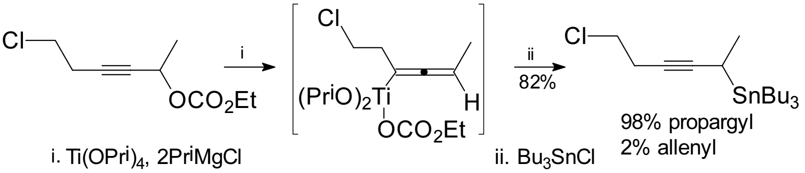
(9-37)

An alternative route is the alkylcupration of an alkynylstannane.[90]



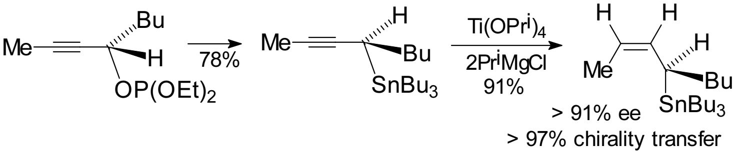
(9-38)

Propargylstannanes have usually been prepared by the reaction of a propargylmagnesium halide with a tin halide,[91, 92] but the Grignard reagents are not always readily accessible. A more general method makes use of organotitanium chemistry, for example:[93]



(9-39)

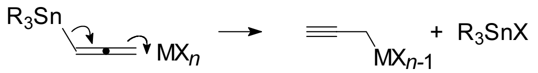
Optically active propargylstannanes have been prepared by this route from the optically active phosphates, and then reduced to the corresponding allylstannanes, again using titanium chemistry.[8]



(9-40)

9.2.2 Reactions

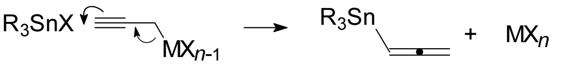
Transmetallation of allenylstannanes with Lewis acid electrophiles MX_n (e.g. BBr_3, Me_2BBr, $AsCl_3$, $SbCl_3$, Vin_2SbCl, $GeCl_4$, $SnCl_4$, $VinSnCl_3$, $SnBr_4$), occurs by the S_E2' mechanism to give the corresponding propargyl-MX_{n-1} compounds (though the propargyl-phosphorus, -arsenic, and -germanium compounds thermally rearrange to the more stable allenyl compounds).[94] This provides a further route for preparing allenyltin compounds, particularly the allenyltin trichlorides. Tin tetrabromide reacts with allenyltributyltin itself at –80 °C to give propargyltin tribromide, which rearranges at –20 °C to allenyltin tribromide, but even at –80 °C, tin tetrachloride reacts with allenyltributyltin to give allenyltin trichloride. With butyltin trichloride, the transmetallations and isomerisation are both much slower.[95]



(9-41)

(MX_n = BBr_3, Me_2BBr, PBr_3, $AsCl_3$, $SbCl_3$, $GeCl_4$, $SnCl_4$, $VinSnCl_3$, etc.)

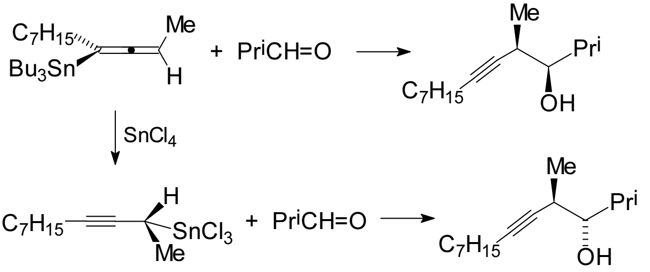
Conversely, the propargylstannanes react with MX_n by a similar S_E2' mechanism to give the allenylstannanes.[94]



(9-42)

(MX_n = BBr_3, Me_2BBr, PBr_3, $AsCl_3$, $SbCl_3$, $GeCl_4$, $SnCl_4$, $VinSnCl_3$, $SnBr_4$, etc.)

Allenylstannanes add to aldehydes in the presence of equimolar boron trifluoride etherate, or magnesium dibromide etherate to give homopropargyl alcohols.[37] If the aldehyde has a branched alkyl group, the *syn* adduct is formed (equation 9-43) through an acyclic transition state. Propargylstannanes similarly add, but through a cyclic transition state, to give the homoallenyl alcohols at –80 °C, and this reaction occurs when the allenylstannanes are converted *in situ* into the corresponding propargyltrichlorostannanes with $SnCl_4$.[89, 95, 96]



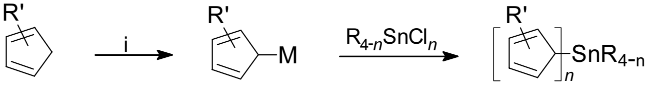
(9-43)

9.3 Cyclopentadienylstannanes[97, 98]

The cyclopentadienyltin compounds are interesting because of the stability of both the tin(IV) and tin(II) monomeric species, because of the special nature of the bonding of the cyclopentadienyl ligand, and because of the high heterolytic and homolytic reactivity of the Sn–Cp bond. In the Sn(IV) derivatives, the cyclopentadienyl group is monohapto bonded, and rapidly fluxional, and these compounds are dealt with in this chapter, together with the stannylated metallocenes. Multihapto bonding is associated with the Sn(II) oxidation state (the cyclopentadienylstannylenes), and these compounds are discussed in Section 21.5.

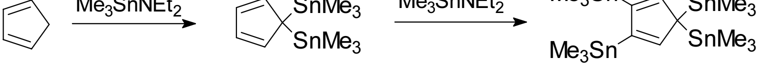
9.3.1 Formation

The acidity of the cyclopentadienes makes the cyclopentadienyltin compounds readily accessible[97] either through the reaction of other cyclopentadienylmetal derivatives with tin(IV) halides (equation 9-44),[99] or by acidolysis of an aminostannane with a cyclopentadiene (equation 9-45).[100, 101] Ferrocenylstannanes can also be obtained from ferrocenylmercury compounds and organotin sulfides (equation 9-54).[102]



(9-44)

i. BuLi, Na, K, or MeMgI



(9-45)

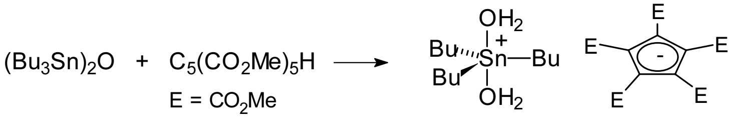
Bis(pentamethylcyclopentadienyl)tin dibromide[103] and pentaphenylcyclopentadienyltin trichloride[104, 105] (though not the tribromide) can be prepared by oxidative addition of the cyclopentadienyl halide to Sn or Sn(II) as appropriate.

$$C_5Me_5Br \xrightarrow{Sn} C_5Me_5SnBr \xrightarrow{C_5Me_5Br} (C_5Me_5)_2SnBr_2 \qquad (9\text{-}46)$$

$$C_5Ph_5Cl \xrightarrow{SnCl_2} C_5Ph_5SnCl_3 \qquad (9\text{-}47)$$

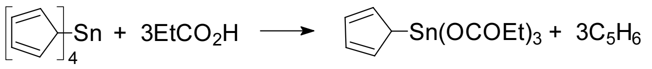
The pentamethylcyclopentadienyl-tin(IV) and -tin(II) compounds have attracted a lot of attention.[106] Pentamethylcyclopentadienyllithium (Cp*Li) will alkylate $SnCl_4$ to give Cp^*SnCl_3 (as intense red needles) and $Cp^*_2SnCl_2$ (as golden yellow crystals).[107] At –80 °C, lithium naphthalenide or dilithium cyclooctatetraenide will reduce $Cp^*_2SnCl_2$ and $Cp^*_2SnBr_2$ to η^5-$Cp^*_2Sn(II)$,[108] and this can be oxidised back to $Cp^*_2SnX_2$ with Br_2, I_2, $SnCl_4$, or $HgCl_2$.

Pentakis(methoxycarbonyl)cyclopentadiene, which is a strong protic acid, reacts with bistributyltin oxide in benzene at room temperature to give a salt between the diaquotributyltin cation and the cyclopentadienide anion as shown in equation 9-48.[109] The cation has a trigonal bipyramidal structure, with the water molecules in the apical positions, and these can be replaced by other ligating molecules such as HMPT and DMF.



(9-48)

The derivatives Cp_nSnX_{4-n} can be prepared by partial alkylation of SnX_4, or by controlled acidolysis of Cp_4Sn with the appropriate acid HX (equation 9-49), or by the Kocheshkov comproportionation between Cp_4Sn and $SnCl_4$.[110]



(9-49)

Nickelocene reacts with the tin(II) diamine $Me_2Si(NBu^t)_2Sn$**:** to give the Sn–Ni bonded compound **9-2** in which one cyclopentadienyl group remains η^5-bonded to the nickel, but the other is π-bonded to two tin atoms and is rapidly haptotropically rearranging both in solution and in the solid state[111, 112]

(9-2)

(9-50)

9.3.2 Properties

Some examples of cyclopentadienyltin(IV) compounds are shown in Table 9-1.

The cyclopentadienyltin(IV) compounds are usually yellow oils or crystals, which are sensitive to air, light, and moisture (though some preparations have been worked up using a hydrolytic procedure), and tetrakis(cyclopentadienyl)tin has been reported to inflame in the air.[99] On standing, they darken in colour, which is probably due, at least in part, to Diels-Alder polymerisation.

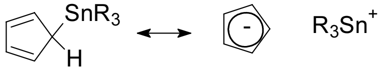
The effect of the electronic configuration in conferring special characteristics on the cyclopentadienyltin(IV) compounds is discussed in Section 3.1.2.3.

A number of properties of cyclopentadienyltin compounds emphasise that the electronegativity of the cyclopentadienyl ligand is greater than that of an alkyl ligand. The Mössbauer spectra of the compounds R_3SnCp and R_2SnCp_2 show a substantial

Table 9-1 η^1-Cyclopentadienyltin(IV) compounds.

Compound	M.p./°C or b.p./°C(mmHg)	Ref.
$(C_5H_5)_4Sn$	81–82	99
$(C_5H_5)_3SnMe$	115(0.001)	113
$(C_5H_5)_2SnMe_2$	85(0.001)	113
$C_5H_5SnMe_3$	85(10)	113
$C_5H_5SnMe(Pr^i)(Ph)$	110(0.01)	114
$(MeC_5H_4)_4Sn$	71–73	115
2-$(Ph_3C)C_5H_4SnMe_3$-5		116
$Me_5C_5SnMe_3$	50(2.3)	107
$C_5H_5FeC_5H_4SnMe_3$	90(0.1)	102
$(Me_3SnC_5H_4)_2Fe$	280(0.1)	117
$Bu_3Sn(OH_2)_2{}^+C_5(CO_2Me)_5{}^-$	decomp. 92	109
$(Me_5C_5)_2SnCl_2$	95	107
5,5-$(Me_3Sn)_2C_5H_4$		101
2,3,5,5-$(Me_3Sn)_4C_5H_2$	solid, 120–125(0.1–0.05)	101

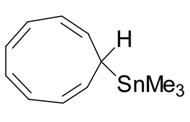
quadrupole splitting, and the behaviour of the radicals $R_nCp_{3-n}Sn^{\bullet}$ is closer to that of the radicals $R_nCl_{3-n}Sn^{\bullet}$ than $R_3Sn^{\bullet}$.[118] Again, if a ligand such as HMPT, DMF, or LiCl is added to a solution of $CpSnMe_3$, the $^{117/119}Sn-H$ coupling in the ^1H NMR spectrum is lost, indicating that the tin is undergoing intermolecular exchange. These effects can be rationalised if the structure of R_3SnCp is regarded as a resonance hybrid of the structures (**9-3**) and (**9-4**).



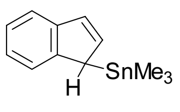
(**9-3**) (**9-4**)

The property that has attracted most attention is the rapid sigmatropic migration of the tin around the cyclopentadienyl ring (fluxionality or "ring whizzing").[119] This occurs with all the Group 14 elements, the mobility increasing down the group, C < Si < Ge < Sn, Pb. On the NMR time scale, the fast migration at "high" temperature can render magnetically equivalent the carbon atoms and attached protons (or other groups) of the ring, and by following the change in the ^1H or ^{13}C NMR spectra with temperature, the barrier to migration can be measured. In $CpSnMe_3$ this is found to be 32.6 ± 4 kJ mol^{-1}, but in Cp^*SnMe_3 the migration is too fast to measure, and the barrier is estimated to be < 21 kJ mol^{-1}. The values in the corresponding derivatives of the other Group 14 metals are $CpSiMe_3$ 54.3 ± 4, $CpGeMe_3$ 38.5 ± 4, Cp^*SiMe_3 64 ± 0.8, and Cp^*GeMe_3 47.6 ± 5.4 kJ mol^{-1}.[119]

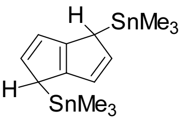
Similar fluxional behaviour is observed in structurally related compounds such as cyclononatetraenyltrimethyltin (**9-5**),[120] indenyltrimethyltin (**9-6**), the mono- and di-trimethylstannyl derivatives of dihydropentalene (**9-7**), and the stannyl derivative of indacene (**9-8**),[119] but not in the bowl-shaped distannylacepentalene (**9-9**),[121] or its tribenzo derivative.[122]



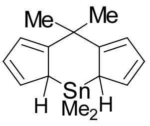
(**9-5**)



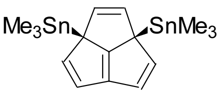
(**9-6**)



(**9-7**)

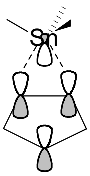


(**9-8**)

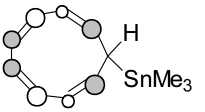


(**9-9**)

Evidence for the mechanism of the migration is provided by the NMR spectrum of $C_5H_5SnMe(CHMe_2)Ph$,[114] which, because of the rapid migration of the stannyl substituent round the ring, shows a single signal for the ring protons, δ 6.19, $J^{117/119}Sn$ 22 Hz, and for the ring carbon atoms, δ 112.8, $J^{117/119}Sn$ 14 Hz. The chirality at the tin centre renders the two methyl groups of the isopropyl ligand magnetically non-equivalent, but this non-equivalence would be lost if the migration involved inversion of configuration at the tin centre. In fact, the two methyl groups show separate ^{13}C NMR signals over a range of temperature, and it is concluded that the migration involves retention of configuration. This conclusion is supported by analogous studies on similar silicon and germanium compounds in which the barrier to migration is larger, and the region of slow exchange can be reached. This is in line with the predictions of the Woodward-Hoffmann frontier orbital model for the [1,5]-migration of an sp^3 radical across a 1,3-pentadienyl radical, involving the transition state (**9-10**).



(**9-10**)



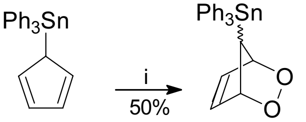
(**9-11**)

The symmetry of the cyclononatetraene LUMO (**9-11**) is similarly appropriate for providing symmetry-enhanced hyperconjugative stabilisation of the C–Sn bond at the *sp*^{3}C position, and there is strong evidence for [1,9]-migration of the tin under symmetry control, with $E^{\neq}$ 25.1(2.5) kJ mol^{-1}. In 7-stannylcycloheptatrienes, however, the *sp*^{3}C position lies in the nodal plane of the LUMO, and the *sp*^{3}C-Sn bond is not subject to hyperconjugative stabilisation (see Section 3.1.2.3).

9.3.3 Reactions

Bipyridyl adds to Cp_2SnCl_2 to give Cp_2SnCl_2,bipy, but reacts with $Cp^*{}_2SnCl_2$ to give $SnCl_2$,bipy and Cp*–Cp*.[107]

The cyclopentadienyltin(IV) compounds undergo Diels-Alder cycloadditions with reactive dienophiles such as maleic anhydride, diethyl maleate, and diethyl acetylenedicarboxylate,[99] and an endoperoxide has been identified from the reaction with singlet oxygen.[123]

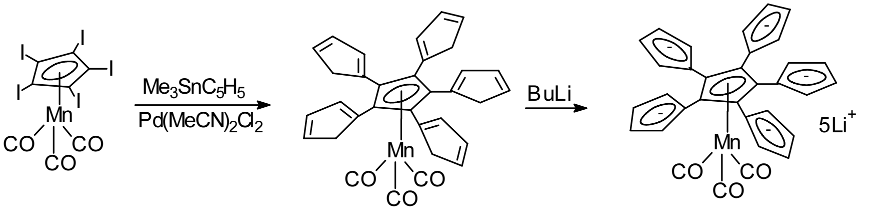


(9-51)

i. O$_2$, Rose Bengal, *h*ν, -20 °C

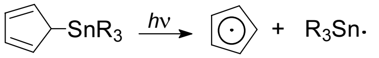
Protic reagents (e.g. equation 9-49) and other electrophiles (e.g. halogens) readily cleave the Cp–Sn bond, and the Kocheshkov reaction with $SnCl_4$ occurs rapidly even at –60 °C.[110]

Cyclopentadienyltin(IV) compounds can act as cyclopentadienylating agents in the Stille reaction (Section 22.2), and $Me_3SnC_5H_5$ reacts with $C_5I_5Mn(CO)_3$ to give $C_5(C_5H_5)_5Mn(CO)_3$ and thence the pentaanion (equation 9-52).[124]



(9-52)

The cyclopentadienyltin compounds (and cyclopentadienyl derivatives of other metals such as mercury and lead) are very sensitive to photolysis, and on irradiation with UV light in an ESR spectrometer they show the spectrum of the cyclopentadienyl radical; the stannyl radical is difficult to observe directly under these conditions, but its presence is established by the reactions which it shows with substrates such as alkyl halides. This provides a useful route to a variety of stannyl radicals (see Section 20.1.1), and a method of generating cyclopentadienyl radicals for study by ESR spectroscopy.[125] It would be interesting to extend these ESR studies to the more complex compounds **9-6–9-9**, which are known to be photosensitive.

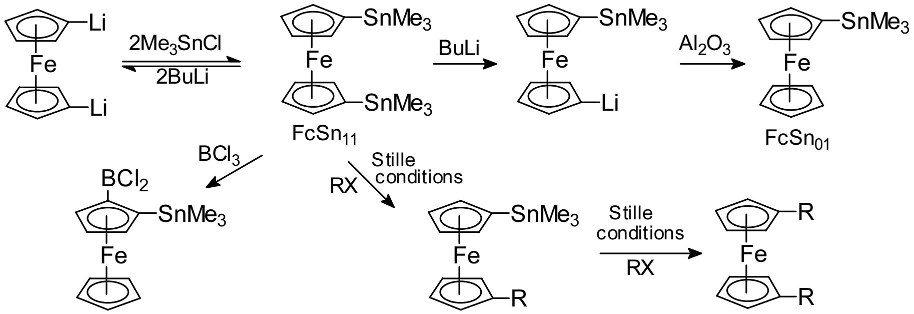


(9-53)

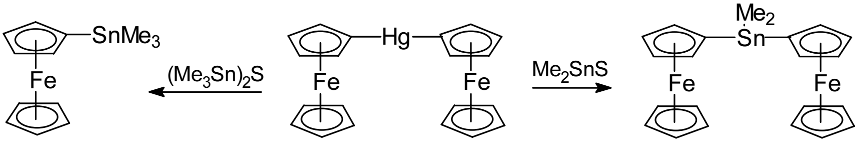
If the cyclopentadienyl radical carries substitutents, these can interact with the degenerate π-molecular orbitals of the ring to break the degeneracy, and the resulting ESR spectrum can be interpreted to show whether the nature of that interaction is electron repelling or electron attracting. In this way, photolysis of $C_5H_4(SnMe_3)_2$ provides the spectrum of the radical $Me_3SnC_5H_4^{\bullet}$, which shows that the trimethylstannyl substituent is weakly electron attracting; in comparison, the Me_3Si group is more strongly electron attracting, the Me_3C group is electron repelling, and the Me_3Ge group has a negligible electron repelling effect.[126] In contrast (see below), electrochemical studies indicate that, in ring-stannylated ferrocenes, the stannyl groups are net electron-releasing.

9.3.4 Stannylmetallocenes

There have been substantial developments in the chemistry of the stannnylmetallocenes, particularly the stannylferrocenes, in recent years. These can be prepared by transmetallation of the metallated ferrocenes (Scheme 9-5 and equation 9-54),[102] or of a lithium stannylcyclopentadiene with $FeCl_2$ (Scheme 9-6).[127] The products can be symbolised by the shorthand $FcSn_{xy}$, where the subscripts x and y indicate the numbers of stannyl groups in the separate cyclopentadienyl rings. The stannylruthenocenes can be prepared in a similar way.[128]

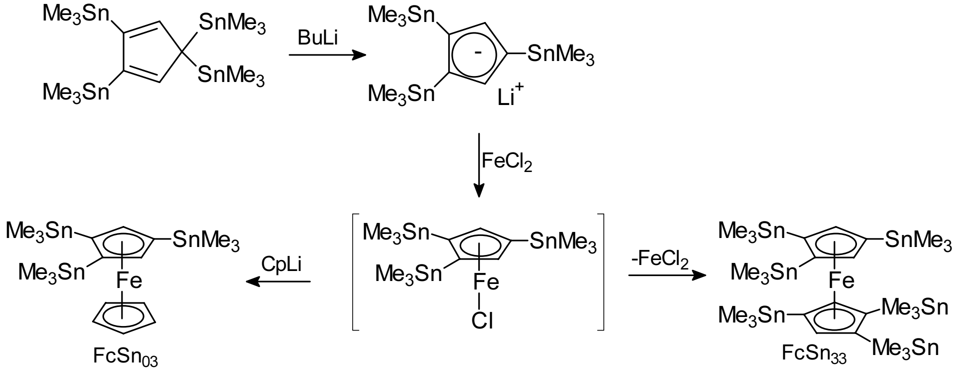


Scheme 9-5 Preparation of stannylferrocenes by transmetallation of metalloferrocenes.



(9-54)

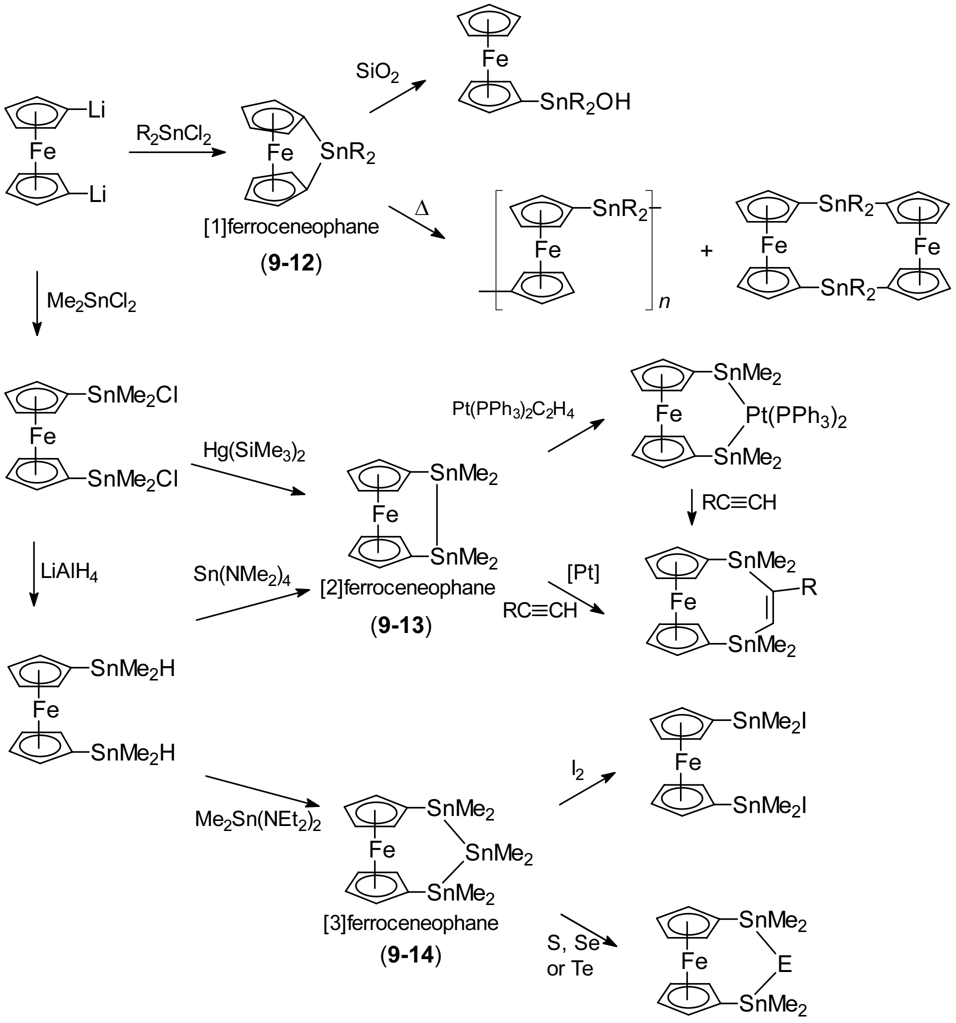
A variety of multiply stannylated ferrocenes (FcSn$_{01}$, FcSn$_{02}$, FcSn$_{03}$, FcSn$_{11}$, FcSn$_{22}$, FcSn$_{33}$) have been prepared by the reactions exemplified in Scheme 9-6.[127] The energy barriers for ring rotation are $\Delta G^{\#}$ 10.5(2) kcal mol^{-1} for FcSn$_{22}$, and 11.0(2) kcal mol^{-1} for FcSn$_{33}$. These stannylferrocenes are more easily oxidised than ferrocene itself (see above), the redox potential becoming about 15 mV more negative for each stannyl group that is introduced, and this is ascribed to a strong σ-donor (+I) effect, and a weak π-acceptor (–M) effect by the substituent.



Scheme 9-6 Preparation of multiply stannylated ferrocenes.

Stille reactions of FcSn$_{01}$ and FcSn$_{11}$ with heterocyclic halides RX give the substituted ferrocenes (RC_5H_4)Fe(C_5H_5) and (RC_5H_4)$_2$Fe.[129–131] Butyllithium reacts with FcSn$_{11}$ by mono- and di-transmetallation, but BCl_3 surprisingly gives a rearranged product.[132]

Ferrocenophanes with one, two, or three tin atoms in the bridge have been prepared by the methods shown in Scheme 9-7.

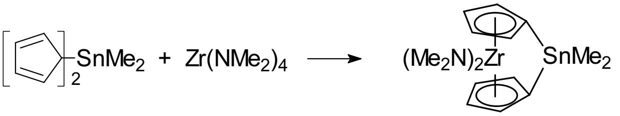


Scheme 9-7 Stannaferroceneophanes.

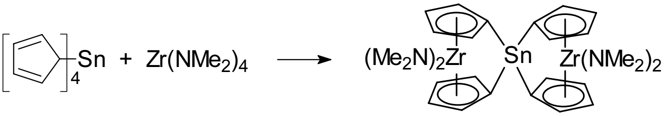
The tin-bridged stanna[1]ferroceneophanes (**9-12**) are stable only with two bulky ligands on the tin such as t-butyl or mesityl, when the tilt angles between the two rings are 14.1(2)° and 15.2(2)°, respectively. On being heated, or in solution, particularly in the presence of acid or base, ring opening occurs to give a polyferrocenylstannane and some cyclic dimer.[133–136]

1,1,2,2-Tetramethyl-1,2-distanna[2]ferroceneophane[137, 138] (**9-13**) shows the characteristic reactions of the Sn−Sn bond, reacting with $Pt(PPh_3)_2C_2H_4$ to give a 1,3-distanna-2-platina[3]ferrocenophane,[139] in which the platinum can be displaced by an alkyne.[140, 141] In the hexamethyl-1,2,3-tristanna[3]ferroceneophane (**9-14**) the rings are parallel but twisted by 62°, and the central Me_2Sn unit can be replaced by sulfur, selenium, or tellurium, to give a 1,3-distanna-2-chalcogena[3]ferroceneophane.[137, 139]

Stanna[1]zirconoceneophanes have been prepared by taking advantage of the acidity of the cyclopentadiene ring in stannylcyclopentadienes (equations 9-55 and 9-56);[142] the products are more effective than the silicon analogues in polymerising ethylene.



(9-55)



(9-56)

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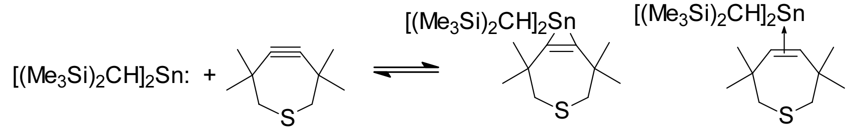
10 Stannacycloalkanes[1]

10.1 Monostannacycloalkanes, $R_2Sn(CH_2)_n$[2]

The first stannacycloalkane, $Et_2Sn(CH_2)_5$, was prepared in 1917 from the reaction of $ClMg(CH_2)_5MgCl$ with Et_2SnCl_2,[3] and compounds of this type have continued to attract attention because of the special physical and chemical properties that can be conferred by angle strain in the ring. The oligomers, $[R_2Sn(CH_2)_n]_m$, are interesting also because they can be regarded as the Lewis acid counterparts of the familiar crown ether Lewis bases, and might be expected to bind anions selectively, particularly when R = Cl.[4]

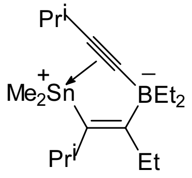
No stannacyclopropane, $R_2Sn(CH_2)_2$, appears to have been yet reported, but the stannacyclopropene **10-1** has been obtained from the corresponding stannylene and acetylene as pale yellow crystals.[5] Its structure in the solid state has been confirmed by X-ray diffraction, but in solution above –16 °C it is in equilibrium with its factors, and its bonding is probably best described in terms of a π-complex (**10-2**).



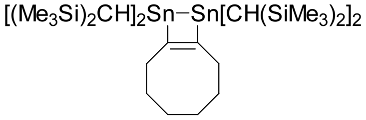
(**10-1**) (**10-2**)

(10-1)

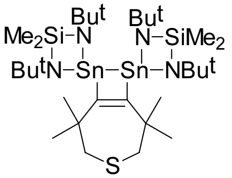
Similarly the adduct **10-3** formed between bis(3-methylbutynyl)dimethylstannane and triethylborane (see Section 8.2.2) has been represented as involving a π-adduct between a C≡C triple bond and a stannyl cation.[6]



(**10-3**)



(**10-4**)



(**10-5**)

The reaction of cyclooctyne or 3,3,7,7-tetramethyl-5-thiacycloheptyne with 2 equivalents of the appropriate stannylene gives the distannacyclobutenes **10-4**[7] and **10-5**[8] with *r*SnSn 281.7 and 280.3 pm, respectively.

The higher homologues $R_2Sn(CH_2)_n$ are known where $n = 3–6$, and have been prepared by the reaction of the di-Grignard reagents $XMg(CH_2)_nMgX$ with the organotin dichlorides R_2SnCl_2 (Method **A**, equation 10-2)[9] or by thermolytic disproportionation of the bis(trialkylstannyl)alkanes $R_3Sn(CH_2)_nSnR_3$ alone or, better, in the presence of $ZnCl_2$ (Method **B**, equation 10-3).[10] When R = Me or Ph, the halides $XRSn(CH_2)_n$ and

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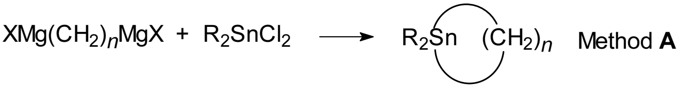
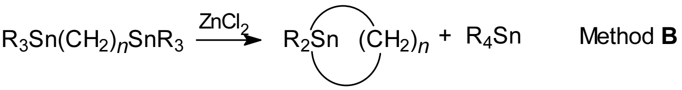
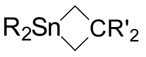
$X_2Sn(CH_2)_n$ can then be obtained by selective cleavage of the R–Sn bonds with bromine, iodine, HX or $HgCl_2$.



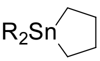
(10-2)



(10-3)



(**10-6**)



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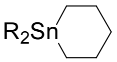

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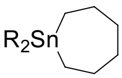
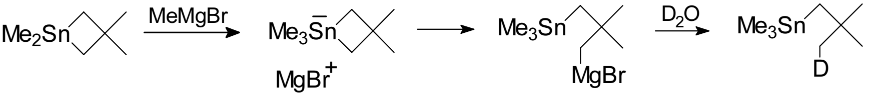


(**10-9**)

Attempts to prepare dimethylstannacyclobutane (**10-6**, R = Me, R′ = H) by Method **A** gave mainly the cyclic oligomers $(Me_2SnCH_2CH_2CH_2)_n$, $n = 2$, 3, or 4, but the monomer could be detected in solution by NMR spectroscopy.[11] By a similar method **10-6**, R = R′ = Me, was isolated in 48% yield as a colourless liquid which polymerised slowly in solution, and reacted with air to give a white solid. The effect of angle strain in causing the rehybridisation of the tin is evident from the NMR spectra, and from the fact that the compound readily forms ate complexes in which angle strain is relieved as the geometry changes from pseudo-tetrahedral to pseudo-trigonal bipyramidyl (equation 10-4).

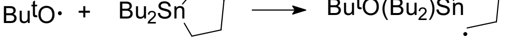


(10-4)

A large number of stannacyclopentanes, **10-7**, have been prepared by both methods **A** and **B**,[12] for example $R_2 = Me_2$, Et_2, Bu_2, $Bu^t{}_2$, $Pe^{neo}{}_2$, Ph_2, MeCl, MePh, $MePe^{neo}$; method **A** usually gives a mixture of oligomers $[R_2Sn(CH_2)_4]_n$, which have to be separated. In polar solvents, the monomers slowly oligomerise, and thermolysis of the oligomers $(Me_2SnCH_2CH_2CH_2CH_2)_n$ regenerates the monomers. In the air, they are oxidised slowly to peroxides, which decompose to give mainly diols (e.g. equation 10-5).[13]

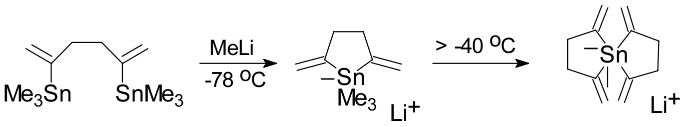
(10-5)

A partial X-ray structure of diphenylstannacyclopentane[14] gave the C–Sn–C angle within the ring as 95° (whereas MM2 calculations give a value of 87.1°).[15] The effect of the angle strain shows up in the ^{119}Sn NMR chemical shift {e.g. δ^{119}Sn, $Ph_2Sn(CH_2)_4$ 0 ± 2, $[Ph_2Sn(CH_2)_4]_2$ -74 ± 2},[14] and in an enhanced homolytic and heterolytic reactivity. For example, t-butoxyl radicals react at the tin centre with ring opening to give a carbon-centred radical which can be observed by ESR spectroscopy, whereas unstrained tetraorganostannanes undergo reaction at hydrogen rather than at tin.[16]

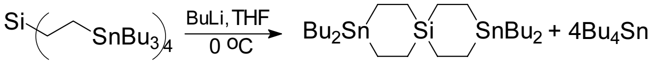


(10-6)

The tin again shows an enhanced tendency to form 5-coordinate complexes and an example of an ate complex formed from an unsaturated stannacyclopentanes is shown in equation 10-7.[17] The ring-closure occurs through a series of Sn/Li transmetallations (Section 22.1), and a similar mechanism is involved in the formation of 1-sila-4-stannacyclohexanes as illustrated in equation 10-8.[18]

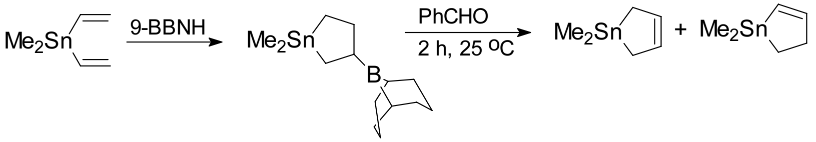


(10-7)



(10-8)

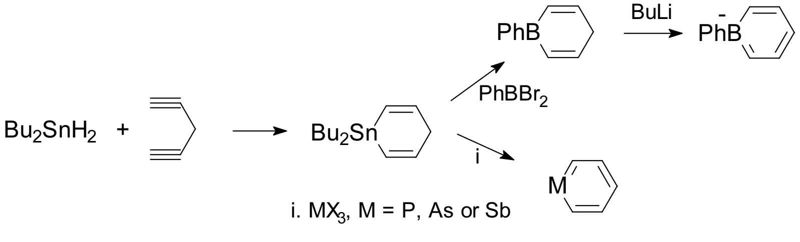
The hydroboration of dimethyldivinylstannane can lead to stanna-cyclopentanes and -cyclopentenes through a series of intramolecular rearrangements.[19] Tetravinylstannane similarly gives the diborylated spirostannane.



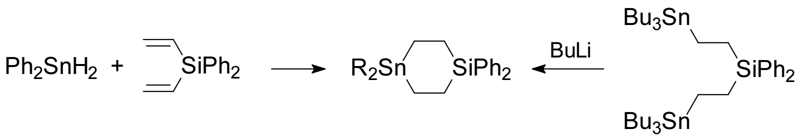
(10-9)

The stannacyclohexanes **10-8** and stannacycloheptanes **10-9** have been prepared by both methods **A** and **B**. There is now less strain in these larger rings, and these compounds have conventional characteristics.

The stannacyclopentadienes are treated separately below. Some further examples of the preparation of monostannacycloalkanes are shown in equations 10-10[20] and 10-11.[18, 21]

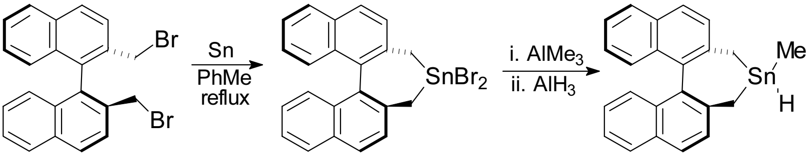


(10-10)



(10-11)

The optically active dibromostannepin **10-10** can be made by the direct reaction between the benzylic bromide and metallic tin, and then converted into the methylhydride by monomethylation then reduction.[22] The dibromide has been used in the kinetic resolution of diols by monobenzoylation,[23] and the hydride in the asymmetric reduction of an α-bromoketone.[22]

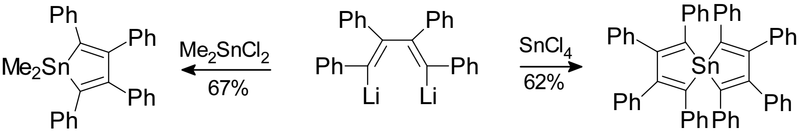


(**10-10**)

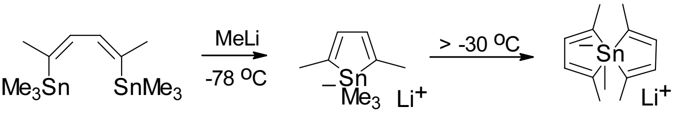
(10-12)

10.2 Stannacyclopentadienes

Stannacylopentadienes (stannoles) can be prepared from butadienyllithium compounds and tin halides (equation 10-13)[24] and by Sn/Li transmetallations (equation 10-14);[17] the electronegative character of the double bonds, and the ring strain, render the ate complexes unusually stable.

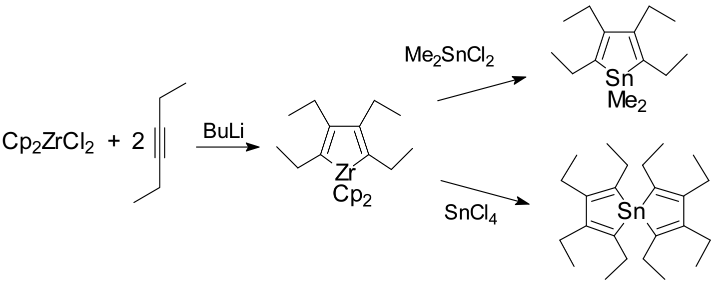


(10-13)



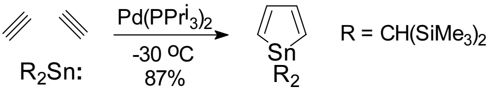
(10-14)

The accessibility of the zirconiacyclopentadienes provides a further method of transmetallation;[25, 26] the reaction is subject to copper catalysis.[27]

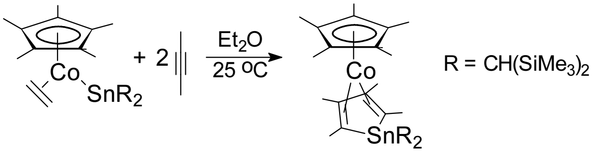


(10-15)

Stannoles can also be formed by a 2 + 2 + 1 cycloaddition between two acetylene units and a stannylene,[28] and an analogous reaction of a cobalt-bonded stannylene gives an η^4-bonded stannole.[29]

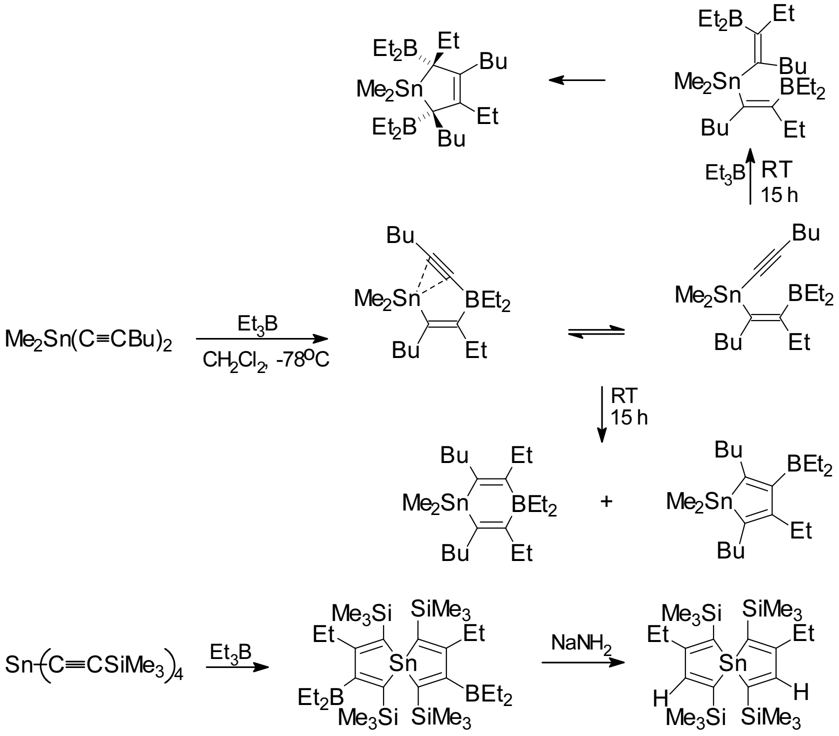


(10-16)



(10-17)

Finally, Wrackmeyer's chemistry involving alkynylmetallic compounds and organoboranes can be used in stannole synthesis (Scheme 10-1).[6, 30–32]

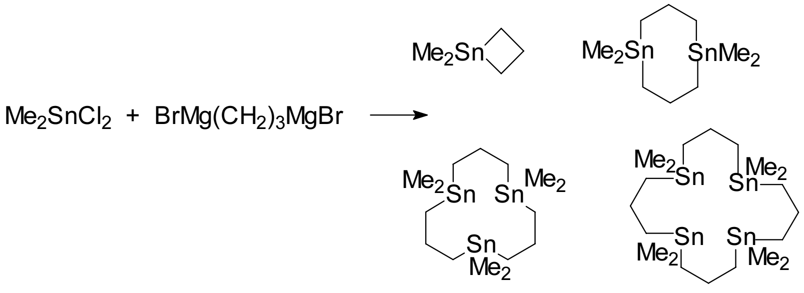


Scheme 10-1 Formation of stannoles by alkylboration of alkynylstannanes.

10.3 Oligostannacycloalkanes, $[R_2Sn(CH_2)_n]_m$[2]

10.3.1 Formation

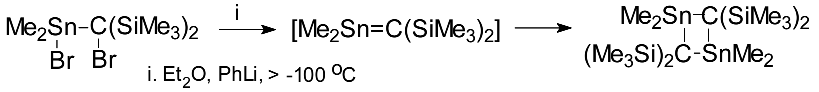
Cyclic oligostannacycloalkanes, $[R_2Sn(CH_2)_n]_m$, can be prepared from the reaction between tin dihalides and organodimetallic compounds, or tin dimetallic compounds and organic dihalides. Many of these reactions give mixtures of oligomers from which the individual compounds are separated, usually by chromatography, and sometimes in only low yield (e.g. equation 10-18).[11]



(10-18)

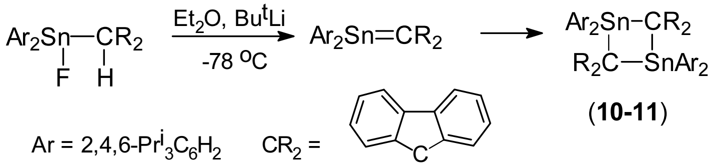
When R in $[R_2Sn(CH_2)_n]_m$ is Ph, reaction with HCl in ether gives the chlorides $[ClPhSn(CH_2)_n]_m$ and $[Cl_2Sn(CH_2)_n]_m$.[33]

Two 1,3-distannacyclobutanes have been prepared, both by dimerisation of the corresponding stannenes as shown in equations 10-19[34] and 10-20.[35, 36] The 4-membered ring in **10-11** is planar with rSnC 228.8–229.3 pm.



$$Me_2Sn(Br)\text{-}C(Br)(SiMe_3)_2 \xrightarrow[\text{i. Et}_2\text{O, PhLi, > -100 °C}]{\text{i}} [Me_2Sn{=}C(SiMe_3)_2] \longrightarrow \begin{array}{c} Me_2Sn\text{-}C(SiMe_3)_2 \\ | \quad\ | \\ (Me_3Si)_2C\text{-}SnMe_2 \end{array}$$

(10-19)



(**10-11**)

(10-20)

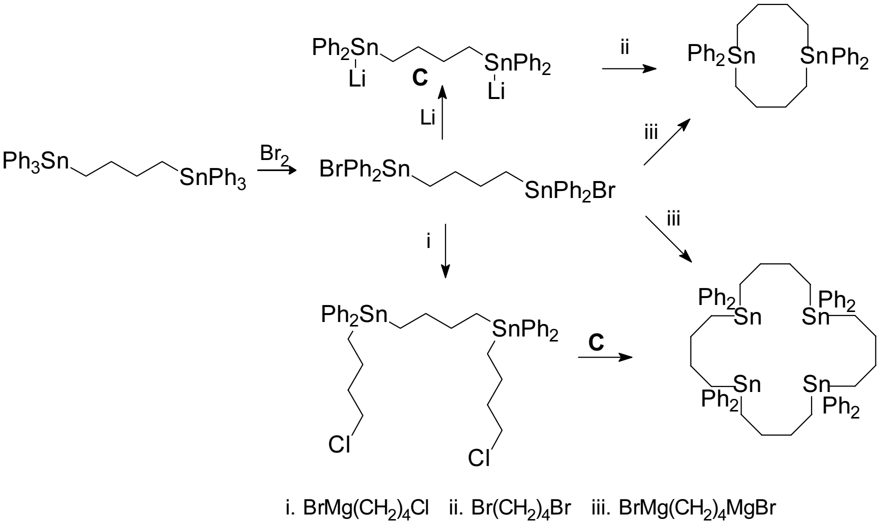
Otherwise, the smallest distannacycloalkanes without SnSn bonds, which have been reported are the 1,5-distannacyclooctanes ($n = 3$, $m = 2$), and no compounds $[R_2Sn(CH_2)_n]_m$ appear to be known where $n = 2$.

A number of stannacycloalkanes have been prepared which contain an Sn–Sn bond, but these compounds show principally the characteristics of distannanes, and are considered in Section 18.4.

A list of 29 compounds $[R_2Sn(CH_2)_n]_m$, where R = Me or Et, and $n = 1$, 3–6, 8, 10, or 12, and $m = 2$–4, is given in Chapter 8 of the first edition of this book.[11, 14, 37–40]

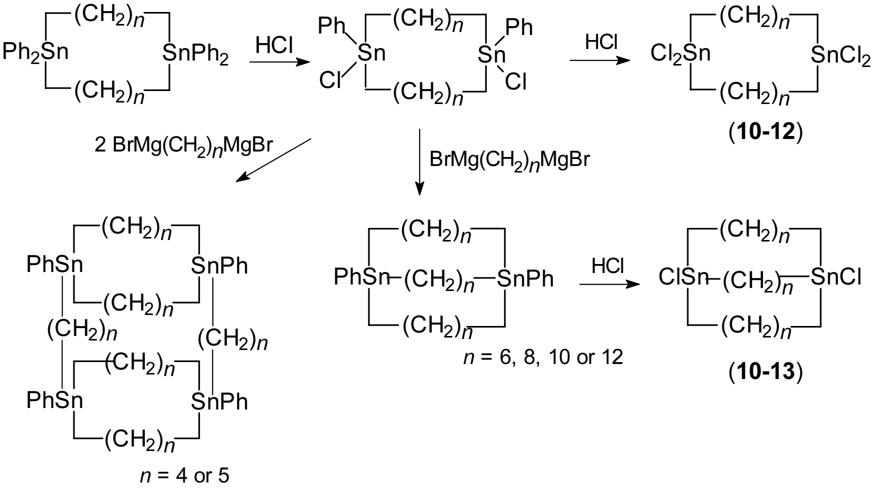
Typical preparative methods are shown in Scheme 10-2.[39] The structures of the compounds $[Ph_2Sn(CH_2)_4]_2$ and $[Ph_2Sn(CH_2)_4]_4$ have been determined by single crystal X-ray diffraction.[14, 15]

Distannabicycloalkanes can then be made by chlorodephenylation of the monocyclic compounds, and treatment of the resulting chlorides with dimetallic reagents (Scheme 10-3).[41] With different proportions of reagents, tetrastannatricycloalkanes can also be obtained.[42]



i. $BrMg(CH_2)_4Cl$ ii. $Br(CH_2)_4Br$ iii. $BrMg(CH_2)_4MgBr$

Scheme 10-2 Examples of the preparation of oligostannacycloalkanes.



Scheme 10-3 Polycyclic oligostannacycloalkanes.

10.3.2 Structures and Properties

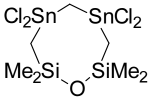
A critical factor with regard to the ability to bind anions is expected to be the intramolecular Sn...Sn separation; in the chlorostannyl compounds (**10-12**), the corresponding values of *n* and *r*SnSn are: 5, 589.2; 7, 785.7; 8, 756.6; 9, 1048; 10, 1033.6 pm.[43] This binding ability can be monitored by ^{119}Sn NMR spectroscopy. For example, progressive addition of tetrahexylammonium chloride to $ClBuSn[(CH_2)_{10}]_2SnBuCl$ in $CDCl_3$ causes a smooth upfield shift of δ Sn from 150, characteristic of four-coordinate tin, to -50, characteristic of 5-coordinate tin.[41]

The monocyclic bis(dichlorostannanes) **10-12**, *n* = 8, 10, and 12, rapidly bind 2 Cl^- per host, with low binding selectivity, only a small cooperative effect, and little dependence on ring size.[44] The bicyclic compounds $ClSn[(CH_2)_n]_3SnCl$, *n* = 8, 10, and 12, bind one Cl^- per host more strongly,[41] when they show a single NMR signal for tin, with δ Sn about half way between that for 4- and 5-coordinate tin, which would be compatible with either bidentate tin or rapid exchange of the halide between the two tin sites. When *n* = 6, addition of F^- ion causes the singlet signal of the tin at δ 1410.5 to be replaced by a doublet at –6.5, *J*(SnF) ca. 1090 Hz, characteristic of 5-coordinate tin.

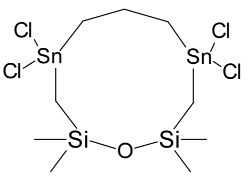
The bicyclic bis(monochlorostannane) **10-13**, *n* = 8, binds Cl^- to give an anion with a stannane-stannate structure; the chloride ion is located in the middle of the molecule, but one tin is strongly bound (*r*SnCl 261.0 pm) and one weakly bound (*r*SnCl 388.8 pm). In solution the chloride ion exchanges between the tin two sites with an activation energy of 23 kJ mol^{-1}.[44] The smaller compound **10-13**, *n* = 6, binds F^- to give an anion $ClSn[(CH_2)_6]_3SnClF^-$ in which both tin atoms have hemistannate character, with the fluoride ion almost symmetrically placed between the two tin atoms (*r*Sn ... F 212 and 228 pm), and the F^- exchanges between the two sites of minimum energy with an activation energy of 12 kJ mol^{-1}.

Similar ^{119}Sn NMR studies on the tristannacyclododecanes $(R_2SnCH_2CH_2CH_2)_3$ show that, when $R_2 = Me_2$, there is negligible interaction with Cl^-, but when R_2 = MeCl or Cl_2, complexes are formed with one and with two chloride ions.[40] The X-ray structure of the complex $(Cl_2SnCH_2CH_2CH_2)_3 \cdot Cl^-$ $[Ph_3P{=}N{=}PPh_3]^+$ shows that the chloride ion is bonded symmetrically to two tins, with close to trigonal bipyramidyl geometries.

Functional groups have been introduced into the distannacycloalkane rings so that they may be subject to ring opening polymerisation (ROP) and give compounds that can be incorporated into polymers to give ion-selective electrodes. The distanna compound **10-14**, with an 8-membered ring, forms complexes with F^- and Cl^- in which the halide anion asymmetrically bridges the two tin atoms, with *r*SnF 222.5 and 227.1 pm, and *r*SnCl 278.1 and 289.1 pm, but the ring is too stable to show ROP under either acidic or basic conditions.[45] The equivalent compound **10-15**, with a 10-membered ring, incorporates Cl^- between the two tin atoms, with *r*SnCl 268.6 and 281.2 pm. In CH_2Cl_2 for several days, **10-15** is converted into the cyclic dimer **10-16**, and in the presence of acid, both **10-15** and **10-16** underwent ROP to give the linear polymer **10-17**.[46]



(10-14)



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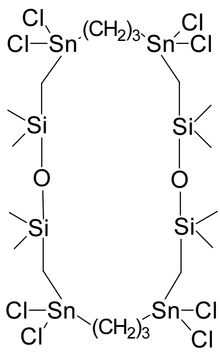

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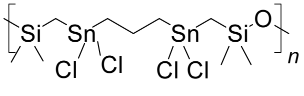

(10-17)

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11 Organotin Halides[1–3]

11.1 Preparation

The organotin halides R_nSnX_{4-n} provide the starting materials from which most other functional organotin compounds R_nSnY_{4-n} ($Y = H$, OR', NR'_2, $OCOR'$ etc.) are prepared (see Chapter 1), and a number of the halides are available commercially.

The principal methods by which they can be prepared are:

1. The "direct" reaction between an organic halide and tin metal or a tin(II) halide.
2. The reaction of a tetraorganostannane with a halogen X_2, halogen acid HX, or metal halide (MX_n, e.g. M = Hg).
3. The reaction of an organometallic compound RM with SnX_4.
4. The comproportionation reaction between a tetraorganostannane and a tin tetrahalide.
5. The reaction of an organotin hydroxide or oxide with a halogen acid, HX, or acid halide.
6. Anionic exchange at tin.
7. The cleavage of an Sn-Sn bond with a halogen, X_2.

The first two of these reactions have been adequately described in Sections 4.1, 4.3, 5.3, and 7.1. We are concerned here with the other five methods.

11.1.1 The Reaction of RM with SnX_4

The reaction of an organomagnesium or organolithium compound with tin tetrachloride is often difficult to stop at a specific stage of partial alkylation. The reaction is usually therefore taken to the stage of complete tetraalkylation, then the organotin halides are prepared by thermal comproportionation between the tetraorganostannane and a tin(IV) tetrahalide, as described in the following section. However, a number of patents describe how, by careful control of the reaction conditions (e.g. by using $SnBr_4$ rather than $SnCl_4$, and organoaluminium rather than organomagnesium reagents), satisfactory yields of the organotin halides can be obtained.[1]

Two circumstances in particular make the organotin halides directly accessible. First, if the group R is bulky, steric hindrance to further reaction becomes progressively more severe as the number n in R_nSnX_{4-n} increases, and the compounds R_2SnX_2 or R_3SnX may be isolated. For example, tricyclohexyltin chloride, trineophyltin chloride, di-t-butyltin dichloride, and dimesityltin dichloride can be prepared from the corresponding Grignard reagents.

A more general route depends on the fact that the acetylacetonate ligand on tin is more rapidly displaced than a chloro or bromo ligand, and an alkyl or aryl Grignard reagent, RMgX, reacts with $(acac)_2SnX_2$ (X = Cl or Br) at room temperature or in refluxing ether to give the product R_2SnX_2.[4, 5]

$$2RMgBr + (acac)_2SnBr_2 \xrightarrow[\text{reflux 2-3 h}]{Et_2O/C_6H_6} R_2SnBr_2 \qquad (11\text{-}1)$$

R = Et, yield = 93%. R = Pr, yield = 75%. R = Ph, yield = 61%.

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11.1.2 The Kocheshkov Reaction

In the absence of a solvent, but sometimes in the presence of a catalyst such as aluminium chloride,[6–8] tetraorganostannanes and tin tetrahalides (or, more generally, any organotin compound, R_nSnX_{4-n}, and tin halide, R_mSnX_{4-m}) undergo a redistribution of the alkyl and halogen groups.This reaction is commonly known as the Kocheshkov reaction, after its discoverer.[9]

$$n\mathrm{R_4Sn} + 4\text{-}n\mathrm{SnX_4} \xrightarrow{\Delta} 4\mathrm{R}_n\mathrm{SnX}_{4-n} \tag{11-2}$$

The reactivity follows the sequence R = phenyl > benzyl > vinyl > methyl > ethyl > higher alkyl, and X = Cl > Br > I. When R = alkyl and X = halide, the first stage of the reaction (equation 11-3) takes place rapidly at room temperature.

$$\mathrm{R_4Sn} + \mathrm{SnCl_4} \longrightarrow \mathrm{RSnCl_3} + \mathrm{R_3SnCl} \tag{11-3}$$

With a 1:3 ratio of reagents, R_3SnCl is formed in good yield when R is aryl or a straight-chain alkyl group, but yields are sometimes low for branched-chain alkyl homologues. Tributyltin chloride and triphenyltin chloride are prepared commercially by this reaction.

When R > Me, heating, usually to about 200 °C, is needed to induce the next stage of the reaction:

$$\mathrm{R_3SnCl} + \mathrm{RSnCl_3} \longrightarrow 2\mathrm{R_2SnCl_2} \tag{11-4}$$

Thus when Bu_4Sn and $SnCl_4$ are heated at 240 °C for 3 h, Bu_2SnCl_2 is formed in 95% yield,[10] but again yields can be low if R is a branched alkyl group. Dibutyltin dichloride and dioctyltin dichloride are prepared in this way commercially.

The reaction of R_2SnCl_2 with $SnCl_4$ to give $RSnCl_3$ requires prolonged heating in the presence of coordinating additives (e.g. DMSO, $POCl_3$, or P_2O_5), and alkyltin trichlorides are usually prepared industrially by taking the reaction to the stage of $RSnCl_3$ and R_2SnCl_2, then separating these by distillation. In the presence of a Pt(II) or Pd(II) catalyst, however, the reaction occurs readily in refluxing toluene.[11]

The low reactivity of the cyclohexyl-tin bond has been exploited in preparing the spacer bridged bistrichlorides, $Cl_3SnSpSnCl_3$ (Sp = alkylene, arylene, or aryldimethylene) by the Kocheshkov reaction of $Cy_3SnSpSnCy_3$ with $SnCl_4$.[12] From these hexachlorides, a variety of compounds $R_3SnSpSnR_3$ (e.g. R = MeC≡C) can be prepared.

Some examples of the Kocheshkov reaction are given in Table 11-1.

In what might be regarded as a related reaction, tetramethylstannane reacts with tetrakis(trifluoromethyl)stannane to give the mixed tetraalkylstannanes.[23]

$$\mathrm{Me_4Sn} + \mathrm{(CF_3)_4Sn} \xrightarrow[\text{30 min}]{\text{RT}} + \mathrm{(CF_3)_3SnMe} + \mathrm{CF_3SnMe_3} \tag{11-5}$$

Table 11-1 Organotin halides prepared by the Kocheshkov reaction.

Reactant	T/°C	Time/h	Product	Yield/%	Ref.
Et_4Sn	200	3	Et_3SnCl	86	13, 14
Et_4Sn	205	1.5	Et_2SnBr_2	76	10
Et_4Sn	210	1.5	Et_2SnCl_2	85	10
Et_4Sn	reflux	24	$EtSnCl_3$	15	10
Pr_4Sn	125	0.75	Pr_3SnCl	91	10
	200	2			
Bu_4Sn	220	1.5	Bu_3SnCl	96	10
Bu_4Sn	240	3	Bu_2SnCl_2	95	10
Vin_4Sn	30	1	Vin_3SnCl	96	15
Cp_4Sn	-60	45 s	Cp_2SnCl_2		14
	220	4.5	Cp_2SnCl_2	86	16
Ph_4Sn	220	2	Ph_3SnCl	70	17
	220	3	Ph_2SnCl_2	85	18
	220	3	$PhSnCl_3$	78	18
Bu_2SnCl_2 [a]	110	12	$BuSnCl_3$	80	11
$Cl_2Sn(CH_2CH_2CO_2Bu)_2$	100	3	$Cl_3Sn(CH_2CH_2CO_2Bu)$	90	19
Mes_2SnX_2	150	3	$MesSnX_3$	30	20
$Me_2(cycloC_6H_{11})_2Sn$			$Me(cycloC_6H_{11})_2SnCl$	97	14, 21
$CH_2(SnMe_2Cl)_2$	60	ca.15	$CH_2(SnMeCl_2)_2$	70	22

[a] In presence of $PtCl_2(PPh_3)_2$

11.1.3 Preparation from Organotin Oxides or Hydroxides

Triorganotin hydroxides R_3SnOH or oxides $(R_3Sn)_2O$, diorganotin oxides, R_2SnO, and stannonic acids, $RSnO_2H$ (and the corresponding alkoxides), react with halogen acids HX, to give the corresponding organotin halides, R_nSnX_{4-n}.[24] Some examples of these reactions are given in equations 11-6,[6] 11-7,[25] and 11-8.[26]

$$(Bu_3Sn)_2O + 2HCl \longrightarrow 2Bu_3SnCl + H_2O \tag{11-6}$$

$$Bu_2SnO + 2HI \xrightarrow[1.5\ h.\ 51\%]{H_2O/C_6H_6} Bu_2SnI_2 \tag{11-7}$$

$$Pr^iSnO_2H + 3HBr \longrightarrow Pr^iSnBr_3 \tag{11-8}$$

Alternative halogenating agents which have sometimes been used are PCl_3, PCl_5, $SnBr_4$, $SOCl_2$, and $COCl_2$ (equation 11-9)[27] and compounds containing the Sn-N or Sn-H bond can be used in place of Sn-O bonded compounds.

$$Bu_2SnO + 2COCl_2 \xrightarrow[warm]{PhMe} [Bu_2SnCl(OCOCl)] \xrightarrow{79\%} Bu_2SnCl_2 + CO_2 \tag{11-9}$$

A further convenient technique is to heat an organotin hydroxide, oxide, or alkoxide in toluene or methylcyclohexane with an ammonium halide or pseudohalide. Ammonia and water are evolved, and the halide or pseudohalide can be isolated in good yield.[28] A similar reaction of NH_4X (X = F, Cl, Br, or I) in refluxing aqueous dioxane may give either the dihalides R_2SnX_2 or the dihalogeno-distannoxanes $XR_2SnOSnR_2X$.[29] Isocyanates can also be prepared by heating together a trialkyl- or dialkyl-tin oxide and isocyanic acid, urea, or biuret.[30]

$$(\mathrm{Pr_3Sn})_2\mathrm{O} + 2\mathrm{NH_4Br} \xrightarrow[8\ \mathrm{h},\ 80\%]{\mathrm{C_6H_{11}Me}} 2\mathrm{Pr_3SnBr} + 2\mathrm{NH_3} + \mathrm{H_2O} \tag{11-10}$$

$$\mathrm{Bu_2SnO} + 2\mathrm{NH_4NCS} \xrightarrow[8\ \mathrm{h},\ 80\%]{\mathrm{C_6H_{11}Me}} \mathrm{Bu_2Sn(NCS)_2} + 2\mathrm{NH_3} + \mathrm{H_2O} \tag{11-11}$$

$$(\mathrm{Et_3Sn})_2\mathrm{O} + 2\mathrm{NH_2CONH_2} \xrightarrow[1.5\ \mathrm{h}.\ 92\%]{135\ ^{\circ}\mathrm{C}} 2\mathrm{Et_3SnNCO} + \mathrm{H_2O} + 2\mathrm{NH_3} \tag{11-12}$$

11.1.4 Exchange of Anionic Groups at Tin

Electronegative ligands X on tin frequently undergo ready exchange with electronegative ligands Y on other metals or on tin, providing a method of preparing other halides and pseudohalides from the chlorides which are more readily available.

$$\mathrm{R}_n\mathrm{SnX}_{4-n} + m\mathrm{MY} \rightleftharpoons \mathrm{R}_n\mathrm{SnX}_{4-m-n}\mathrm{Y}_m + m\mathrm{MX} \tag{11-13}$$

Thus the chlorides $\mathrm{R}_n\mathrm{SnCl}_{4-n}$ can be converted into the corresponding bromides or iodides by heating them with the appropriate sodium halide in acetone, after which the sodium chloride which is formed can be filtered off.

In organic syntheses using organotin reagents such as tributyltin hydride, the resulting tin compounds are often separated as the insoluble organotin fluorides. The trialkyltin chloride or bromide can then be recovered by heating the fluoride with sodium chloride or bromide under reflux in THF for 3–5 days.[31]

$$\mathrm{Bu_3SnF} + \mathrm{NaBr} \xrightarrow[5\ \mathrm{days},\ 86\%]{\mathrm{THF,\ reflux}} \mathrm{Bu_3SnBr} + \mathrm{NaF} \tag{11-14}$$

A general method for the interhalide conversions, including those from a heavier halide to a lighter halide, is to heat the tin halide in a saturated solution of the required ammonium halide in ether; conversions are essentially quantitative in 2 h. The reaction of tin fluorides requires a rather different technique: the fluoride, suspended in tetrahydrofuran, is mixed with an aqueous solution of the ammonium halide, and heated under reflux until the solution is clear.[32]

Halogen exchange can also be brought about between a tin halide and a halogenosilane, the heavier halogen preferring the heavier metal (equation 11-15). This provides an alternative method for recovering a tin chloride or bromide from a tin fluoride (equation 11-16).[33] t-Butyltin trichloride has been prepared from the reaction between t-butyltris(diethylamino)stannane and chlorotrimethylsilane, but it rapidly decomposes at room temperature into tin(II) chloride and t-butyl chloride (equation 11-17) (which is the reverse of the familiar "direct" synthesis of alkyltin trichlorides from $\mathrm{SnCl_2}$ and RCl).[34]

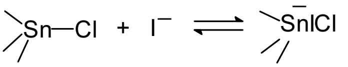
$$\mathrm{Me_2SnCl_2} + 2\mathrm{Me_3SiI} \xrightarrow[85\%]{\Delta,\ \mathrm{overnight}} \mathrm{Me_2SnI_2} + 2\mathrm{Me_3SiCl} \tag{11-15}$$

$$\mathrm{Bu_3SnF} + \mathrm{Et_3SiBr} \xrightarrow[88\%]{\Delta,\ 6\ \mathrm{h}} \mathrm{Bu_3SnBr} + \mathrm{Et_3SiF} \tag{11-16}$$

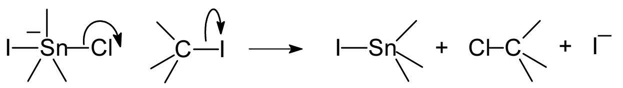
$$\mathrm{Bu^tSn(NEt_2)_3} + 3\mathrm{Me_3SiCl} \xrightarrow[43\%]{\mathrm{RT,\ 1\ h}} \mathrm{Bu^tSnCl_3} \xrightarrow[t_{1/2},\ 28\ \mathrm{h}]{\mathrm{C_6H_6},\ 20\ ^{\circ}\mathrm{C}} \mathrm{Bu^tCl} + \mathrm{SnCl_2} \tag{11-17}$$

Tributyltin bromide or iodide and dibutyltin dibromide or diiodide can be prepared from the corresponding chlorides by reaction with alkyl bromides or iodides in the presence of a tetrabutylammonium halide catalyst. It is suggested that the reaction involves the coordination of halide ion to the tin, then nucleophilic substitution by the chloride ligand at the carbon centre (equations 11-18, 11-19 and 11-20).[35]

$$Bu_2SnCl_2 + EtI \xrightarrow[150\ ^{o}C,\ 5\ h;\ 86\%]{6\ mol\%\ Bu_4N^+\ I^-} Bu_2SnI_2 + EtCl \qquad (11\text{-}18)$$



(11-19)



(11-20)

The exchange reaction between two diorganotin compounds R_2SnX_2 and R_2SnY_2 can lead to the formation of new organotin halides R_2SnXY when X and/or Y is halogen (equation 11-21).[36] The reactions usually occur merely on mixing the reagents at room temperature. A mixture of R_2SnX_2 and R'_2SnZ (Z = O, S, or NR″) gives the distannoxane, distannathiane, or distannazane, respectively, $XR_2SnZSnR'_2X$ (equation 11-22, $n = 2$); a lot of attention has been given to these halogenodistannoxanes (Z = O), and they are discussed in Section 14.2. Similarly $RSnX_3$ and R'_2SnZ give the compounds $X_2RSnZSnR_2X$, and R_3SnX and R'_2SnZ give the compounds $R_3SnZSnR'_2X$ (equation 11-22, $n = 1$ or 3, respectively).

$$R_2SnX_2 + R_2SnY_2 \longrightarrow 2R_2SnXY \qquad (11\text{-}21)$$

$$R_nSnX_{4\text{-}n} + R'_2SnZ \longrightarrow X_{3\text{-}n}R_nSnZSnR'_2X \qquad (11\text{-}22)$$

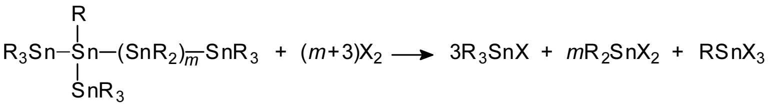
Examples of these reactions are given in Table 11-2.

Table 11-2 Diorganotin halides prepared by exchange reactions.

Reagents		Product	Ref.
Bu_2SnCl_2	Bu_2SnBr_2	$Bu_2SnClBr$	25
Bu_2SnBr_2	$Bu_2Sn(OAc)_2$	$Bu_2Sn(OAc)Br$	25
Me_2SnCl_2	Me_2SnH_2	Me_2SnHCl	37
Pr_2SnF_2	$Pr_2Sn(OMe)_2$	$Pr_2Sn(OMe)F$	36
Bu_2SnCl_2	$Bu_2Sn(SBu)_2$	$Bu_2Sn(SBu)Cl$	36
Bu_2SnCl_2	Bu_2SnO	$ClBu_2SnOSnBu_2Cl$	38
Me_2SnCl_2	$(Me_2SnNR)_3$	$ClMe_2SnN(R)SnMe_2Cl$	39
Me_2SnCl_2	Me_2SnS	$ClMe_2SnSSnMe_2Cl$	40
$MeSnCl_3$	Bu_2SnS	$Cl_2MeSnSSnBu_2Cl$	40
Bu_3SnCl	Oct_2SnO	$Bu_3SnOSnOct_2Cl$	41

11.1.5 The Reactions of Halogens with Sn-Sn Bonded Compounds

Halogens react rapidly and quantitatively with Sn-Sn bonded compounds, to give the two corresponding tin halides.[24] This has limited value as a preparative method because Sn-Sn bonded compounds are usually prepared, directly or indirectly, from tin halides, but it does provide a procedure for the identification and quantitative titration of Sn-Sn bonds. The nature of the products defines the nature of the bonding, as illustrated in equation 11-23.



$$\mathrm{R_3Sn{-}}\underset{\substack{|\\ \mathrm{SnR_3}}}{\overset{\substack{\mathrm{R}\\ |}}{\mathrm{Sn}}}\mathrm{{-}(SnR_2)}_{\overline{m}}\mathrm{SnR_3} + (m{+}3)\mathrm{X_2} \longrightarrow 3\mathrm{R_3SnX} + m\mathrm{R_2SnX_2} + \mathrm{RSnX_3} \qquad (11\text{-}23)$$

For example, the reaction of hexaethyldistannane with chlorine in CCl_4 at −70 °C gives triethyltin chloride, tetrabutyldiacetoxydistannane with bromine gives dibutylacetoxybromostannane,[42] and octa-t-butylcyclotetrastannane with one molar equivalent of iodine gives 1,4-diiodo-octa-t-butyltetrastannane.

$$\mathrm{Et_3SnSnEt_3} + \mathrm{Cl_2} \longrightarrow 2\mathrm{Et_3SnCl} \qquad (11\text{-}24)$$

$$\mathrm{AcOBu_2SnSnBu_2OAc} + \mathrm{Br_2} \xrightarrow{\mathrm{CCl_4}} 2\mathrm{Bu_2Sn(OAc)Br} \qquad (11\text{-}25)$$

$$(\mathrm{Bu^t{}_2Sn})_4 + \mathrm{I_2} \longrightarrow \mathrm{I(Bu^t{}_2Sn)_4I} \qquad (11\text{-}26)$$

11.2 Physical Properties and Structures

The organotin fluorides are usually insoluble in organic solvents and water, but the other halides are readily soluble in organic solvents. The fluorides are usually high-melting solids; within any series of alkyltin halides R_nSnX_{4-n}, when R is small the melting points normally decrease down the homologous series. The physical properties of some common examples are shown in Table 11-3.

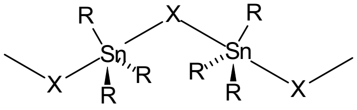
Table 11-3 Organotin halides R_nSnX_{4-n}; m.p. (°C) or b.p. (°C/mm Hg).

R_n	X = F	X = Cl	X = Br	X = I
R_3SnX				
Me_3	375dec	37–38	26–27	67–68/15
Et_3	302	210/760	224/760	234/760
Pr_3	275	98–100/4	133/13	147–148/20
Bu_3	248–252	152–156/14	120–122/2	108/0.07
Ph_3	357dec	105	124–125	122–124
Bz_3	242	142–144	125–128	102–103
R_2SnX_2				
Me_2	>300	107–108	75–77	43–44
Et_2	310–320	84	63	44
Pr_2	262–270	81	49	270–273/760
Bu_2	156–157	40–41	20(96/0.1)	145/6
Oct_2	125–127	47	–	225–230/1
Ph_2	>300	41–42	37	72–73
Bz_2	–	163	123–124	88
$RSnX_3$				
Me	321–327	45–46	55	85
Et	269–272	86/12	46/0.1	181–184.5/19
Pr	296–299	98–99/12	–	200/16dec
Bu	337–338	93/10	77–79/0.2(d)	154/5
Ph	ca. 220	128/15	182–183/29	31–32

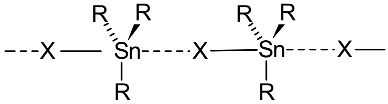
In the vapour phase, the alkyltin halides are simple near-tetrahedral monomers, e.g. Me_3SnBr, *r*SnBr, 247.9 pm, CSnBr 105.5 °;[43] Me_3SnI, *r*SnI, 269.5 pm, CSnI, 107.3 °.[44]

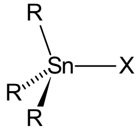
X-Ray crystallography shows that, in the solid state, many organotin halides R_nSnX_{4-n} are self-associated (and this has often required conclusions based on earlier Mössbauer spectra to be revised). The structure is determined by the value of *n* and the nature of the halogen (the tendency to associate decreasing in the sequence n = 2 > 1, and F > Cl > Br > I), and by the size of the organic group. Spectroscopic methods such as NMR and IR spectroscopy show that in solution these complexes tend to dissociate into small oligomers, dimers, or monomers.

In the triorganotin monohalides the structures vary from zig-zag polymers with trigonal bipyramidal geometry about the tin (**A**), through linear rod-like polymers or oligomers (**B**), to tetrahedral monomers (**C**).



A





Examples of X-ray structures for triorganotin halides are shown in Table 11-4.

Table 11-4 Crystal structures of triorganotin halides.

Compound	Structure	Ref.	Compound	Structure	Ref.
Me_3SnF	**A**	45	Me_3SnCl	**A**	46
Ph_3SnF	**B**	47	Cy_3SnCl	**C**	48
Me_2PhSnF	**B**	49	$(PhMe_2CCH_2)_3SnCl$	**C**	50
Cy_3SnF	**C**	51	$(PhMe_2SiCH_2)_3SnCl$	**C**	50
Mes_3SnF	**C**	52	Ph_3SnCl	**C**	53
$(Me_3SiCH_2)_3SnF$	**C**	49, 54	Cy_3SnBr	**C**	51
$(PhMe_2Si)_3CSnMe_2F$	**C**	55	$(PhMe_2CCH_2)_3Sn\,Br$	**C**	56
$(Me_3Si)_3CSnMe_2F$	**C**	55	Cy_3SnI	**C**	51

Trimethyltin fluoride exists in the crystal as a polymer with a structure close to **A**. The Me_3Sn units are planar, and the non-linear Sn-F-Sn bridges are somewhat asymmetric, with Sn-F distances ca. 210 and 220–260 pm, respectively.[57] This structure is not easily disrupted, and trimethyltin fluoride, like the the other lower trialkyltin fluorides, is insoluble in unreactive organic solvents. The solid state ^{119}Sn NMR spectrum shows effectively equal coupling to the two adjacent fluorine atoms with $^1J(SnF)$ 1300 Hz.[58]

Triphenyltin fluoride is a rod-shaped polymer (**B**), presumably as a result of minimising the repulsion of the larger phenyl groups. The two Sn-F distances are both 214.58(3) pm, and in the solid state ^{119}Sn NMR spectrum, the tin is equally coupled to two fluoride atoms with $^1J(SnF)$ 1500 Hz.[58]

The more severe steric hindrance in trimesityltin fluoride causes it to be a tetrahedral monomer (**C**), with Sn-F 195.7–196.5 pm.[52] There are two crystallographically distinct molecules in the unit cell, and the solid state ^{119}Sn NMR spectrum shows coupling to one ^{19}F of 2256 and 2300 Hz, respectively.[58] This, and the other bulky organotin fluorides shown in Table 11-4, which are similarly tetrahedrally four-coordinate, are more soluble in organic solvents.

This general insolubility of organotin fluorides is made use of in the removal of organotin residues from organic syntheses. The organotin compound is converted into the fluoride by anion exchange with, for example, KF, then the fluoride which separates is removed by filtration (see Section 22.3).[59, 60]

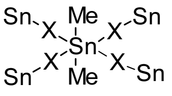
Trimethyltin chloride exists in the crystal as a zig-zag polymer; the geometry about the tin is closer to trigonal bipyramidal than to tetrahedral, with SnClSn 150.39°, CSnC 117(3)°, and *r*Sn–Cl 243.0(2) and 326.9 pm. Tricyclohexyltin fluoride, chloride, bromide and iodide all exist as tetrahedral monomers [*r*Sn–F 245(1), Sn–Cl 241(1), SnBr 252(1), Sn–I 254(1) pm]. Triphenyltin chloride at room temperature and 110 K exists as a slightly distorted tetrahedron [*r*Sn–Cl 235.38(14) pm], but in trineophyltin chloride, the very bulky ligands cause serious distortion [C–Sn-C 117.2°, *r*Sn–Cl 231.15(4) pm].

The pseudohalide $Me_3SnC{\equiv}N$ has a rod-like structure (**B**), bridged through C and N; the isothiocyanates $R_3SnN{=}C{=}S$ (R = Me or Ph) have a zig-zag structure (**A**), bridged through N and S,[3] but the azide Me_3SnN_3 has the structure (**A**) bridged through only the α-nitrogen atom.

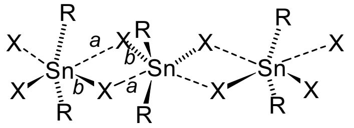
Crystallographic data for some diorganotin dihalides and pseudohalides are shown in Table 11-5.

Table 11-5 Structures of diorganotin dihalides and pseudohalides.

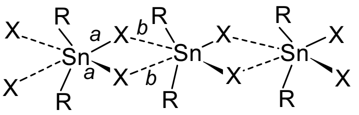
Compound	Structure	Ref.	Compound	Structure	Ref.
Me_2SnF_2	**D**	61	Cy_2SnBr_2	**E**	62
Me_2SnCl_2	**E**	63	$MePhSnCl_2$	**E**	64
Et_2SnCl_2	**E**	65	Et_2SnI_2	**F**	65
Et_2SnBr_2	**E**	65	$(ClCH_2)_2Sn(CN)_2$	**F**	66
Bu_2SnCl_2	**E**	67	$Me_2Sn(CN)_2$	**F**	68
Cy_2SnCl_2	**E**	62, 69	$Me_2Sn(NCS)_2$	**F**	70, 71



D



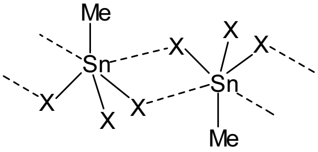
E



F

Dimethyltin difluoride consists of infinite 2-dimensional sheets of tin and fluorine atoms with octahedral geometry about the tin as shown in **D**; the Sn-F distances are all 212(1) pm; SnF_4 has the same structure, with fluorine atoms in place of the methyl groups. In dimethyltin dichloride, the interaction is weaker and the structure consists of a one-dimensional polymer (**E**) with Sn–Cl distances *a* 240 pm and *b* 354 pm, and Me-Sn-Me 123.5°. The structure about the tin can be considered to be distorted from tetrahedral towards octahedral by the interaction. The other dihalides Et_2SnCl_2, Et_2SnBr_2, Bu_2SnCl_2, Cy_2SnCl_2, Cy_2SnBr_2, and $MePhSnCl_2$ have a similar structure, but diethyltin diiodide, bis(chloromethyl)tin dichloride, dimethyltin dicyanide and dimethyltin diisothiocyanate have the alternative structure **F**, in which the two primary bonds in each bridge are formed by ligands on the *same* tin atom. In Et_2SnI_2, the Sn–I distances are *a* 217.8 and *b* 271.9 pm.

In the gas phase, $MeSnCl_3$ is tetrahedral,[72] and in the crystal, $MeSnCl_3$[73] and $MeSnBr_3$ [74] are essentially isostructural, with near-tetrahedral molecules very weakly bridged through two of the three halogen atoms, as shown in **11-1**, and the halogen NQR spectra show the presence of two types of halogen atom in the ratio of 1:2.[75] In $MeSnI_3$ the discrete tetrahedral molecules show no significant interaction.[76]



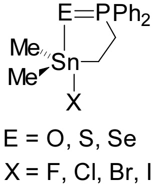
(11-1)

11.3 Coordination Complexes

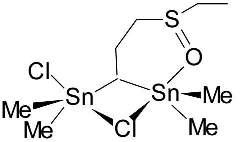
The Lewis acid strengths of the organotin halides R_nSnX_{4-n} decrease as n increases and when the halide is varied in the sequence Cl > Br > I.[77] When $n = 4$, intermolecular complexes ($R_4R'Sn^- M^+$) are usually formed only when M is an alkali metal, but functionally-substituted arylstannanes can become 5- or 6-coordinate by intramolecular coordination by heteroligands. When $n = 3$, five-coordinate complexes, R_3SnXL, are commonly formed, in which the three carbon-bonded ligands are normally equatorial in a trigonal bipyramid. When $n = 2$ or 1, five- or six-coordinate complexes, $R_nSnCl_{4-n}L$ and $R_nSnCl_{4-n}L_2$ are usually formed; in the complexes $R_2SnX_2L_2$, the two groups R are usually *trans*, but the ligands X_2 and L_2 can be *cis* or *trans*. Examples of 7-coordinate complexes are also known, usually where L is an intramolecular ligand. Evidence for this coordination comes from the upfield chemical shift in the ^{119}Sn NMR spectrum in the solid state, and of course from single crystal X-ray diffraction studies.[78]

α,ω-Bis(trichlorostannyl)alkanes, $X_3Sn(CH_2)_nSnX_3$ (X = Cl or Br; n = 1, 3, 4, or 8) form the 5-cordinate adducts $[X_4Sn(CH_2)_nSnX_4]^{2-}$ with Cl^- or Br^-, and the 5-coordinate adducts $[F_4Sn(CH_2)_nSnF_4]^{2-}$ with F^-, and there is no evidence for their behaviour as bidentate Lewis acids.[79] The *o*-phenylene halogenostannanes $o\text{-}C_6H_4(SnMe_2X)_2$ (X = Cl or F), on the other hand, do behave as bidentate Lewis acids, and give adducts such as $[o\text{-}C_6H_4(SnMe_2Cl)_2 \cdot Cl]^-$, $[o\text{-}C_6H_4(SnMe_2F)_2 \cdot F]^-$, and $o\text{-}C_6H_4(SnMe_2Cl)_2 \cdot (Me_2N)_3PO$.[80]

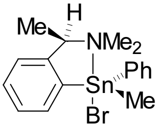
Some examples of intramolecularly coordinated organotin halides are shown in structures **11-2,**[81] **11-3**,[82] **11-4** and **11-5**.[83]



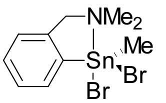
(11-2)



(11-3)



(11-4)



(11-5)

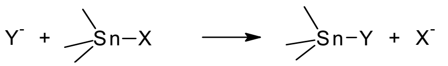
A solution of the *R*(C)*R*(Sn) diastereomer of **11-4** is optically stable at –30 °C, but begins to epimerise through inversion at tin at –13 °C to give a 40:60 mixture of the *R*(C)*R*(Sn) and *R*(C)*S*(Sn) isomers. The dibromide **11-5** shows only one resonance pattern from –80 to +100 °C and it is suggested that rapid epimerisation occurs through the intermediate dimer.[83]

The nature of the self-association depends on steric factors. In the ω-acetoxyalkyltin trichlorides, $Cl_3Sn(CH_2)_nOCOMe$, the alkoxyl group is intramolecularly bonded to the tin in a 5-membered ring when $n = 3$, but intermolecular bonding by the carbonyl groups occurs when n = 4 or 5, giving dimers with 16- or 18-membered rings, respectively.[84]

A number of complexes of the diorganotin dihalides such as $R_2SnCl_2 \cdot$ bipy and $R_2SnCl_2 \cdot$ phen, modelled on the cisplatin platinum drugs, have been tested in cancer therapy. They show reproducible activity against P388 lymphocytic leukaemia in mice, and though their activity is generally lower than that of cisplatin, their toxic side effects are usually less.[85, 86]

11.4 Reactions

The most characteristic property of the organotin halides is their ready nucleophilic substitution as shown in equation 11-27, where Y = HO^-, RO^-, R_nMO^-, R_2N^-, RCO_2^-, R^-, H^-, R_3Sn^-, etc... These reactions are covered in the sections dealing with the appropriate derivatives containing the SnY group.[77]



(11-27)

Hydrolysis of the monohalides gives the corresponding hydroxides, R_3SnOH which are usually unstable and form the oxides $(R_3Sn)_2O$. The dihalides give initially an important family of compounds, the tetraorganodihalogenodistannoxanes, $XR_2SnOSnR_2X$, then the halide-hydroxides $XR_2SnOSnR_2(OH)$, and ultimately the polymeric oxides, $(R_2SnO)_n$. Halides $M(OSnR_2Cl)_n$, where M is an organotin or organoheterometallic group, can also be prepared by telomerisation between the organometallic halide and R_2SnO. These compounds are dealt with in Chapter 12 on Sn-O bonded compounds.

Cleavage of an alkyl-tin bond by an S_H2 reaction (see Section 5.3.6) occurs more readily with the alkyltin halides (and carboxylates) than with the tetraalkylstannanes.[87, 88] These reactions were first identified by ESR spectroscopy in the photolysis of di-t-butyl peroxide in the presence of organotin halides, which provides a very convenient technique for ESR studies of alkyl radicals, for example equations 11-28 and 11-29.[89]

$$Bu^tOOBu^t \xrightarrow{h\nu} 2\ Bu^tO^\bullet \qquad (11\text{-}28)$$

$$Bu^tO^\bullet + Pr_3SnCl \longrightarrow Pr_2Sn(OBu^t)Cl + Pr^\bullet \qquad (11\text{-}29)$$

Photoexcited ketones react in the same way as alkoxyl radicals, and if, for example, a solution containing acetophenone and tripropyltin chloride is irradiated with UV light, the superimposed spectra of the propyl radical and the stannyloxyalkyl radical can be observed.[89]

$$PhMeCO^T + Pr_3SnCl \longrightarrow PhMe\dot{C}OSnPr_2Cl + Pr^\bullet \qquad (11\text{-}30)$$

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12 Organotin Hydroxides and Oxides[1]

Hydrolysis of organotin derivatives R_nSnX_{4-n}, where X = halide, OCOR′, OR′, NR'_2 *etc.*, gives a series of the corresponding hydroxides and oxides. The principal types of product which can be isolated are shown in equations 12-1 to 12-3,[1] though examples of oxides with more complicated compositions are also known, particularly when derived from the compounds R_2SnX_2 or $RSnX_3$. There is a recent thorough review by Chandrasekhar.[2]

$$R_3SnX \xrightarrow{H_2O} R_3SnOH \longrightarrow R_3SnOSnR_3 \qquad (12\text{-}1)$$

$$\begin{tikzcd} & R_2SnX_2 \arrow[r, "H_2O"] & R_2Sn(X)OH \arrow[r] & XR_2SnOSnR_2X \arrow[d] \\ (R_2SnO)_n & & HOR_2SnOSnR_2OH \arrow[ll] & HOR_2SnOSnR_2X \arrow[l] \end{tikzcd} \qquad (12\text{-}2)$$

$$RSnX_3 \xrightarrow{H_2O} RSn(OH)X_2 \longrightarrow RSn(OH)_2X \longrightarrow [RSn(OH)O]_n \qquad (12\text{-}3)$$

Aqua complexes of the ions R_3Sn^+ and R_2Sn^{2+} have been studied in aqueous solution,[3–5] and bipyramidal $Bu_3Sn(OH_2)_2^+$ (equation 9-48)[6] and octahedral $R_2Sn(OH_2)_4^{2+}$ (R = Me[7] or Bu[8]) have been identified crystallographically.

12.1 Triorganotin Hydroxides and Oxides

12.1.1 Preparation and Properties

Triorganotin hydroxides and oxides are usually prepared by the hydrolysis of the corresponding chlorides under alkaline conditions. A recent patent reports the formation of trialkyl-, dialkyl-, and monoalkyl-tin oxides by passing an alcohol in the gas phase over tin powder in the presence of a Lewis acid at 200–400 °C,[9] for example:

$$MeOH + Sn \xrightarrow[280\ ^{o}C]{SnCl_2} \underset{91\%}{Me_2SnO} \qquad (12\text{-}4)$$

The simple trialkyltin hydroxides can be obtained as soft, low-melting, waxy solids, when the oxides are stirred with water at 0–5 °C, but on warming they usually readily lose water to give the corresponding oxides.[10] The hydroxides and oxides differ little in their elemental analyses and, in solution, they may exist in equilibrium, and sometimes the two families of compounds have been confused; for example, trineophyltin oxide is readily hydrolysed to the hydroxide under humid conditions, but the compound that is always isolated from solutions is the oxide, and the compound which was initially identified as $(PhMe_2CCH_2)_3SnOH$, is in fact $[(PhMe_2CCH_2)_3Sn]_2O$.[11, 12] The hydroxides

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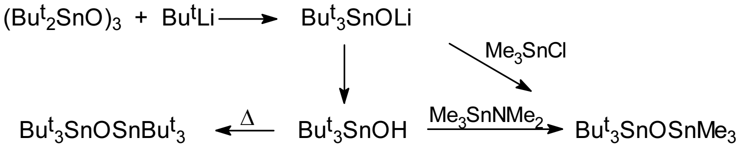
show OH stretching and bending frequencies at about 3620 and 900 cm^{-1}, respectively, though the assignment is complicated by the common presence of water of hydration; the distannoxanes are characterised by ν_{as}(SnOSn) 740–770 cm^{-1}.[10] The observation in the Sn NMR spectra of $^{2}J(^{119}Sn,^{117}Sn)$ coupling between the two tin atoms is a definitive criterion for the distannoxanes (see below).

The principal exception to this pattern of behaviour is trimethyltin hydroxide [ν(OH) 3620, δ(OH) 920 cm^{-1}] which sublimes unchanged above 80 °C; it can be dehydrated with sodium in benzene[13] or with calcium hydride[14] to give the oxide [ν_{as}(SnOSn) 740 cm^{-1}], but this fumes in air as it is hydrolysed back to the hydroxide.

Branching at the α-carbon atom appears to confer enough steric hindrance to inhibit dehydration of the hydroxide. Tricyclohexyltin hydroxide, which is used as an acaricide under the name of *Plictran*, is stable up to about 125 °C when it loses water to give the oxide.[3] Tri-t-butyltin hydroxide can be prepared from tris(di-t-butyltin oxide) as shown in Scheme 12-1, and loses water to give bis(tri-t-butyltin) oxide only when it is heated for several hours under vacuum at 200 °C. The properties of some triorganotin hydroxides and oxides are given in Table 12-1.[15]



Scheme 12-1 Tri-t-butyltin hydroxide and oxides.

Table 12-1 Properties of triorganotin hydroxides and oxides.

R	R_3SnOH M.p./°C	Ref.	$R_3SnOSnR_3$ M.p./°C or b.p./°C(mm Hg)	Ref.
Me	118	10	86(24)	10
Et	48–50	10	76–79(0.1)	10
Pr	30–32	10	104–106(0.1)	10
Bu	15–16	10	154–158(0.25)	10
Bu^t	34dec	15	$99(10^{-4})$	15
Cy	120dec	16	195–198	16
Bn	122–124	17	120	17
Ph	116–120dec	18	122–123	18
Mes	74dec	19		

Thermogravimetric analysis shows that triphenyltin hydroxide loses water at 80–100 °C to give the oxide,[18] but tri-*o*-tolyl- and tri-*o*-anisyl-tin hydroxides can be characterised only in solution, and revert to the oxides when they are isolated.[20]

The tin in distannoxanes is readily transferred between different oxygen atoms, and mixtures of the simple compounds $(R_3Sn)_2O$ and $(R'_3Sn)_2O$ on warming in solution come into equilibrium with the mixed distannoxanes $R_3SnOSnR'_3$ in the ratio 1 : 1 : 2, and these can be distinguished by their ^{119}Sn chemical shifts and $^{2}J(^{119}Sn,^{117}Sn)$ coupling constants. An example is shown in Scheme 12-2.[21] The only mixed bis(trialkytin) oxide which has been isolated appears to be $Bu^t_3SnOSnMe_3$ (m.p. 35 °C) (Scheme 12-1).[15]

	$(Bu_3Sn)_2O$	+ $(Cy_3Sn)_2O$	$\rightleftharpoons$	$2Bu_3SnOSnCy_3$
δSn	82.9	-7.6		79.9 -3.4
$^2J(^{119}Sn,^{117}Sn)$	458	618		540 ± 1

Scheme 12-2 NMR Spectra of simple and mixed distannoxanes.

It has been suggested that there is a correlation between the values of $^2J(^{119}Sn,^{117}Sn)$ and the SnOSn angle θ, reflecting the increasing *s*-character of the contribution of the oxygen to the OSn bond as the angle θ increases (Table 12-2),[22, 23] and the relationship shown in equation 12-5 has been proposed. Sometimes the value of ^2J falls when the distannoxane is dissolved [e.g. for (o-Anis)$_3$SnOSn(o-Anis)$_3$, from 650.6 to 471.2 Hz] implying that the SnOSn angle is smaller in solution than it is in the crystal.[20]

$$\text{Sn-O-Sn} = 0.086\ ^2J(^{119}\text{Sn},^{119}\text{Sn}) + 98.6, \quad r = 0.990\ (n = 8) \tag{12-5}$$

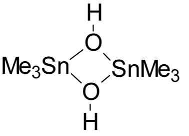
Table 12-2 Values of $^2J(^{119}Sn,^{117}Sn)^a$ in distannoxanes, $R_3SnOSnR_3$.

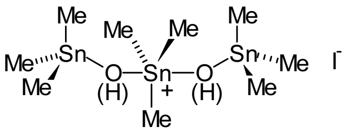
R	Ph	Pr	Bu	Neophyl	Pr^i	Bz	Bu^s	Bu^t
$^2J(^{119}Sn,^{117}Sn)$/Hz	420.6	446.8	451.7	532.1	615.4	617.9	650.7	916.0

^{a} $^2J(^{119}Sn,^{119}Sn) = 1.046\ ^2J(^{119}Sn,^{117}Sn)$

The polarity of the $Sn^{\delta+}–O^{\delta-}$ bond enhances the Lewis acidity of the tin, and the Lewis basicity of the oxygen towards protic and Lewis acids, and that Lewis acid may be the same or a different tin compound. This shows itself in the formation of more complex structures by association, and in promoting a variety of catalytic or stoichiometric reactions, the electrophilic tin and the nucleophilic oxygen sometimes apparently exerting their effects in concert.

Thus, in solution, trimethyltin hydroxide exists as a hydroxide-bridged dimer (**12-1**). A complete crystal structure has not been reported, but it is clear that it is a hydroxide-bridged polymer.[24, 25]


(12-1)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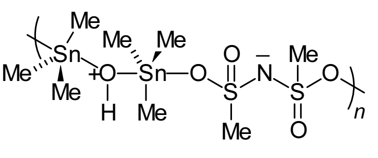
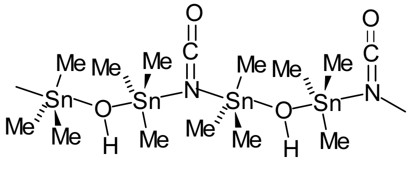
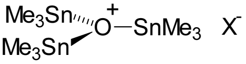
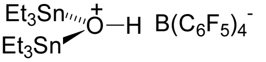

(12-3)


(12-4)

Trimethyltin hydroxide and trimethyltin iodide react to give the complex compound **12-2** (though the position of the hydrogen atoms was not determined and had to be inferred from spectroscopic methods).[26] Trimethyltin hydroxide and trimethyltin di(methylsulfonyl)amide, $Me_3SnN(SO_2Me)_2$, give **12-3**, which can be regarded as being comprised of alternating $[(Me_3Sn)_2OH]^+$ and $[(MeSO_2)_2N]^-$ ions.[27, 28] The compounds $Me_3SnOH.Me_3SnNCO$ and $Me_3SnOH.Me_3SnN_3$ are isomorphous, bridging through the α-nitrogen to form zig-zag chains (e.g. **12-4**).[29]

Bis(trimethyltin) oxide in the gas phase has *r*SnO 194 pm, SnOSn 140.8°. It reacts with trimethyltin chloride or bromide to give the compounds **12-5** with a trigonal planar cation.[30] In the crystal, the chloride ($X = Cl^-$) has *r*SnO 209.99(4) pm, and SnOSn 120.0(0)°, and the chloride ion intermolecularly bridges two tin atoms to give a graphite-like layer lattice.[30]


(**12-5**)


(**12-6**)

Triethyltin hydroxide in the crystal forms zig-zag Sn–O(H)–Sn–O(H) chains with *r*SnO 215.6 and 222.4 pm, and SnOSn 145.5°. Hydrolysis of $Et_3Sn^+ B(C_6F_5)_4^-$ gives the oxonium salt **12-6** in which the SnO bond is long (212 pm) and the tetrahedra about the tin are flattened, indicating a pronounced stannylium character (see Section 7.2).[31]

In the crystal, triphenyltin hydroxide forms a linear polymer with trigonal bipyramidal tin, and Sn–O distances 217.97(17) and 225.00(17) pm and SnOSn 137.66(10)°.[32, 33]

Trimesityltin hydroxide exists as a tetrahedral monomer[19, 34] with *r*SnO(av.) 196.1 pm, which has been proposed to represent the standard for the length of an SnO single bond.

12.1.2 Reactions

The compounds R_3SnOH and $R_3SnOSnR_3$ provide a source of mildly nucleophilic oxygen and electrophilic tin, and many of their reactions involve substitution or addition reactions with reagents N–E or N=E, where N is a nucleophile and E is an electrophile. The distannoxanes are less reactive in this sense than are the alkoxides R_3SnOR' (and those less so than the amino compounds $R_3SnNR'_2$), but equilibrium reactions can be driven to completion by removing water with a desiccant such as magnesium sulfate, or molecular sieves, or as an azeotrope with boiling benzene, toluene, or xylene. The nucleophilic power of the oxygen can also be enhanced by the addition of a good ligand (L) for tin, such as MeCN or DMF, or by halide ion, particularly F^-, when the reactant is $R_3Sn{-}OSnR_3L$, and can act as a transfer agent for O^{2-}.[35]

$$R_3Sn\text{-}OSnR_3 + N\text{-}E \longrightarrow R_3Sn\text{-}N + E\text{-}OSnR_3 \qquad (12\text{-}6)$$

$$R_3Sn\text{-}OSnR_3 + N{=}E \longrightarrow R_3SnN\text{-}EOSnR_3 \qquad (12\text{-}7)$$

Simple examples of the substitution reactions are shown in Table 12-3. Protic acids HX react to give water and the compounds R_3SnX, providing the most common route to derivatives such as the halides or carboxylates. The reactions can often be conveniently carried out by azeotropic dehydration in a Dean and Stark water separator. Hydrogen sulfide gives the corresponding sulfides $(R_3Sn)_2S$. Alcohols react to give the alkoxides,[36] and alkyl hydroperoxides to give the peroxides.[37] Carboxamides[38] and sulfonamides[39] can be *N*-stannylated under similar conditions.

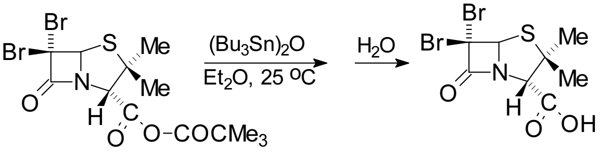
Metal hydrides such as lithium aluminium hydride provide nucleophilic hydrogen for reducing distannoxanes to tin hydrides; poly(methylsiloxane), which is a byproduct of the commercial production of dimethyldichlorosilane, provides a convenient and cheap alternative, as the tin hydride which is formed can be distilled off the involatile polymer.[40]

Alkyl iodides or benzyl bromides, RX, will react with tributyltin oxide in the presence of a source of fluoride ion to give the corresponding ether, R_2O, in excellent yield, the distannoxane acting as a transfer agent for O^{2-}; the reactivity increases in the sequence CsF < CsF.18-crown-6 < $Bu_4N^+ F^-$.[35]

Table 12-3 Substitution reactions of bis(triorgano)tin oxides.

Stannoxane	Reagent	Conditions	Product	Ref.
$(Bu_3Sn)_2O$	$MeCO_2H$	120–130 °C, 20 min	$Bu_3SnOCOMe$	16
$(Et_3Sn)_2O$	H_2S	EtOH; room temp.	$(Et_3Sn)_2S$	41
$(Bu_3Sn)_2O$	(–)-Menthol	PhH azeotrope	$Bu_3SnOMenthyl$	36
Ph_3SnOH	$PhCMe_2OOH$	PhH azeotrope	$Ph_3SnOOCMe_2Ph$	37
$(Et_3Sn)_2O$	PhC≡CH	PhH azeotrope	$Et_3SnC{\equiv}CPh$	42
Et_3SnOH	HCONHPh	Xylene azeotrope	$HCONPhSnEt_3$	35
$(Bu_3Sn)_2O$	$PhSO_2NHPr$	PhMe azeotrope	$PhSO_2NPrSnBu_3$	39
$(Pr_3Sn)_2O$	$[MeSi(H)O]_\infty$	Vacuum distillation	Pr_3SnH	40
$(Et_3Sn)_2O$	$(MeCO)_2CH_2$	PhH azeotrope	$MeCOCH{=}CMeOSnEt_3$	42
$(Bu_3Sn)_2O$	$PhCH_2Br$	MeCN, CsF, 18-c-6	$(PhCH_2)_2O$	35
$(Bu_3Sn)_2O$	$MeO_2C(CH_2)_2CO_2Bu^t$	PhMe, 80 °C	$HO_2C(CH_2)_2CO_2Bu^t$	43
$(Oct_3Sn)_2O$	$(MeO)_2CO$	130–135 °C	Oct_3SnOMe	36

Carboxylic esters react with bis(tributyltin) oxide under mild conditions to give the corresponding tin carboxylates and tin alkoxides, providing a method of deprotecting esters in aprotic solvents under neutral conditions, tolerant of other functional groups,[43–46] for example:



(12-8)

Carbonic esters react on heating to give the alkyl stannyl carbonates, which decarboxylate on heating, providing the best route to triorganotin methoxides and ethoxides.[36]

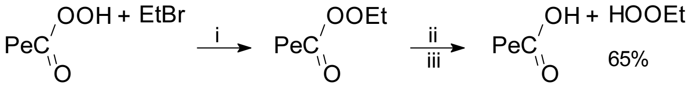
$$R_3SnOSnR_3 + (R'O)_2C{=}O \longrightarrow R_3SnOR' + R'OC(O)OSnR_3 \tag{12-9}$$

$$R'OC(O)OSnR_3 \longrightarrow R'OSnR_3 + CO_2 \tag{2-10}$$

$$R_3SnOSnR_3 + (R'O)_2C{=}O \longrightarrow 2R_3SnOR' + CO_2 \tag{12-11}$$

Diketene similarly reacts readily with tributyltin oxide in THF at room temperature[47] to give the stannyl 3-stannyloxybut-3-enoate which rearranges to the 2-enolate; this enolate will then give an ene reaction with an aldehyde,[48] or react with an alkyl halide,[49] followed by decarboxylation, providing a route to ketones, enones, and ketoaldehydes. Similar reactions with bromomethyl β- or γ-lactones result in the formation of β-hydroxy-γ-lactones or γ-hydroxy-δ-lactones.

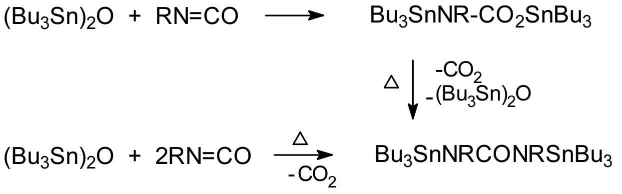
Peroxyesters derived from primary or secondary alkyl hydroperoxides undergo a carbonyl-forming elimination under basic conditions, but hydroysis can be achieved under mild neutral conditions with bis(tributyltin) oxide, providing a route to hydroperoxides which otherwise are difficult to prepare.[50]



(12-12)

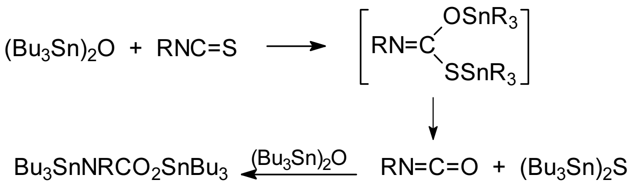
i. $Et_3O^+ BF_4^-$ ii. $(Bu_3Sn)_2O$, -10 °C, 12 h. iii. H_2O, CO_2

Bis(trialkyltin) oxides usually react rapidly, and often exothermically, with the acceptor molecules shown in Table 12-4.[51] Isocyanates exothermically give trialkyltin *N*-trialkylstannylcarbamates; these decompose on distillation to give the trialkylstannylureas, which can also be prepared by heating the tin oxide with the isocyanate in the ratio of 1 : 2.



(12-13)

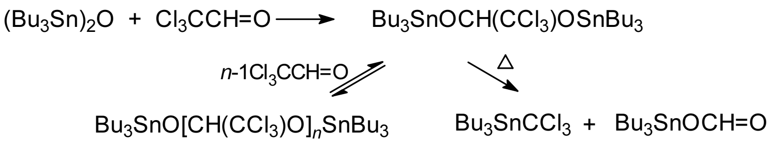
Isothiocyanates react rapidly, but bis(tributyl)tin sulfide is eliminated, and the same oxide-isocyanate adduct is formed, probably by the route shown in equation 12-14.



(12-14)

The triorganotin oxides and hydroxides absorb carbon dioxide from the air to give the carbonates, and react with carbon disulfide to give dithiocarbonates, and there are a number of erroneous IR and NMR data in the literature which arise because these reactions were ignored.

Aldehydes, and certain more reactive ketones, react to form distannyl acetals or ketals, and with an excess of chloral, repetition of this process leads to the formation of polychloral. If an attempt is made to distil the 1:1 adduct, elimination occurs to give the trialkyltrichloromethyltin and trialkyltin formate.



(12-15)

Similar addition reactions occur with the Sn-O bond of organotin alkoxides [e.g. $Bu_3SnOMe + PhN{=}CO \rightarrow Bu_3SnNPhC(O)OMe$], and, by recycling through the alkoxides, the bis(trialkyltin) oxides will catalyse the addition reactions of alcohols and similar compounds. These catalysed reactions are discussed in Section 14.1.2.

Table 12-4 Addition reactions of bis(tributyltin) oxide.

Co-reagent	Product	Ref.
$MeN{=}CO$	$Bu_3SnNMeCO_2SnBu_3$	52
$S{=}CNPh$	$Bu_3SnSC({=}NPh)OSnBu_3$	53
$O{=}CO$	$Bu_3SnOC(O)OSnBu_3$	53
$S{=}CS$	$Bu_3SnSC(S)OSnBu_3$	53
$O{=}CHCCl_3$	$Bu_3SnOCH(CCl_3)OSnBu_3$	54
$PhN{=}CNPh$	$Bu_3SnNPhC({=}NPh)OSnBu_3$	53
$O{=}SO$	$Bu_3SnOS(O)OSnBu_3$	53
$TolN{=}SNTol$	$Bu_3SnNTolS(O)NTolSnBu_3$	55
$TolSO_2N{=}SO$	$TolSO_2N(SnBu_3)SO_2SnBu_3$	56
$N{\equiv}CCCl_3$	$Bu_3SnN{=}C(CCl_3)OSnBu_3$	53
$CH_2{=}CO$	$Bu_3SnCH_2CO_2SnBu_3$	57

12.2 Diorganotin Hydroxides and Oxides

More details of the hydrolysis pathway of diorganotin dihalides are shown in equation 12-16. A lot of attention has been paid to the various intermediates **12-7**–**12-12** that are formed, in part because of their potential use as catalysts.

$$\begin{tikzcd}
R_2SnX_2 \arrow[r] & \begin{array}{c}R_2SnX_2.H_2O\\ \mathbf{(12\text{-}7)}\end{array} \arrow[r] & \begin{array}{c}[R_2SnX(OH)]_2\\ \mathbf{(12\text{-}8)}\end{array} \arrow[r] & \begin{array}{c}[XR_2SnOSnR_2X]_2\\ \mathbf{(12\text{-}9)}\end{array} \arrow[d] \\
\begin{array}{c}[R_2SnO]_n\\ \mathbf{(12\text{-}13)}\end{array} & \begin{array}{c}[R_2Sn(OH)_2]_2\\ \mathbf{(12\text{-}12)}\end{array} \arrow[l] & \begin{array}{c}[HOR_2SnOSnR_2OH]_2\\ \mathbf{(12\text{-}11)}\end{array} \arrow[l] & \begin{array}{c}[HOR_2SnOSnR_2X]_2\\ \mathbf{(12\text{-}10)}\end{array} \arrow[l]
\end{tikzcd} \tag{12-16}$$

A bulky organic group R stabilises the hydroxo compounds against dehydration, and limits the size (*n*) of the ultimate diorganotin oxide **12-13** which is obtained. This sequence of hydrolysis has been traced out for R_2SnCl_2 where $R = Me_3SiCH_2$, $X = Cl$,[58] and the compounds **12-7**, **12-9**, **12-11**, **12-12**,[59] and **12-13** ($n = 3$), were identified crystallographically. To avoid the complications that sometimes accompany hydrolysis under aqueous conditions, oxygen-transfer from di-t-butyltin oxide has often been used to give a cleaner reaction (equation 12-17).

$$2{\equiv}SnX + 1/3(Bu^t{}_2SnO)_3 \longrightarrow {\equiv}SnOSn{\equiv} + Bu^t{}_2SnX_2 \tag{12-17}$$

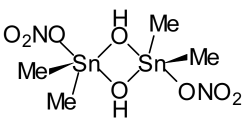
$R_2SnX_2 \cdot H_2O$

In the crystal, the hydrate **12-7** ($R = Me_3SiCH_2$, $X = Cl$) has $R_2SnCl_2(OH_2)$ units linked by Cl–Sn ... Cl bridges so that the tin is octahedrally 6-coordinate. It dissociates in an organic solvent into the parent dichloride and water, and the ^{119}Sn chemical shift changes from –53.9 in the solid to 146.6 in $CDCl_3$.[58]

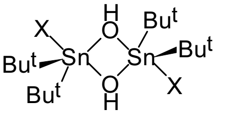
$[R_2Sn(X)OH]_2$

Like many triorganotin hydroxides, the diorganotin hydroxides $R_2Sn(OH)X$ (**12-8**) are readily dehydrated and are difficult to purify and characterise. For example, if dibutyltin dichloride in methanol is added to a large volume of water, a white solid is formed which is probably $Bu_2Sn(OH)Cl$, but it very readily dehydrates to $(ClBu_2Sn)_2O$.[60] The hydroxide nitrates, $R_2Sn(OH)NO_3$ (R = Me, Et, Pr, Bu), are more stable,[61, 62] and X-ray diffraction shows that the methyl compound has the dimeric structure **12-14**, with bridging hydroxyl groups.[63] Larger organic groups inhibit condensation, and the compounds $Bu^t_2Sn(OH)X$, X = F, Cl, Br, I,[64] OH[65] and OAc,[66] are relatively stable, and are again hydroxyl-bridged dimers (**12-15**). Dibutyltin hydroxide triflate forms a hydroxyl-bridged dimer in which the two tin atoms are rendered 6-coordinate by the addition of two water molecules, and di-t-butyltin hydroxide triflate similarly forms a hydrate, but with the 5-coordinate structure **12-16**.[67]

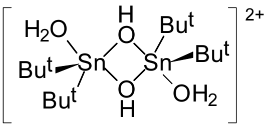
The hydroxide hydride $[(Me_3Si)_2CH]_2Sn(OH)H$, on the other hand, is hydrogen bonded by O–H … O bridges into a dimer, with *r*SnH 173(2) pm.[68]



(**12-14**)



(**12-15**)



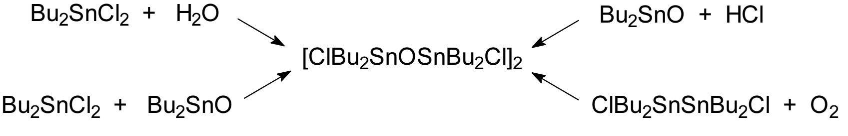
(**12-16**)

$[R_2Sn(OH)_2]_2$

The dihydroxo compound (**12-12**) is known as the complexes which it forms with distannaboratrioxanes and distannasilatrioxanes (see **12-50** and **12-55** below).

$[(XR_2Sn)_2O]_2$

With the above exceptions, the first products which are usually isolated from the hydrolysis of the compounds R_2SnX_2 are the tetraorganodistannoxanes, $XR_2SnOSnR_2X$, (**12-9**) and sometimes they are formed when the dihalides are simply exposed to air.[69] They can also be prepared by treating the polymeric diorganotin oxide R_2SnO with R_2SnX_2 or with HX, or by aerobic oxidation of the distannanes XR_2SnSnR_2X (Scheme 12-3) and, indeed, some compounds which were reported in the early literature to be distannanes are in fact distannoxanes.[60] They are often encountered adventitiously under a variety of conditions; for example, they often separate from samples of triorganotin halides which have been stored for long periods, and the compound $ClAr_2SnOSnAr_2Cl$ [Ar = 2,4,6-tris(trifluoromethyl)phenyl] was obtained from an attempt to recrystallise the stannylene Ar_2Sn: from hexane in the presence of Cl^-.[70]



Scheme 12-3 Routes to tetraorganodistannoxanes.

Examples of the distannoxanes $XR_2SnOSnR_2X$ are known where X = F, Cl, Br, I, RCO_2, ArO, RO, HO, Me_3SiO, NO_3, NCO, NCS, N_3, ROO, $OctOCOCH_2S$, $(RO)_2BO$, $(RO)_2PSO$, RSO_3, or CrO_4. The alkoxides, $(R'O)R_2SnOSnR_2(OR')$, are formed when the appropriate alcohol and the dialkyltin oxide are azeotropically dehydrated in benzene or toluene[36], and from them, further derivatives such as the dicarboxylates can be prepared.[71] When X = halide or carboxylate, the compounds $XR_2SnOSnR_2X$ can often be prepared by heating R_2SnO with NH_4X in aqueous dioxane, and this reaction probably provides the best route to the fluorides, X = F.[72]

Distannoxanes carrying one carboxylate and one alkoxide group can be obtained from the reaction between dialkyltin oxides and esters (equation 12-18).[73, 74] Under similar conditions, dibutyltin oxide reacts with diphenyl carbonate to give the di-phenoxide $(PhO)Bu_2SnOSnBu_2(OPh)$ presumably through decarboxylation of $(PhOCO)Bu_2SnOSnBu_2OPh$,[74] and a polymeric distannoxane carrying aryloxy and carboxylate groups is formed when vanillic acid (3-methoxy-4-hydroxybenzoic acid) is heated with trimethyltin chloride and water in a sealed tube at 130 °C.[75]

$$2R_2SnO + R'CO_2R'' \longrightarrow (R'CO_2)R_2SnOSnR_2(OR'') \tag{12-18}$$

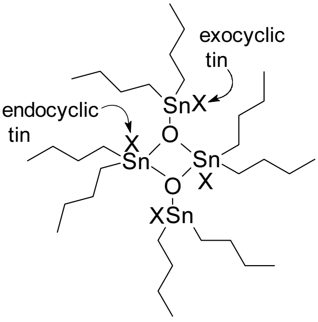
The compounds $XR_2SnOSnR_2X$ are solids, often highly crystalline, and very soluble in non-polar solvents; they show some interesting structural features and some useful properties as catalysts for organic reactions, and have attracted a lot of attention since they were first identified in 1961.[76]

The only examples that have been shown to be monomeric in the solid state appear to be $ClAr_2SnOSnAr_2Cl$ [Ar = 2,4,6-$(CF_3)_3C_6H_2$] (SnOSn 144.8°),[70] $HOR_2SnOSnR_2OH$ [R = $(Me_3Si)_2CH$],[77] and $NO_3MeRSnOSnMeRNO_3$ [R = $(Me_3Si)_3C$].[78] Otherwise these distannoxanes are dimeric in solution and the solid state (though there may be some monomer in equilibrium in solution), and in the ^{119}Sn NMR spectra they show the presence in solution of two non-equivalent types of tin atoms. Thus $[ClBu_2SnOSnBu_2Cl]_2$ shows $\delta(^{119}Sn)$ –139.8 and –92.0, $^2J(Sn\text{-}Sn)$ 73.2 Hz, and $[ClBu_2SnOSnBu_2OH]_2$ shows $\delta(^{119}Sn)$ –175.0 and –158.6, $^2J(Sn\text{-}Sn)$ 195.3 and 78.1 Hz.[79, 80]

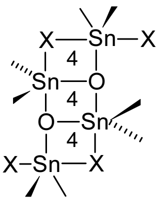
This dimeric structure (**12-17**) comprising a polar central core with peripheral alkyl groups (or more poetically, "highly polar stannoxane islands dispersed in a less polar ocean"),[81] has the properties of a reversed micelle, and it is this structure that confers the high solubility in non-polar solvents.

The X-ray crystal structures of many of these dimeric distannoxanes have now been determined; 28 examples are listed in the first edition of this book; many more have now been described, and details can be retrieved from the database on the CD ROM that accompanies this second edition.[82] All have the common feature of dimerisation to give a central SnOSnO ring as shown in **12-17**, but the detailed structures depend on the identity of the groups X.[83]

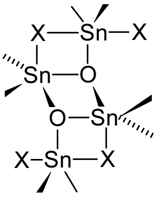
The ligands X on the central tin atoms usually bridge to the terminal tin atoms, rendering both types of tin 5-coordinate. When X is a monodentate ligand, this causes the central SnOSnO ring to be fused to two SnOSnX rings (referred to here as a 4-4-4 formation); the three 4-membered rings usually lie in one plane (**12-18**), but sometimes they may be stepped (**12-19**), and these are often described as ladder or staircase arrangements, respectively. When X = carboxylate, the OC=O group may act as a bidentate ligand and bridging often occurs through the carbonyl oxygen atom, giving a 6-4-6 formation (**12-20**);[72, 84, 85] the tetramethyldistannoxanes derived from the dibasic acids nitroterephthalic acid or diphenic acid give linear or sheet polymers, respectively.[86] When X = ON=CMe(2-pyridyl), the bridging involves the O and N of the oxime to give a 5-4-5 structure.[87] Some examples are illustrated in structures **12-21**,[88] **12-22**,[89] and **12-23**.



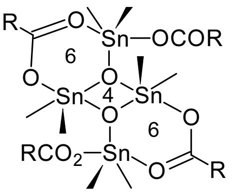
(**12-17**)



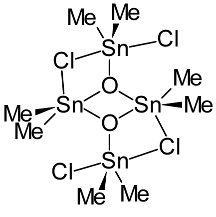
(**12-18**)



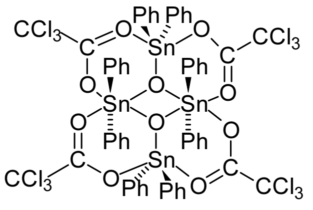
(**12-19**)



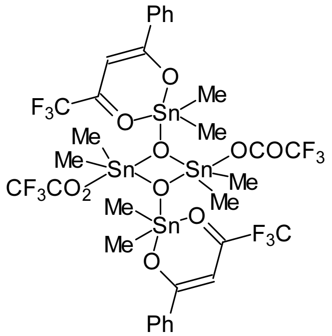
(**12-20**)



(**12-21**)

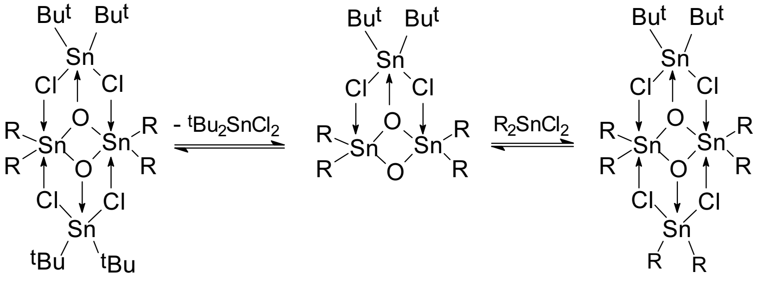


(**12-22**)



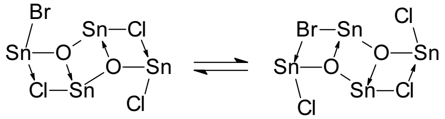
(**12-23**)

Distannoxanes with mixed alkyl groups, $[XR_2SnOSnR'_2X]_2$, can be prepared from the reaction of R_2SnX_2 with R'_2SnO (R = Me, Et, Pr^i, Bu, R′ = Bu^t;[90] R = Me_3SiCH_2, R′ = Bu^t;[91] R = Pr^i, R′ = Me[92]). In $[ClBu^t_2SnOSnR_2Cl]_2$, R = Me or Pr^i, the large t-butyl groups are bonded in the crystal to the two exocyclic tin atoms and the chlorine atoms are only weakly bonded to the endocyclic tin, so that the compounds may be regarded as $(R_2SnO)_2$ rings stabilised by two $Bu^t_2SnCl_2$ units (equation 12-19). These compounds are stable in the solid state, but in solution they rearrange to give a number of distannoxanes, and the exchange is thought to proceed through a dissociative mechanism (equation 12-19).[90] In $[FBu_2SnOSnBu^t_2F]_2$[93] and in $[X(Me_3Si)_2SnOSnBu^t_2Y]_2$ (X = Y = OH; X = Cl, Y = OH; or X = Y = Cl)[91] the t-butyl groups are again at the exocyclic position, but it is surprising that in the dimer of $ClMe_2SnOSnPr^i_2Cl$, the bulky isopropyl groups are bonded to the endocyclic tin.[92]

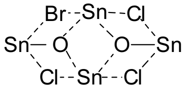


(12-19)

When two different functional groups are present in the compounds $[R_4Sn_2XYO]_2$,[94] the one that can act as the stronger donor ligand is bonded to the endocyclic tin,[95] for example EtO in $[EtOMe_2SnOSnMe_2I]_2$[96] or OH in $[HOBu^t{}_2SnOSn(CH_2SiMe_3)_2Cl]_2$[91] or in $[HOCy_2SnMe_2OSnBu^t{}_2Cl]_2$.[97] When X and Y have similar donor strengths, for example Cl and Br, their position become randomised and a mixture of $[Bu_4Sn_2Cl_2O]_2$ and $[Bu_4Sn_2Br_2O]_2$ in solution shows ^{119}Sn signals for the two parents and five further isomers $Bu_8Sn_4Cl_mBr_nO_2$, ($m + n = 4$); the number of observable possible isomers is reduced by a rapid equilibration in solution between structures such as **12-24** and **12-25**, which renders them equivalent (**12-26**) on the NMR time scale.[95]



(**12-24**) (**12-25**)



(**12-26**)

The reaction of R_2SnO with R_2SnX_2 to give $XR_2SnOSnR_2X$ (Scheme 12-3) can be regarded as the insertion of an R_2SnO unit into an SnX bond, and the oxygen-transfer that is shown by di-t-butyltin oxide (equation 12-17) is obviously closely related. Similar insertion reactions take place with the reagents R_3SnX and $RSnX_3$, for example dibutyltin oxide dissolves when it is warmed in a solution of trimethyltin chloride in benzene to give the pentaalkylchlorodistannoxane which is monomeric in benzene (equation 12-20). Similarly dibutyltin oxide reacts exothermically with ethyltin trichloride in benzene to give the trialkyltrichlorodistannoxane (equation 12-21), which again is monomeric in benzene. If a good ligand for tin is added to the trifunctional trialkyldistannoxanes $X_2RSnOSnR'_2X$, the adduct reacts to give the complex $R'_2SnX_2.L_2$ derived from the initial R'_2SnX_2, but the other product, which might be expected to have the composition $(XRSnO)_n$, has not been identified.[98]

$$Me_3SnCl + Bu_2SnO \xrightarrow[10\ min]{C_6H_6,\ 80\ ^oC} Me_3SnOSnBu_2Cl \qquad (12\text{-}20)$$

$$EtSnCl_3 + Bu_2SnO \xrightarrow[1\ min]{C_6H_6,\ 80\ ^oC} Cl_2EtSnOSnBu_2Cl \qquad (12\text{-}21)$$

$XR_2Sn(OSnR_2)_nX$

Similar reactions might be expected for the products of these insertion reactions which should lead to the formation of oligodistannoxanes, and indeed dibutyltin oxide will react progressively with dibutyltin dichloride and butyltin trichloride (but not tributyltin chloride) to give oligomers which are the equivalent of a soluble form of dibutyltin oxide (e.g. equations 12-22 and 12-23). They react with 2,2′-bipyridyl or 9,10-phenanthroline to give the derivatives of dibutyltin dichloride, and they are monomeric in benzene; if coordination does occur from oxygen to tin, it can apparently be accomplished intramolecularly.[98]

$$BuSnCl_3 + 12Bu_2SnO \xrightarrow[80\ ^oC]{C_6H_6} BuSn[(OSnBu_2)_4Cl]_3 \qquad (12\text{-}22)$$

$$Bu_2SnCl_2 + 12Bu_2SnO \xrightarrow[80\ ^oC]{C_6H_6} ClBu_2Sn(OSnBu_2)_{12}Cl \qquad (12\text{-}23)$$

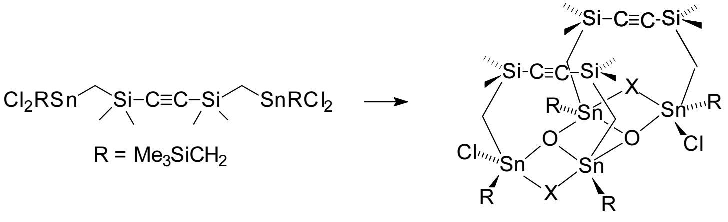
The reaction of the dichloride R_2SnCl_2 or of the corresponding dichlorodistannoxanes with sodium azide in water gives the tristannoxanes $[N_3R_2SnOSnR_2OSnR_2N_3]_2$ (R = Me, Et, Pr, or Bu), which, when R = methyl, reacts in boiling methanol to give the distannoxane $[N_3Me_2SnOSnMe_2OMe]_2$.[99] The tristannoxane $[N_3Bu_2SnOSnBu_2OSnBu_2N_3]_2$ has the structure of a near-planar 6-rung ladder, with three central SnOSnO rings and two outer SnOSnN rings.[100] Dioctyltin dichloride, on the other hand, reacts with aqueous sodium azide to give the diazidotetrastannoxane $[N_3R_2SnOSnR_2OSnR_2OSnR_2N_3]_2$,[99] and partial hydrolysis of Me_2SnCl_2 has given the ionic complex $[NHEt_3]^+[(SnMe_2Cl)_5O_3]^-$.[101]

$XR_2SnOSnR_2OH$

On further hydrolysis of the distannoxanes $XR_2SnOSnR_2X$, the compounds $XR_2SnOSnR_2OH$ (**12-10**) can often be isolated. They are unusual in providing a family of stable tin hydroxides, and they react with alcohols to give the corresponding alkoxides. The compound $ClPh_2SnOSnPh_2OH$ has been shown to have a dimeric 4-4-4 ladder structure, with bridging OH groups, and chlorine bonded to the central ring,[102] and $Cl(Me_3SiCH_2)(Bu^t)SnOSn(Bu^t)(CH_2SiMe_3)OH$ also has the structure of a 4-4-4 dimer. The 1,3-dihydroxydistannoxanes $(HO)R_2SnOSnR_2(OH)$ are stable only when bulky groups R inhibit dehydration; the compound $HO[(Me_3Si)_2CH]_2SnOSn[CH(SiMe_3)]_2OH$ is a monomer,[77] but $HO[(Me_3Si)_2CH]_2SnOSnBu^t_2OH$ is a dimer.[91]

Bridged bis(distannoxanes)

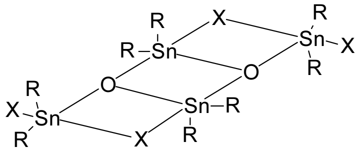
More complex structures can be obtained from compounds $X_2RSn \sim\sim SnRX_2$ in which two $RSnX_2$ units are linked by a bridge, which leads to the formation of bridged distannoxanes. The acetylene-bridged precursor **12-27** reacts with $(Bu^t_2SnO)_3$ to give the *cis*-bridged dimeric distannoxane **12-28** (X = Cl), which can then be hydrolysed to **12-28** (X = OH).[103]



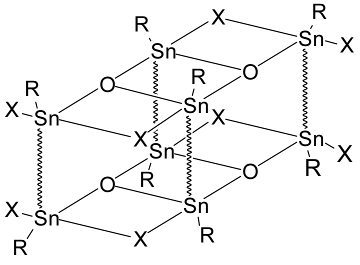
(**12-27**) (**12-28**)

(12-24)

If the precursor $X_2RSn \sim SnRX_2$ carries a polymethylene bridge, hydrolysis or oxygen transfer from $(Bu^t_2SnO)_3$ gives two parallel units of the familiar 4-4-4 motif (**12-29**), now joined by four bridges (**12-30**). Examples are given in Table 12-5.



(**12-29**)



(**12-30**)

Table 12-5 Bridged dimeric tetraorganodistannoxanes (**12-30**).

Entry	R	X	Bridge	Ref.
1	Me_3SiCH_2	Cl	$CH_2CH_2CH_2$	104, 105
2	Me_3SiCH_2	Cl, OH	$CH_2CH_2CH_2$	105
3	Me_3CCH_2	Cl	$CH_2CH_2CH_2$	104
4	Me_3SiCH_2	Cl	$CH_2CH_2CH_2CH_2$	104
5	Me_3CCH_2	Cl	$CH_2CH_2CH_2CH_2$	104
6	Me_2CHCH_2	Cl	$CH_2CH_2CH_2CH_2$	104
7	Me_3SiCH_2	Cl	$CH_2SiMe_2CH_2$	104
8	Me_3SiCH_2	OAc	$CH_2CH_2CH_2$	104
9	Me_3SiCH_2, Ph	Cl	$CH_2CH_2CH_2$	106
10	Me_3CCH_2, Me_2CHCH_2	Cl	$CH_2CH_2CH_2CH_2$	106
11	Me_3CCH_2, Me_3SiCH_2	Cl	$CH_2CH_2CH_2CH_2$	106
12	Me_3SiCH_2	Cl	p-$(CH_2SiMe_2)_2C_6H_4$	107
13	Me_3SiCH_2	Cl	m-$(CH_2CH_2)_2C_6H_4$	107
14	Ph	I, OH	CH_2	108

Entry 2 was obtained by treating entry 1 with aqueous ethanolic KOH.[105]

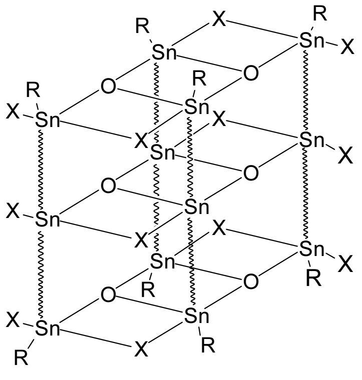
The acetate (entry 8) was obtained by treating the chloride (entry 1) with silver acetate.

Entry 9 represents a mixture of the five possible isomers which are formed when the mixed bridged tetrachloride $Cl_2PhSn(CH_2)_3Sn(CH_2SiMe_3)Cl_2$ is treated with $(Bu^t{}_2SnO)_3$.

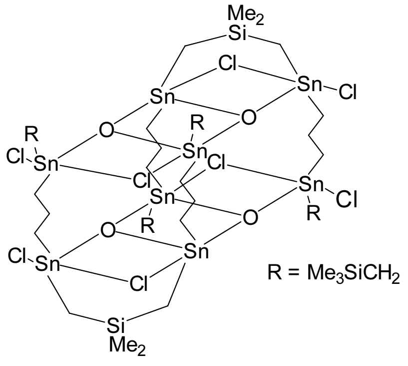
Entries 10 and 11 were obtained by the reaction of the bridged tetrachlorides $Cl_2RSn(CH_2)_4SnRCl_2$ with the polymeric bridged oxides $[R'(O)Sn(CH_2)_4Sn(O)R']_n$. In the crystal, the neopentyl groups occupy the outer four corners of the tetrameric block; in solution, the tetramers are in equilibrium with their corresponding mixed dimers.

In entry 12, which includes a p-phenylene unit in the bridge, the top ladder layer is twisted with respect to the bottom layer, resulting in a helical structure with no centre of symmetry, and in which all eight tin atoms are chiral. In the m-phenylene equivalent (entry 13), on the other hand, the top and bottom layers are parallel. Entry 14 can be obtained solvent free, but also forms a 4 THF and a 3 CH_2Cl_2 complex, and all three forms have a twist angle of 28–29°.

The doubly-bridged tristannane $Cl_2RSn(CH_2)_3SnCl_2(CH_2)_3SnRCl_2$ ($R = Me_3SnCH_2$) reacts with $(Bu^t{}_2SnO)_3$ to give the three-layered chlorostannoxane (**12-31**)[109], and $Cl_2RSn(CH_2)_3SnCl_2CH_2SiMe_2CH_2SnCl_2(CH_2)_3SnRCl_2$ gives the double-layered compound (**12-32**).[109]



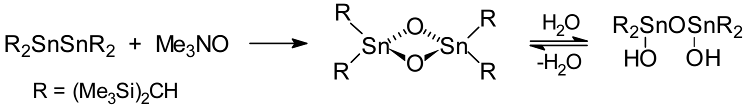
(12-31)



(12-32)

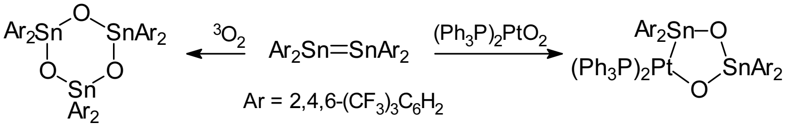
$(R_2SnO)_n$

No dihydroxides, $R_2Sn(OH)_2$, or monomeric stannanones, $R_2Sn{=}O$, which might be expected to result from complete hydrolysis, appear to have yet been characterised, but bulky groups R can stabilise low oligomers of $R_2Sn{=}O$. Tetrakis[bis(trimethylsilyl)-methyl)]-distannene reacts with trimethylamine oxide to give the dimeric stannoxane, which can be hydrolysed to the dihydroxydistannoxane, and this can be converted back into the cyclic dimer by azeotropic dehydration in toluene.[77]



(12-25)

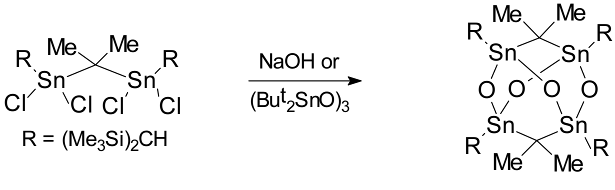
When R = t-butyl or t-pentyl, the smallest oligomers $(R_2SnO)_n$ that can be isolated are the planar cyclic trimers,[110] but $[(Me_3Si)(Me)SnO]_3$ has the structure of a severely flattened boat.[77] Hexakis[di(2,6-diethylphenyl)]tristannoxane[111] and hexakis[di(2,4,6-triisopropylphenyl)]tristannoxane[112] have almost planar rings. Tetrakis[2,4,6-tris(trifluoromethyl)phenyl]distannene in the solid state or in toluene solution reacts with dioxygen to give the cyclotristannoxane which has a non-planar ring, and reaction with $(Ph_3P)_2PtO_2$ gives the interesting stable compound **12-33** with a Pt−Sn bond and again a non-planar ring.[113]



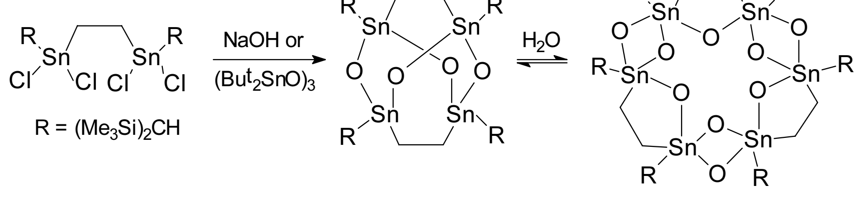
(12-26)

(12-33)

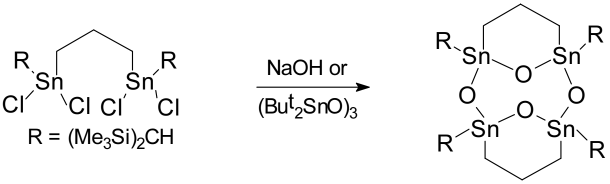
If two dichlorostannane units which carry a bulky group R are linked by a bridge as in $Cl_2RSn{-}Z{-}SnRCl_2$, the oxide $(R_2SnO)_n$ which is obtained on hydrolysis or non-aqueous transfer of oxygen from $(t\text{-}Bu_2SnO)_3$ may have a more complex structure in the products (equations 12-24[103] and 12-27–12-29[114]).



(12-27)

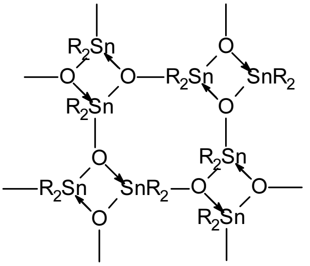


(12-28)



(12-29)

With smaller organic groups and no bridge, loss of water from the 1,3-dihydroxydistannoxanes gives the polymeric stannoxanes, $(R_2SnO)_n$, as high-melting, insoluble, amorphous polymers. Their exact structures are not known but the Mössbauer quadrupole coupling (Me_2SnO, QC 2.06 mm s^{-1}, Bu_2SnO, QC 2.09 mm s^{-1}), and the high resolution solid state ^{119}Sn NMR spectra[115] [Me_2SnO, δ −152, Bu_2SnO, δ −177, cf. $(Bu^t_2SnO)_3$ δ −84.3)] support the assumption that these compounds are crosslinked polymers, probably containing 5-coordinate tin. A possible structure is shown in **12-34**.



(**12-34**)

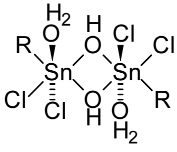
The exchange reaction between the Sn−O bond in dialkyltin oxides, R_2SnO, and the SnCl bond in organotin halides is discussed in Section 12.4.

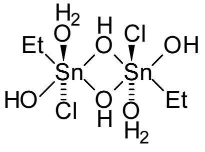
12.3 Monoorganotin Hydroxides and Oxides

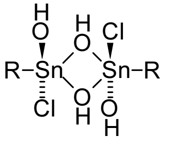
Hydrolysis of monoorganotin compounds can give rise to a wider variety of hydroxides and oxides through a combination of hydrolysis, dehydration, and aggregation reactions,[116] but less work has been done in this field. In moist air, ethyl-, butyl- and octyl-tin trichloride are hydrolysed as far as the hydrated hydroxide dichlorides, $RSnCl_2(OH) \cdot H_2O$ (R = Et, m.p. 94−96 °C; Bu, m.p. 80−87 °C, Oct, m.p. 45−56 °C),[117] which, in the crystal, exist as hydroxyl-bridged dimers (**12-35**) with octahedral coordination about the tin atoms.[118–120] The trichlorides dissolve in water where they are hydrolysed to give acid solutions, (and the reaction can be followed by ^{1}H and ^{119}Sn NMR spectroscopy),[121] but if the water is distilled off, the trichloride is recovered.

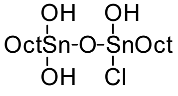
In the presence of one molar equivalent of alkali, hydrolysis proceeds to the stage of the chloride dihydroxides, (e.g. $EtSn(OH)_2Cl \cdot H_2O$, m.p. > 225 °C, $BuSn(OH)_2Cl$, m.p. 107−112 °C, $OctSn(OH)_2Cl$ m.p. 122−127 °C).[117] The structures of these compounds have not yet been determined crystallographically, but they are probably again hydroxyl-bridged dimers as shown in **12-36** and **12-37**. The compounds $(H_2O)Cl_3Sn(CH_2)_3SnCl_3(H_2O)$ and $(H_2O)_2Cl_3Sn(CH_2)_3SnCl_3(H_2O)_2$ are non-associated in the crystal, but the further hydrolysis product $[H_2O(OH)Cl_2Sn(CH_2)_3SnCl_2(OH)H_2O \cdot 2\,H_2O]_n$ is HO-bridged in the sense shown in **12-36**.[122]

When the compounds **12-36** and **12-37** are heated they lose water to give glasses with the composition $[RSn(O)Cl]_n$, for example $[BuSn(O)Cl]_n$, $n = 6$.[123] With three molar equivalents of alkali, complete hydrolysis of the trichlorides takes place to give the stannonic acids. From $EtSnCl_3$, $HO[EtSn(OH)O]_nH$, $n = 3$, has been isolated as an infusible solid, but after several weeks, n had increased to 13.8, when the formula approximated to $RSn(O)OH$.[117] From the hydrolysis of octyltin trichloride at room temperature, the distannoxane **12-38** has been isolated, but if the solution is heated under reflux for several hours, the stannonic acid, $OctSn(O)OH$, is formed.[117]


(**12-35**)


(**12-36**)


(**12-37**)



$$\mathrm{Oct}\overset{\mathrm{OH}}{\underset{\mathrm{OH}}{\mathrm{Sn}}}\text{-O-}\overset{\mathrm{OH}}{\underset{\mathrm{Cl}}{\mathrm{Sn}}}\mathrm{Oct}$$

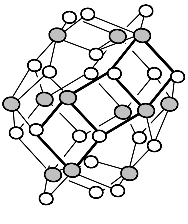
(**12-38**)

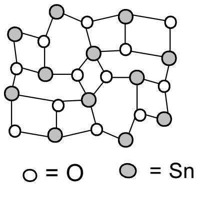
If $Pr^iSn(OH)_2Cl.3/4H_2O$, from the alkaline hydrolysis of Pr^iSnCl_3, is dissolved in DMSO and exposed to air for some weeks, crystals with the composition $(Pr^iSn)_9O_8(OH)_6Cl_5 \cdot 6\,DMSO$ separate. This compound has a pyramidal cage structure built up of tin atoms with trigonal bipyramidal or octahedral coordination geometry, bridged by η^3-oxygen atoms or η^2-hydroxyl groups.[124]

Treatment of $Pr^iSn(OH)_2Cl\,.\,3/4\,H_2O$ in DMF under the same conditions gives the compounds $[(Pr^iSn)_{12}O_{14}(OH)_6]^{2+}\,Cl^-{}_2.\,3\,H_2O$ and $[(Pr^iSn)_{12}O_{14}(OH)_6]^{2+}\,Cl^-{}_2\,.\,2\,DMF$, in which the structure of the cation (**12-39**) can be viewed as a sphere with an equatorial ring of six square-pyramidal $RSnO_4$ units, with polar caps each of three $RSnO_5$ units; the presence of the familiar 4-4-4 motif is indicated.[118, 124]

Similarly, by the slow base hydrolysis of $BuSnCl_3$, the compound $[(BuSn)_{12}O_{14}(OH)_6]^{2+}Cl^-{}_2\,.\,2\,H_2O$ is obtained. It has the structure **12-39** both in the solid state and in solution, with δ ^{119}Sn -283.1 and -468.1 for the 5- and 6-coordinate tin centres, respectively, and electrospray mass spectrometry showing the molecular ion m/z 1218 for $[(BuSn)_{12}O_{14}(OH)_6]^{2+}$; in methanol, exchange of OH and MeO groups occurs to give the molecular ion $[(BuSn)_{12}O_{14}(OMe)(OH)_5]^{2+}$ at m/z 1232.[123]

Again, the hydrolysis of the alkyltin trialkoxides $BuSn(OR')_3$[125] or the trialkynylstannanes $RSn(C{\equiv}CR')_3$ [R = Bu, $4\text{-}(CH_2{=}CH)C_6H_4(CH_2)_4$, $AcO(CH_2)_5$, or $MeCH{=}CHCO_2(CH_2)_5$] [126] gives the closo clusters $[(RSn)_{12}O_{14}(OH)_6](OH)_2\,.\,2\,H_2O$. These compounds have attracted interest as possible catalysts,[127] and a simple route to $[(BuSn)_{12}O_{14}(OH)_6](Tos)_2\,.\,2Diox$ has been developed by the azeotropic dehydration of butylstannonic acid and toluene *p*-sulfonic acid.[128] Hydrolysis of $X_3Sn(CH_2)_3SnX_3$ ($X = ClCH_2CO_2$), gives $[Sn(CH_2)_3Sn]_6X_{14}(OH)_2O_{10}$ (**12-40**) with a flat Sn_{12} core.[129]

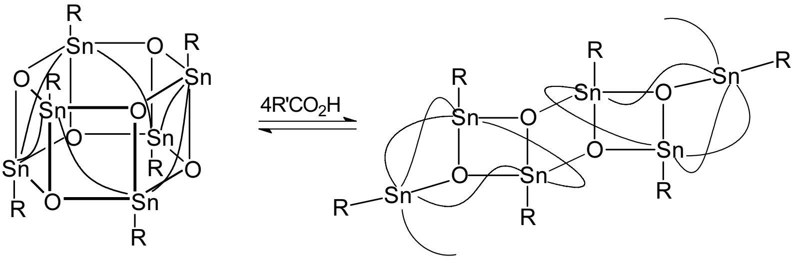

(**12-39**)



(**12-40**)

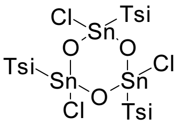
Metal ions (e.g. Na^+) can be enclosed within the cage **12-39**,[130] and the equatorial RSn groups (the filled circles) can be replaced by one, two, three or six VO groups.[131]

By the hydrolysis of organotin tricarboxylates or the reaction of stannonic acids with carboxylic acids, a family of hexameric organotin carboxylates can be obtained with the composition $[RSn(O)O_2CR']_6$, where R = Ph, R′ = Cy;[132] R = Bu, R′ = Bu, Cy, or Ph;[133] R = Me, R′ = Me;[134] R = $MeO_2CCH_2CH_2$, R′ = Me;[135] or R = Pr^i, R′ = Me.[136] Their structures are based on a drum, with the sides consisting of Sn_2O_2 rings, and the ends of Sn_3O_3 rings, the carboxylate groups bridging between the tin atoms on each face as shown in **12-41**.[83, 120, 136] In solution they are in equilibrium with the open-chain ladder structure **12-42**.[89, 133] When the carboxylate bridging groups are $C_5H_5FeC_5H_4CO_2$ or 2,4,6-$Me_3C_6H_2CO_2$, C−H ··· O hydrogen bonding between the carboxylate oxygen and the ferrocenyl C−H or 6-Me C−H groups, respectively, binds the molecules into a 2-dimensional grid-like structure.[137]

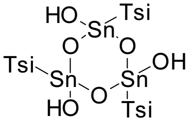


(12-41) **(12-42)**

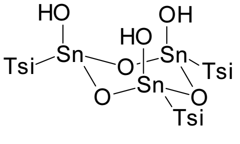
Smaller oligomers can be isolated when the group R is large. Hydrolysis of $(Me_3Si)_3CSnCl_3$ ($TsiSnCl_3$) gives the trimers $(TsiSnClO)_3$ (**12-43**) and $[TsiSnO(OH)]_3$ (**12-44**) which has the structure **12-45**,[138] and hydrolysis of $TsiSnBr_3$ gives the adamantane-shaped tetramer $(TsiSn)_4O_6$ (**12-46**).[139]



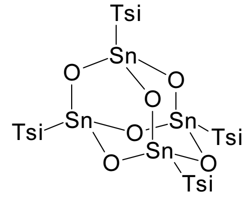
(12-43)



(12-44)



(12-45)

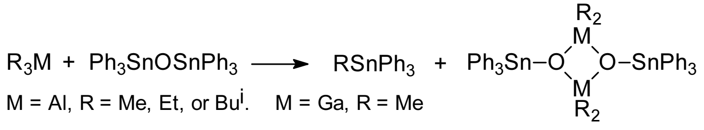


(12-46)

12.4 Stannametalloxanes[140]

Stannametalloxanes containing the unit SnOM, where M is a metal or an organometallic group, can generally be prepared by the reaction of MOLi or MONa with a tin halide, or by the azeotropic dehydration of MOH and a tin oxide or hydroxide,[141] or by the cohydrolysis of MCl and an organotin halide.

Trialkylaluminiums and trimethylgallium, R_3M, react with hexaphenyldistannoxane to give the mixed metal oxides $R_2MOSnPh_3$, which exist in the crystal as dimers across the M−O bonds.[142]



$$R_3M + Ph_3SnOSnPh_3 \longrightarrow RSnPh_3 + Ph_3Sn{-}O\underset{\underset{R_2}{M}}{\overset{\overset{R_2}{M}}{\diamond}}O{-}SnPh_3 \qquad (12\text{-}30)$$

M = Al, R = Me, Et, or Bu^i. M = Ga, R = Me

Functionally substituted metallostannoxanes (M = Si, Ge, Pb, Tl, Hg; X = halogen or carboxylate) can also be prepared by reaction between the appropriate metal halide MX and diorganotin oxide R_2SnO (e.g. equation 12-31). Little is known about the structures and reactions of these compounds.[143]

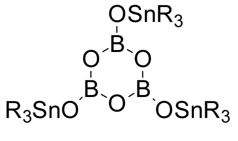
$$PhHgCl + Bu_2SnO \longrightarrow PhHgOSnBu_2Cl \qquad (12\text{-}31)$$

The compounds that have been studied in most detail are the borastannoxanes and, particularly the silastannoxanes, because of their relation to metalloxane polymers. A thorough recent review of the silastannoxanes is available.[144]

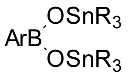
Stannyl orthoborates (**12-47**), metaborates (**12-48**), and boronates (**12-49**), can be prepared by azeotropic dehydration of the corresponding boron acids and organotin oxides,[145] and the cyclic distannaboroxane, prepared from boronic acid and distannoxane, forms a complex (**12-50**) with di-t-butyltin dihydroxide.[146] Adventitious hydrolysis of $B(OSnPh_3)_3$ gave the distannyl borate $HOB(OSnPh_3)_2$, in which the three oxygen atoms are coplanar with the boron.[147] The Lewis acidity is enhanced in the stannyloxy compounds over that in the corresponding alkoxy compounds.[148]

$B(OSnR_3)_3$

(**12-47**)

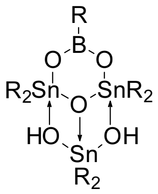


(**12-48**)



$$ArB(OSnR_3)_2$$

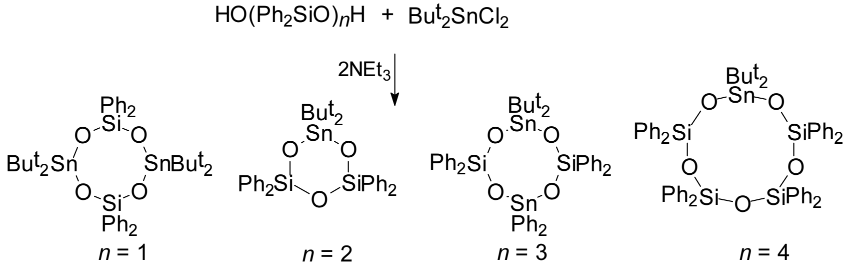
(**12-49**)



(**12-50**)

Simple stannasiloxanes such as $Me_3SiOSnPh_3$ or $(Ph_3SiO)_2SnMe_2$ can be prepared by azeotropic dehydration of the appropriate silanol and distannoxane[141] and disiloxydistannoxanes such as $Me_3SiOMe_2SnOSnMe_2OSiMe_3$ by the cohydrolysis of the appropriate chlorosilane and dichlorostannane.[149]

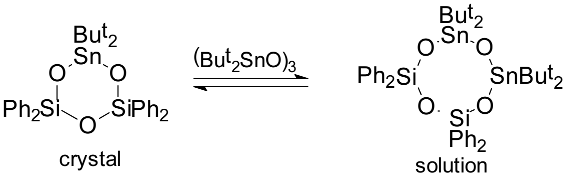
Silanediols react with di-t-butyltin dichloride under basic conditions to give a series of cyclic stannasiloxanes.[144, 150]



(12-32)

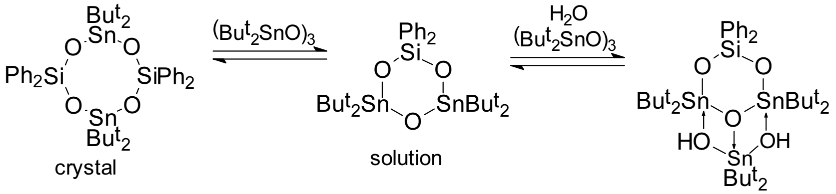
Compound **12-51** is monomeric in solution but undergoes ring-opening polymerisation (ROP) on crystallisation to give the linear stannasiloxane $[-OSnBu^t{}_2OSiPh_2OSiPh_2-]_n$. In the presence of $(Bu^t{}_2SnO)_3$ it undergoes ring expansion to give the eight-membered stannasiloxane **12-52**,[151] whereas, in solution, **12-53** reacts by ring contraction to give the six-membered ring **12-54**. Presumably this difference in behaviour reflects the differences in ring strain. **12-54** Reacts with $(Bu^t{}_2SnO)_3$ in the presence of water to give the complex **12-55**, and a similar complex is formed with $Bu^t{}_2SnF_2$.[152] The compound

$Me_2Si(OSnBu^t_2)_2 \cdot Bu^t_2Sn(OH)_2$ was obtained adventitiously from $Bu^t_2SnCl_2$ and a strong base in the presence of silicone grease.[153] The analogy between these complexes and that of the *cyclo*-boradistannoxane (**12-50**) is obvious.



(**12-51**) (**12-52**)

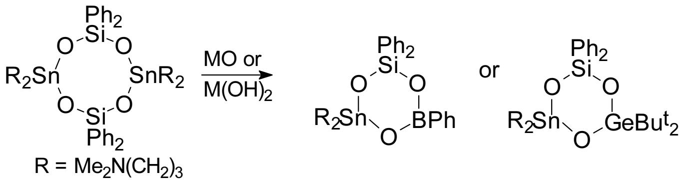
(12-33)



(**12-53**) (**12-54**) (**12-55**)

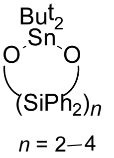
(12-34)

Rings containing three different metals have been formed by the reaction shown in equation 12-35; intramolecular coordination by the nitrogen in R may increase the strain in the 8-ring, but reduce it in the 6-ring.[154]

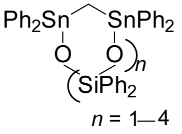


(12-35)

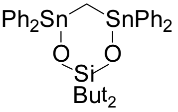
The cyclic stannasiloxanes **12-56** have been obtained from the reaction of the oligosilanes $X(Ph_2Si)_nX$ and $(Bu^t_2SnO)_3$,[144] and the stannyloxy-silanes **12-57** and **12-58** and -germane **12-59** from the reaction between $(HOSnPh_2)_2CH_2$ and the appropriate silanols or germanol.[155]



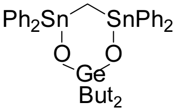
(**12-56**)



(**12-57**)



(**12-58**)



(**12-59**)

The SiOH groups on the surfaces of molecular sieves react with tri- or tetra-alkylstannanes to replace the hydrogen by more bulky SnR_3 groups, and the size of the entrances to the pores can be controlled by a suitable choice of the group R.[156]

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13 Organotin Carboxylates and other Oxyesters. Stannylium Ions

13.1 Organotin Carboxylates[1]

13.1.1 Preparation

Organotin carboxylates, $R_nSn(O_2CR')_{4-n}$, are most commonly prepared[2] by treating the corresponding oxide or hydroxide with the carboxylic acid (equations 13-1 – 13-3), or from the reaction of the corresponding chloride with a metal carboxylate (equation 13-4), or by cleaving a tin-carbon bond with a carboxylic acid (equation 13-5) or a mercury(I) or mercury(II), or lead(IV) carboxylate (equation 13-6).

$$R_3SnOH \text{ or } (R_3Sn)_2O + R'CO_2H \xrightarrow{-H_2O} R_3SnO_2CR' \qquad (13\text{-}1)$$

$$R_2SnO + 2R'CO_2H \xrightarrow{-H_2O} R_2Sn(O_2CR')_2 \qquad (13\text{-}2)$$

$$RSn(O)OH + 3R'CO_2H \xrightarrow{-H_2O} RSn(O_2CR')_3 \qquad (13\text{-}3)$$

$$R_nSnCl_{4\text{-}n} + 4\text{-}nR'CO_2M \longrightarrow R_nSn(O_2CR')_{4\text{-}n} + 4\text{-}nMCl \qquad (13\text{-}4)$$

$$R_4Sn + R'CO_2H \longrightarrow R_3SnO_2CR' + RH \qquad (13\text{-}5)$$

$$R_4Sn + R'CO_2M \longrightarrow R_3SnO_2CR' + RM \qquad (13\text{-}6)$$

The first group of reactions (13-1 – 13-3) can be carried out by mixing aliquots of the tin oxide or hydroxide and acid in a solvent such as methanol (e.g. equation 13-7).[3] The water can often be conveniently removed by azeotropic dehydration in benzene or toluene, but with aryltin compounds it may be better to use molecular sieves, to avoid the risk of cleaving the aryl-tin bonds.[4]

$$Ph_3SnOH + HO_2CCO_2Me \xrightarrow{-H_2O} Ph_3SnO_2CCO_2Me \qquad (13\text{-}7)$$

The products of the reaction of dialkyltin oxides R_2SnO ($R = Bu, Bu^i, Bu^s$, or Bu^t) with carboxylic acids $R'CO_2H$ ($R' = Me, Et, Pr^i$, or Bu^t) (equation 13-8) depend on the size of the groups R and R′ and on the molar ratios.[5]

$$\begin{array}{ccccc} & & R_2SnO + R'CO_2H & & \\ & & \downarrow & & \\ R_2Sn(O_2CR')_2 & \text{or} & (R'CO_2)R_2SnOSnR_2(O_2CR') & \text{or} & R_2Sn(OH)O_2CR' \\ \textbf{(13-1)} & & \textbf{(13-2)} & & \textbf{(13-3)} \end{array} \qquad (13\text{-}8)$$

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With a 1:2 stoichiometry, all combinations of R and R′ gave the dicarboxylates (**13-1**). With a 1:1 ratio, Bu_2SnO reacted with all the acids to give only the distannoxane **13-2**, but $Bu^i{}_2SnO$ gave both the distannoxane **13-2** and the dicarboxylate **13-1**, the proportion of the latter increasing as R′ increases in size, in the order Me < Et < Pr^i < Bu^t. With all the acids, $Bu^s{}_2SnO$ gave the dicarboxylate **13-1**, leaving behind half of the $Bu^s{}_2SnO$ unreacted, and $Bu^t{}_2SnO$ gave only the hydroxide carboxylate **13-3** as an OH-bridged dimer, $[Bu^t{}_2Sn(OH)OCOR]_2$. The reaction of dibutyltin oxide and trichloracetic acid in the ratio of 1:2, however, gave a compound of the composition $Bu_4Sn_2(O_2CCl_3)_3OH$, which can be regarded as one molecule of $Bu_2Sn(O_2CCl_3)OH$ and one of $Bu_2Sn(O_2CCl_3)_2$ doubly bridged by OH from the first molecule and the C=O group of a carboxylate from the other.[6]

The distannoxane derivatives **13-2** can also be prepared by the half hydrolysis of the dicarboxylates $R_2Sn(O_2CR')_2$, or from the reaction between R_2SnO and $R_2Sn(O_2CR')_2$,[7] or via the dialkoxydistannoxanes (Section 12.2), for example:[8]

$$Bu_2SnO \xrightarrow{PrOH} [(PrO)Bu_2Sn]_2O \xrightarrow{CF_3CO_2H} [(CF_3CO_2)Bu_2Sn]_2O \qquad (13\text{-}9)$$

The butyltin oxycarboxylates, BuSn(O)OCOR′, which are formed by azeotropic dehydration of a 1:1 mixture of butanestannonic acid and the acids $R'CO_2H$ (R′ = Pr^i or Bu^t), have been shown to be hexamers with a drum-shaped structure, as described in Section 12.3.[9]

The reaction of organotin halides with metal or ammonium carboxylates (equation 13-4; M = Na, K, Tl, Ag, or R_3NH^+) can be carried out in a solvent such as acetone or carbon tetrachloride, but it is more convenient to prepare the salt *in situ* by adding the acid to a solution of sodium in an alcohol.[10] The sodium carboxylate is formed in a finely-divided form, and then reacts readily with the equivalent amount of the organotin chloride. Alternatively the reaction can be carried out by slowly adding a tertiary amine to a solution of the acid and tin chloride in a solvent such as benzene.[10]

The preparation of organotin carboxylates by cleavage of a carbon-tin bond with a carboxylic acid (equation 13-5) occurs more readily when R is a vinyl, allyl, or aryl group, than when R is alkyl. Thus alkyltrialkynyltin compounds are cleaved by acetic acid to give the alkyltin carboxylates $[RSn(O)O_2CMe]_6$,[11] and the phenyltin trichloroacetates $Ph_2Sn(O_2CCCl_3)_2$, $Ph_6Sn_6(O_2CCCl_3)_{10}O_4$, and $[PhSn(O_2CCCl_3)O]_6 \cdot 3\,C_6H_6$, have been made by the dephenylation of triphenyl- or diphenyl-tin(IV) compounds with trichloroacetic acid.[12]

The reactivity of organotin bonds towards lead tetraacetate (equation 13-6) follows the sequence Ph > Me > Et > Bu >> ^iPr, which is consistent with an electrophilic substitution rather than an electron transfer mechanism.[13]

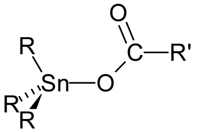
The melting points of some simple carboxylates are given in Table 13.1.

Table 13-1 Properties of organotin carboxylates.

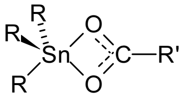
Carboxylate	M.p./°C	Carboxylate	M.p./°C
Me_3SnO_2CH	146	$(PhCH_2)_3SnO_2CMe$	112–113
Me_3SnO_2CMe	196–197	Ph_3SnO_2CMe	121–122
$Me_3SnO_2CCO_2Me$	128	$Et_2Sn(O_2CPh)_2$	121
$Me_3SnO_2OCH_2NH_2$	163–164dec	$Bu_2Sn(O_2CMe)_2$	8.5–10
Et_2BuSnO_2CMe	71–73	$BuSn(O_2CMe)_3$	46
Bu_3SnO_2CMe	85	$PhSn(O_2CEt)_3$	67.5

13.1.2 Structures[14, 15]

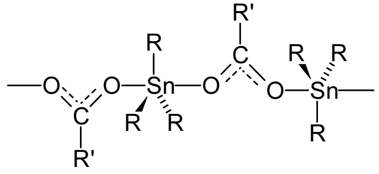
The structures of the triorganotin carboxylates R_3SnO_2CR' can be discussed in terms of the three idealised structures **13-4**, **13-5**, and **13-6**.[14] In **13-4**, the tin is approximately tetrahedral, and the two CO bonds are non-equivalent. In **13-5**, the structure is closer to that of a trigonal bipyramid with facial alkyl groups, and the two CO bonds are equivalent. In **13-6**, the carboxylate groups, with equivalent CO bonds, bridge between planar SnR_3 groups to form a linear polymer.



(13-4)



(13-5)

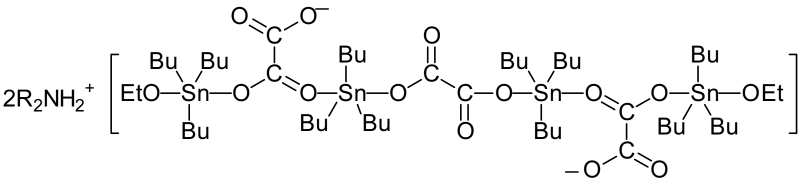


(13-6)

In the solid state, the structures of most compounds R_3SnO_2CR' approximate to the infinite chain polymer **13-6**, in which the oxygen atoms occupy the apical positions in a more or less distorted trigonal bipyramid, and in different compounds there is a continual graduation of SnO and CO bond lengths. For example, in trimethyltin acetate, the Sn–O distances are 220.5(3) and 239.1(4) pm, and the OSnO angle is 171.6(1)°, and in triphenyltin acetate, the corresponding values are 218.5(3) and 234.9(3) pm, and 173.6(1)°.[16] The ^{13}C and ^{119}Sn NMR spectra show that these compounds undergo a 120° propeller-like jump around the Sn-O bonds in the solid state.[17, 18]

Analysis of the X-ray data for the 17 polymeric carboxylates R_3SnO_2CR' for which the structures were known in 1988 showed that the repeat distance in the polymer was approximately constant at 519 ± 21 pm, insensitive to the nature of the groups R and R′.[19]

Bis(tributyltin) oxide reacts with dicyclohexylammonium oxalate to give a stannate which forms an ethanol adduct with the structure shown in **13-7**, in which the configuration about the medial and terminal tin atoms is that of a distorted trigonal bipyramid.[20]

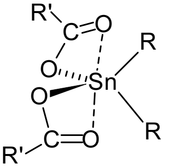


(13-7)

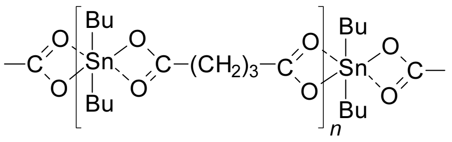
Bulky groups R and R′ might be expected to favour the existence of monomeric molecules R_3SnO_2CR' in the crystal. The only examples which appear to be known are where R = phenyl, cyclohexyl, or neophyl.[21] The closest to the ideal structure **13-4** is tricyclohexyltin trifluoroacetate, with *r*Sn-O 208(4) and 311(4) pm, though this might be regarded as a weakly associated polymer.[13] Triphenyltin (*o*-2-hydroxy-5-methylphenylazo)benzoate approaches the structure **13-5** with *r*SnO 207.0(5) and 246.3(7) pm.[22]

A comparison of the NMR spectra of the carboxylates in the solid and solution states shows that the polymers **13-6** dissociate on dissolution. Thus a series of tributyltin carboxylates in the solid state show δ ^{119}Sn in the range −53 to +39, indicating 5-coordination, but in solution, δ = 109 to 157, characteristic of 4-coordinate tin.[23] In solution, the ^{17}O NMR spectra of tributyltin acetate and of dibutyltin diacetate in both coordinating and non-coordinating solvents show that the two carboxylate oxygen atoms are rendered equivalent by rapid inter- or intra-molecular exchange.[24, 25] Measurements of molecular weight and of IR spectra of triethyltin formate in cyclohexane solution show the presence of a series of oligomers $(Et_3SnO_2CH)_n$, $n = 4.5{-}21.1$, depending on the concentration.[26]

The diorganotin dicarboxylates in the solid state are usually monomolecular as shown in **13-8**. This structure can be described as a tetrahedron built up from two Sn−C and two short Sn-O bonds, which is then doubly capped by weak bonds from the two carbonyl groups, resulting in a very distorted octahedron. For example, in dimethyltin dibenzoate, the CSnC angle is 147.2(7)°, and there are short SnO bonds of 215.6(9) and 212.8(8) pm, and two long ones of 251(1) and 251.0(9) pm.[27] Again, in solution, the ^{17}O NMR spectrum shows only one signal, indicating rapid carboxylate group exchange.[25, 28]



(**13-8**)



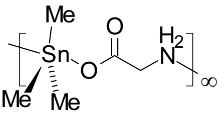
(**13-9**)

In dimethyltin diformate, however, the two carbonyl groups bridge intermolecularly, to form infinite sheets similar to those in dimethyltin difluoride or dimethyltin di(fluorosulfonate).[29] If the linearly polymeric diorganotin carboxylates are dissolved in chloroform, the ^{119}Sn NMR chemical shift moves downfield by 50 to 100 ppm, and is then almost independent of concentration, showing that the compounds are monomeric in solution.[23, 30] Dibutyltin glutarate is a linear polymer as shown in **13-9**.[31]

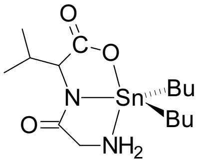
The dicarboxylates of the tetraorganodistannoxanes $R_4Sn_2O(O_2CR')_2$ and of the tetraorganodistannanes $R_4Sn_2(O_2CR')_2$ have special structures, and these are discussed in Sections 12.2 and 18.2.2, respectively.

Little work has been reported on the structures of the monoorganotin tricarboxylates, $RSn(OCOR')_3$. In methyltin tribenzoate, the three carboxyl groups are bidentate, giving 7-coordinate tin.[32] A number of partially hydrolysed monoorganotin carboxylates have been characterised in which the ratio of the groups R to $R'CO_2$ is less than 1 : 3, some of the carboxylate groups being replaced by SnOSn bridges. These compounds are oligomers with rather complex structures, and are discussed in Section 12.3.

There has been a recent, thorough review of the organotin derivatives of amino acids and peptides,[33] and their Mössbauer characteristics are covered also in Barbieri's review.[34] These compounds have attracted interest because they are implicated in the toxicity of organotin compounds, and also because they may have potential in cancer treatment. Typically, trimethyltin glycinate (**13-10**) is a linear amino-bridged polymer in the solid state, with approximately trigonal bipyramidal tin,[35] but cysteine binds to tin through sulfur, rather than through the carboxylate group.[36] A peptide nitrogen is acidic enough to be deprotonated, and, for example, Bu_2SnGly-Val has a monomeric trigonal bipyramidal structure (**13-11**).[37]



(**13-10**)



(**13-11**)

13.1.3 Properties

The triorganotin formates, $R_3SnOCHO$, decarboxylate on heating to give the corresponding hydrides, R_3SnH,[38] and if the formates are prepared from equimolecular amounts of the bis(triorganotin) oxide and formic acid, the hydride reduces the excess oxide to give the hexaorganodistannane, R_3SnSnR_3 (see Section 18.2.1.3).[39]

The triorganotin carboxylates are usually stable to water. The diorganotin dicarboxylates are readily hydroysed as far as the distannoxanes $(R'CO_2)R_2SnOSnR_2(O_2CR')$ and $(R'CO_2)R_2SnOSnR_2(OH)$ (Section 12.2), and the organotin tricarboxylates give the oxycarboxylates $[RSn(O)O_2CR']_n$ (Section 12.3). The dibutyltin halide acetates $Bu_2Sn(O_2CMe)X$, X = Cl or Br [which are formed by mixing $Bu_2Sn(O_2CMe)_2$ and Bu_2SnX_2], smell of acetic acid, and in the air are hydroysed in a few hours to the corresponding dihalogenodistannoxanes, $XR_2SnOSnR_2X$.[10]

Organotin polyoxaalkanecarboxylates, with an increased solubility in water, have been patented for their potential use in anticancer therapy.[40]

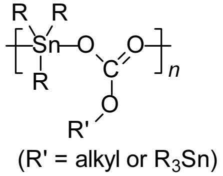
The Lewis acidity of the carboxylates can be measured from the equilibrium constants determined from the ^{31}P NMR chemical shift of the mixture with triethylphosphine oxide:

$$R_3SnO_2CR' + Et_3PO \xrightleftharpoons{K} R_3SnO_2CR'.O{=}PEt_3 \tag{13-10}$$

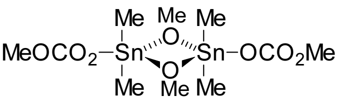
This shows that in benzene or toluene the monocarboxylates (e.g. R = Bu and R′ = Me) form only 1 : 1 complexes, which increase in stability as the acid strength of $R'CO_2H$ increases (e.g. Bu_3SnO_2CMe, $K = 13$, $Bu_3SnO_2CC_6H_3(NO_2)_2$–3,5, $K = 3.2 \times 10^2\ M^{-1}$), and that the carboxylates are weaker Lewis acids than the corresponding chlorides (Ph_3SnO_2CMe, $K = 74$, Ph_3SnCl, $K = 1.7 \times 10^2\ M^{-1}$).[23] The structures of a number of carboxylate complexes have been determined. For example, $Ph_3SnO_2CCCl_3 \cdot MeOH$ has the form of a slightly distorted trigonal bipyramid, with apical carboxylate and alcohol groups, and the equatorial phenyl groups twisted into a paddle-wheel orientation to minimise steric hindrance,[12] and divinyltin bis(trifluoroacetate).bipyridyl is octahedral with *trans*-vinyl groups.[41] Tributyltin acrylates have been incorporated into polymers to serve as self-polishing slow-release antifouling coatings on ships, and dibutyltin dicarboxylates are used as heat-stabilisers for PVC and as catalysts for vulcanising silicone polymers (Section 23.1).

13.2 Carbonates and Carbamates[1]

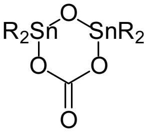
Triorganotin alkoxides and bis(triorganotin) oxides react with carbon dioxide to give the carbonates $R_3SnOC(O)OR'$ or $(R_3SnO)_2CO$, respectively; failure to recognise these reactions has led to some confusion between the tin hydroxides, oxides, and carbonates in the literature. The reactions are reversible, and CO_2 is evolved on heating. The tin alkyl carbonates, $R_3SnOC(O)OR'$, can also be prepared by reaction of the distannoxane $R_3SnOSnR_3$ with dialkyl carbonates, $(R'O)_2CO$, and heating these two reagents together provides a convenient route to the alkoxides R_3SnOR' (see Section 14.1.1). In the crystal, the distannyl carbonates ($R = Me$ or Bu^i) are linear polymers (**13-12**, $R' = R_3Sn$) containing carboxylate-bridged 5-coordinate tin ($R = Me$: δSn −62.2) with pendant 4-coordinate stannyloxyl groups (δSn 123.3).[18, 42] The stannyl alkyl carbonates probably have a similar structure (**13-12**, R′ = alkyl) with pendant alkoxyl groups,[18, 43] but $Me_2Sn(OMe)(OCO_2Me)$ is a methoxyl-bridged dimer (**13-13**).[42]



(**13-12**)



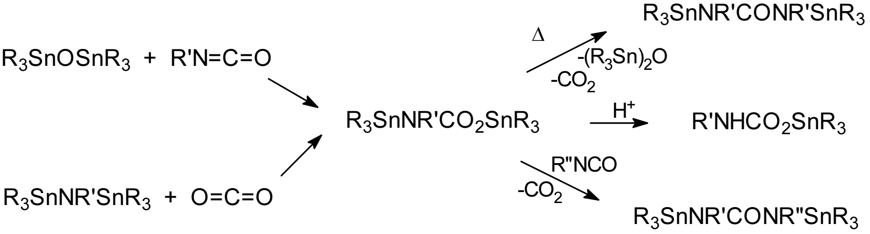
(**13-13**)



(**13-14**)

Dialkyltin dichloride reacts with alkali metal carbonates in water to give oxycarbonates $(R_2Sn)_2OCO_3$ (**13-14**). The Mössbauer spectra (QS 3.0–3.33 mm s^{-1}) indicate that the tin is 5-coordinate, probably through coordination by both the SnOSn and C=O oxygens.[44]

Trialkyltin *N*-stannylcarbamates, $R_3SnNR'CO_2SnR_3$, can be prepared by the addition of bis(trialkyltin) oxides to organic isocyanates, or (less conveniently), of distannazanes to carbon dioxide (Scheme 13-1). Both reactions are reversible; on heating, the carbamates evolve carbon dioxide and give the symmetrical distannylureas, and reaction with a different isocyanate displaces CO_2 to give unsymmetrical distannylureas. The SnN bond is cleaved by protic reagents to give the tin carbamates $R'NHCO_2SnR_3$.[45, 46]

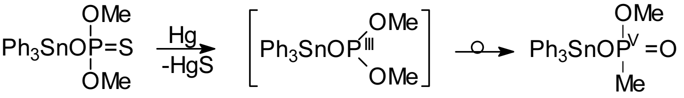


Scheme 13-1 Formation and reactions of trialkyltin carbamates.

13.3 Derivatives of Phosphorus Acids[11, 32]

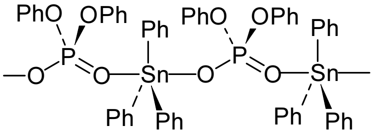
A number of types of organotin derivatives of the phosphorus acids have been prepared, one of the objects being to combine the biological effects of organotin and organophosphorus compounds.

Organotin "esters" of the oxy- and thio-acids of phosphorus can be prepared *inter alia* by azeotropic dehydration of a mixture of the organotin hydroxide or oxide and the acid, or by treating a tin alkoxide or tin amide with the acids, or an organotin halide with a salt of the phosphorus acid. By using different molecular ratios of the reactants, products of different compositions can be obtained. Attempts to prepare phosphites may result in an Arbuzov rearrangement to a phosphorus(V) compound (e.g. equation 13-11).[47]

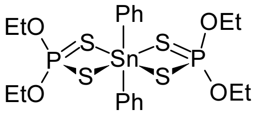


$$\mathrm{Ph_3SnOP(=S)(OMe)_2} \xrightarrow[\mathrm{-HgS}]{\mathrm{Hg}} \left[\mathrm{Ph_3SnOP^{III}(OMe)_2}\right] \longrightarrow \mathrm{Ph_3SnOP^{V}(=O)(OMe)(Me)} \qquad (13\text{-}11)$$

The ^{31}P and ^{119}Sn NMR spectra show that the tributyltin phosphate, phosphonate, and phosphinate, $(Bu_3SnO)_n(Ph)_{3-n}P{=}O$, in solution are all bridged through the O–P=O group.[48, 49] The derivatives of the oxyacids bridge (e.g. **13-15**), whereas those of the dithiophosphorus acids often chelate (e.g. **13-16**), which may be the result, in part, of the different PO, PS, SnO, and SnS bond lengths, and the degree of ring-strain that they may impose.[50]



(**13-15**)



(**13-16**)

The derivatives of the inorganic phosphorus acids are usually intractable powders which are unsuitable for X-ray diffraction, but those of the organic phosphorus acids are often crystalline and a series of complex solid-state structures which have been described as drums, cubes, oxygen-capped clusters, butterfly formations, crowns, and extended clusters[32, 51] have been identified.

Some examples of organotin derivatives of phosphorus acids are given in Table 13-2.

Table 13-2 Organotin derivatives of phosphorus acids.

Compound	Source	Ref.
Phosphates		
$(Me_3SnO)_3P{=}O$	$Me_3SnCl + (AgO)_3P{=}O$	52
$(Me_3SnO)(PhO)_2P{=}O$	$Me_3SnOH + (HO)(PhO)_2P{=}O$	53
$(Bu_3SnO)(Et_2N)_2P{=}O$	$Bu_3SnCl + (KO)(Et_2N)_2P{=}O$	54
$Me_2Sn[S(EtO)_2P{=}S]_2$	$Me_2SnCl_2 + (NaS)(EtO)_2P{=}S$	55
$(Me_3SnO)Cl_2P{=}O$	$Me_3SnCl + (O{=}PCl_2)_2O$	56
Phosphonates		
$(Ph_3SnO)(MeO)(Me)P{=}O$	$Ph_3SnCl + (NaO)(MeO)(Me)P{=}O$	47
$(Bu_3SnO)(EtO)(H)P{=}O$	$Bu_3SnCl + (NaO)(EtO)(H)P{=}O$	57
$Bu_2Sn[OPMe(O)(OH)]_2$	$[(PrO)SnBu_2]_2O + MePO_3H_2$	58
Phosphinates		
$(Me_3SnO)Me_2P{=}O$	$Me_3SnNEt_2 + (HO)Me_2P{=}O$	56
$Bu_2Sn[S(Ph_2)P{=}S]_2$	$(Bu_3Sn)_2O + HS(Ph_2)P{=}S$	59
$(PhCH_2)_2Sn[O(C_6H_{11})_2P{=}O]_2$	$(PhCH_2)_2SnCl_2 + (C_6H_{11})_2PO_2H$	60
Hypophosphites		
$Bu_2Sn[O(H_2)P{=}O]_2$	$Bu_2SnCl_2 + (KO)H_2P{=}O$	52

13.4 Derivatives of Other Oxyacids and of Thioacids[1, 15]

Organotin derivatives of many other oxyacids and thioacids have been prepared by methods analogous to those used for the carboxylates, carbonates, and phosphorus acids, though few systematic studies have been carried out. The derivatives of the stronger acids can usually be prepared also by cleaving an Sn−C bond in R_4Sn or Ar_4Sn with the acid or an anhydride (e.g. SO_2 or SO_3). Some examples are given in Table 13-3.

Table 13-3 Organotin derivatives of oxyacids and thioacids.

Compound	Preparation	M.p./°C	Ref.
$Me_3SnOS(O)_2Ph$	$Me_3SnOH + PhSO_3H$	67–69	61
$Me_3SnOS(O)_2CF_3$	$Me_4Sn + CF_3SO_3H$	327 dec.	62
$Me_3SnOS(O)_2F$	$Me_4Sn + FSO_3H$	144–145	63
Me_3SnONO_2	$Me_3SnBr + AgNO_3$	127–128	64
$Me_3SnSC(S)NEt_2$	$Me_3SnNEt_2 + CS_2$		65
$Me_3SnOClO_3$	$Me_3SnBr + AgClO_4$	125–127	64
$Me_3SnOC(O)NMe_2$	$Me_3SnNMe_2 + CO_2$	153	65
$Bu_3SnOS(O)OMe$	$Bu_3SnOMe + SO_2$		66
$Bu_3SnOS(O)_2CF_3$	$(Bu_3Sn)_2O + (CF_3SO_2)_2O$	41–43	67
$(Bu_3Sn)_2SO_3$	$(Bu_3Sn)_2O + SO_2$		66
$Ph_3SnOS(O)_2CF_3$	$Ph_4Sn + CF_3SO_3H$	290 dec.	62
$(Me_3Sn)_2SO_4$	$Me_3SnOH + H_2SO_4$	138–140	68
$Me_2Sn[OS(O)Me]_2$	$Me_4Sn + SO_2$	206–208	69
$Me_2Sn[SS(O)_2ONa]_2$	$Me_2SnCl_2 + Na_2S_2O_3$	185 dec.	70
$Me_2Sn[OS(O)_2F]_2$	$Me_4Sn + FSO_3H$	253 dec.	63
$Me_2SnCl[OS(O)_2F]$	$Me_2Sn[OS(O)_2F]_2 + Me_2SnCl_2$	108	63
$Et_2Sn(OH)ONO_2$	$Et_2SnO + HNO_3$	214 dec.	71
$O(SnEt_2ONO_2)_2$,	$Et_2Sn(OH)NO_3 - H_2O$	214 dec.	71
Et_2SnSO_3	$Et_2SnO + SO_2$	>300	69
$Bu_2Sn(OMe)OS(O)_2Me$	$Bu_2SnO + Me_2SO_3$		72
$Ph_2Sn[OS(O)_2CF_3]_2$	$Ph_4Sn + CF_3SO_3H$	304 dec.	62
$Ph_2Sn[ONO_2]_2$	$Ph_2SnCl_2 + AgNO_3$		73
$[MeSn(OS(O)_2CF_3)_2O]_2$	$Me_4Sn + CF_3SO_3H$	–	62

Bis(trimethyltin) sulfate and chromate have a polymeric lattice structure in which planar Me_3Sn groups are apically bridged by SO_4 or CrO_4 groups. The dihydrate $(Me_3Sn)_2SO_4 . 2\,H_2O$ has the structure $(H_2O)Me_3SnOS(O)_2OSnMe_3(OH_2)$, again with trigonal bipyramidal geometry about the tin,[68] and the same structural element is found in the nitrate $H_2O.Me_3SnONO_2$ [74] and the benzenesulfonate $H_2O.Me_3SnOS(O)_2Ph$.[61]

The organotin triflates[75, 76] and perchlorates[77] have been recommended as mild Lewis acids for condensation reactions.

As the acid strength of HX increases, the polarity of the corresponding tin compound, $R_3Sn^{\delta+}X^{\delta-}$, similarly increases, and in the limit an ionic compound, $R_3Sn^+ X^-$, should be formed, containing an isolated stannyl cation (stannylium ion). The trigonal bipyramidal dihydrated R_3Sn^+ ion has been identified in the salt $Bu_3Sn(OH_2)_2^+$ $(C_5(CO_2Me)_5^-$ (equation 9-48),[78] and the octahedral tetrahydrated R_2Sn^+ ion in the salt $Bu_2Sn(OH_2)_4^{2+}$ $(2,5\text{-}Me_2C_6H_3SO_3)^-_2$.[79] A number of interesting studies have been carried out with the aim of identifying the three-coordinate species R_3Sn^+, culminating in the isolation of crystalline tris(2,4,6-triisopropylphenyl)stannylium tetrakis(pentafluorophenyl) borate.[80, 81]. This topic is dealt with in Section 7.2.

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14 Organotin Alkoxides, Phenoxides, and Peroxides

14.1 Acyclic Alkoxides and Phenoxides[1]

14.1.1 Preparation

Organotin alkoxides and phenoxides can be prepared from the reaction of an alkali metal alkoxide or phenoxide with the appropriate organotin halide. Triorganotin alkoxides and phenoxides are available from the reaction of bis(triorganotin) oxides with alcohols or phenols or the corresponding carbonates, and the amides $R_nSn(NR''_2)_{4-n}$ react with alcohols to give the corresponding alkoxides.

$$R_nSnX_{4-n} + 4\text{-}nR'OM \longrightarrow R_nSn(OR')_{4-n} + 4\text{-}nMX \tag{14-1}$$

$$(R_3Sn)_2O + 2R'OH \longrightarrow 2R_3SnOR' + H_2O \tag{14-2}$$

$$(R_3Sn)_2O + (R'O)_2CO \longrightarrow 2R_3SnOR' + CO_2 \tag{14-3}$$

$$R_nSn(NR''_2)_{4-n} + 4\text{-}nR'OH \longrightarrow R_nSn(OR')_{4-n} + 4\text{-}nHNR''_2 \tag{14-4}$$

Alkoxystannanes can also be prepared by the addition of an organotin hydride to a carbonyl compound (equation 14-5), and by the S_H2 reaction of alkoxyl radicals with organotin compounds carrying electronegative ligands (Section 11.4), for example equation 14-6, but these reactions have not been widely used for preparative purposes.

$$R_3SnH + R'R''C{=}O \longrightarrow R'R''CH\text{-}OSnR_3 \tag{14-5}$$

$$Bu^tO\cdot + Bu_3SnCl \longrightarrow Bu^tOSnBu_2Cl + Bu\cdot \tag{14-6}$$

Reaction 14-1 can be used for making mono-, di-, or tri-alkoxides (n = 3, 2 or 1) (equations 14-7–14-9) though the reaction between organotin trihalides and sodium alkoxides is complete only when the reagents are heated together in benzene under reflux for some hours.[2, 3]

$$Ph_3SnCl + NaOMe \xrightarrow[93\%]{MeOH,\ 0\ ^oC} Ph_3SnOMe + NaCl \tag{14-7}$$

$$Bu_2SnCl_2 + 2NaOMe \xrightarrow[98\%]{MeOH,\ 0\ ^oC} Bu_2Sn(OMe)_2 + 2NaCl \tag{14-8}$$

$$BuSnCl_3 + 3NaOPr^i \xrightarrow{C_6H_6,\ 80\ ^oC} BuSn(OPr^i)_3 + 3NaCl \tag{14-9}$$

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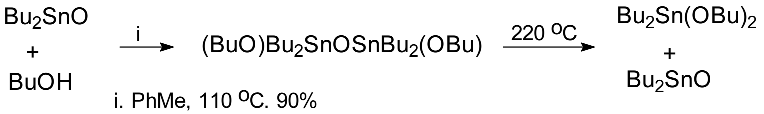
The sodium halide which is formed in these reactions is very finely divided, and may be difficult to filter off.[2] A more convenient way of preparing the triorganotin alkoxides and phenoxides is by the azeotropic dehydration of a mixture of the bis(trialkyltin) oxide and alcohol or phenol in a solvent such as benzene or toluene.[4]

$$(Bu_3Sn)_2O + 2Me_3CCH_2OH \xrightarrow[74\%]{C_6H_6,\ 80\ ^{o}C} 2Bu_3SnOCH_2CMe_3 \qquad (14\text{-}10)$$

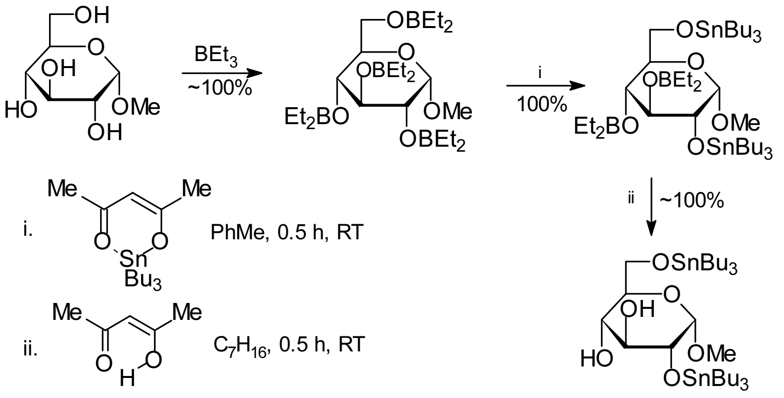
Under these conditions, dialkyltin oxides react to form only the dialkoxydistannoxanes, though if these are heated at about 200 °C under reduced pressure, the dialkyltin dialkoxide can be distilled off, leaving a residue of the dialkyltin oxide.[1] In tetrahydronaphthalene (b.p. 207 °C), however, phenols give the dialkyltin diphenoxides directly.[4]



$$\begin{array}{c}Bu_2SnO\\+\\BuOH\end{array} \xrightarrow{i} (BuO)Bu_2SnOSnBu_2(OBu) \xrightarrow{220\ ^{o}C} \begin{array}{c}Bu_2Sn(OBu)_2\\+\\Bu_2SnO\end{array} \qquad (14\text{-}11)$$

i. PhMe, 110 °C. 90%

Trialkytin alkoxides can be prepared under milder conditions by alcoholysis of a tin alkoxide derived from a lower-boiling alcohol (e.g. Bu_3SnOMe or Et_3SnOEt), or by converting the alcohol first to the borinate derivative, $ROBEt_2$, then stannylating this with the tributylstannylenolate of pentane-2,4-dione, $Bu_3SnOCMe{=}CHCMeC{=}O$ (e.g. equation 14-12).[5]



(14-12)

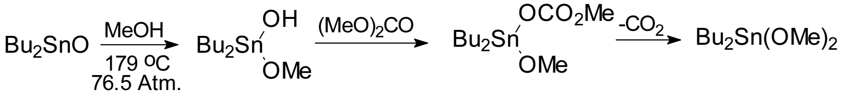
The organotin methoxides cannot readily be prepared from methanol by reaction 14-2 because its boiling point is too low, and it does not form an azeotrope with water. The methoxides and alkoxides derived from other volatile alcohols can, however, readily be prepared by heating together the bis(trialkyltin) oxide and dialkyl carbonate; the exchange reaction between the tin oxide and carbonate gives the tin alkoxide and the alkyltin carbonate (reaction 14-13), which readily decarboxylates to give more alkoxide (reaction 14-14).[4]

$$Bu_3SnOSnBu_3 + (MeO)_2C{=}O \longrightarrow Bu_3SnOMe + MeOC(O)OSnBu_3 \qquad (14\text{-}13)$$

$$MeOC(O)OSnBu_3 \longrightarrow MeOSnBu_3 + CO_2 \qquad (14\text{-}14)$$

$$Bu_3SnOSnBu_3 + (MeO)_2C{=}O \longrightarrow 2Bu_3SnOMe + CO_2 \qquad (14\text{-}15)$$

Under similar conditions, dibutyltin oxide reacts with dimethyl carbonate to give the distannoxane $(MeO)Bu_2SnOSnBu_2(OMe)$, but dibutyltin dimethoxide can also be prepared from the reaction of dibutyltin oxide with methanol and dimethyl carbonate under elevated temperature and pressure.[6, 7]



$$\mathrm{Bu_2SnO} \xrightarrow[\substack{179\ ^{o}C \\ 76.5\ Atm.}]{MeOH} \mathrm{Bu_2Sn(OH)(OMe)} \xrightarrow{(MeO)_2CO} \mathrm{Bu_2Sn(OCO_2Me)(OMe)} \xrightarrow{-CO_2} \mathrm{Bu_2Sn(OMe)_2} \qquad (14\text{-}16)$$

An analogous reaction occurs between dialkyltin oxides and dimethyl sulfite, via $R_2Sn(OMe)OS(O)OMe$, which loses SO_2 to give $R_2Sn(OMe)_2$ and $(MeO)R_2SnOSnR_2(OMe)$ (and ultimately the sulfonate $R_2Sn(OMe)OS(O)_2Me$ through an Arbuzov rearrangement).[8]

The reaction of aminotin compounds with alcohols proceeds in good yield and is particularly useful when the reactivity by alternative routes is low because of steric hindrance or of multiple substitution (equation 14-17).[3, 9, 10]

$$\mathrm{Sn(NEt_2)_4} + 4\mathrm{Bu^tLi} \longrightarrow \mathrm{Bu^tSn(NEt_2)_3} \xrightarrow{Bu^tOH} \mathrm{Bu^tSn(OBu^t)_3} \qquad (14\text{-}17)$$

Monalkyltin trialkoxides can alternatively be prepared by the alcoholysis of alkyltrialkynylstannanes with primary or secondary alcohols (e.g. equation 14-18).[11] *meso*-Tetra-*p*-tolylporphyrinatotin methoxides, $(TTP)Sn(C{\equiv}CPh)OMe$ and $(TTP)Sn(OMe)_2$, can similarly be prepared by the reaction of $(TTP)Sn(C{\equiv}CPh)_2$ with methanol.[12]

$$\mathrm{BuSn(}{-}{\equiv}{-}\mathrm{Me)_3} \xrightarrow[\substack{60\ ^{o}C \\ 16\ h}]{Bu^iOH} \underset{76\%}{\mathrm{BuSn(OBu^i)_3}} \qquad (14\text{-}18)$$

Tributyltin alkoxides can also be prepared under acid conditions by the alcoholyis of tributyltin hydride or allyltributyltin in the presence of a triflic acid catalyst; presumably the reaction involves the tin triflate as an intermediate.[13]

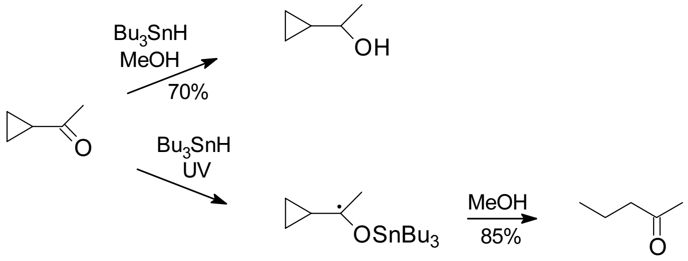
$$\mathrm{Bu_3SnX} + \mathrm{MeOH} \xrightarrow[CD_2Cl_2,\ RT]{CF_3SO_3H} \mathrm{Bu_3SnOMe} + \mathrm{HX} \qquad (14\text{-}19)$$

$$X = H,\ 16\ h.\ 82\% \qquad X = allyl,\ 23\ h.\ 98\%$$

The hydrostannation of carbonyl compounds to give alkoxystannanes (equation 14-5) can follow a homolytic or heterolytic mechanism depending on the structure of the reactants and on the reaction conditions (Section 20.1.3). This existence of alternative mechanisms is elegantly demonstrated in the reduction of cyclopropyl methyl ketone by tributyltin hydride. In methanol, 1-cyclopropylethanol is formed in a polar process, but, with irradiation with UV light, the main product is pentan-2-one, which is formed by ring opening of the cyclopropylmethyl radical by β-scission (Scheme 14-1)[14]

Addition by a homolytic chain mechanism can be promoted with a radical initiator such as AIBN, or by irradiation with UV light.[15]

Addition by nucleophilic attack of hydrogen occurs with a more polar carbonyl compound such as chloral, pentafluorobenzaldehyde, or phenyl pentafluorophenyl ketone (equation 14-20)[16, 17] or with a polar solvent (e.g. methanol),[14] or in the presence of a Lewis acid such as $ZnCl_2$ [18] or $Bu_3SnOSO_2CF_3$ [19] (equation 14-21) which can associate with the oxygen of the carbonyl group and render it more electrophilic.

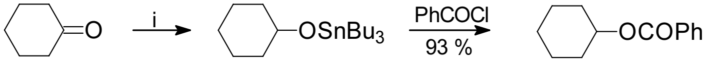


Scheme 14-1 Heterolytic and homolytic hydrostannation of cyclopropyl methyl ketone.

$$\mathrm{Me_3SnH + C_6F_5COPh \xrightarrow[> 90\%]{RT} C_6F_5CH(OSnMe_3)Ph} \qquad (14\text{-}20)$$

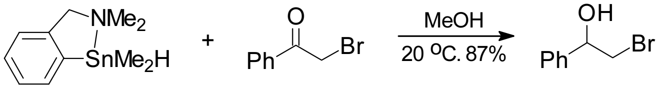
$$\mathrm{Bu_3SnH + Pr^i{}_2C{=}O \xrightarrow[18\ h,\ RT,\ 98\%]{Bu_3SnOSO_2CF_3} Pr^i{}_2CHOSnBu_3} \qquad (14\text{-}21)$$

Lewis bases (e.g. HMPA, or Bu_3PO or F^-) can also promote the polar reaction by associating with the tin hydride and making the hydrogen more nucleophilic (e.g. equation 14-22).[20] and the Lewis base may be incorporated into the tin hydride as shown in equation 14-23.[21]



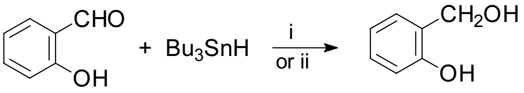
(14-22)

i. Bu_3SnH, Bu_4NF. 60 °C, 5 h



(14-23)

Aldehydes, but not ketones, acyl chlorides, or esters, can be reduced in boiling methanol, or in aqueous methanol or THF, or even (heterogeneously) in water.[22]



(14-24)

i. MeOH, reflux, 4 h. 100% yield. ii. H_2O, 65 °C, 6 h. 81% yield.

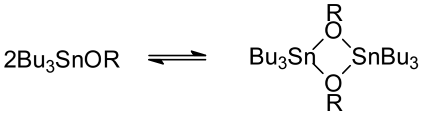
Some typical triorganotin alkoxides and phenoxides are listed in Table 14-1.

Table 14-1 Organotin alkoxides.

Compound	M.p./°C or b.p./°C (mm Hg)	Compound	M.p./°C or b.p./°C (mm Hg)
Me_3SnOMe	45dec	$Me_2Sn(OMe)Cl$	178–180
Me_3SnOPh	109(8)	$Bu_2Sn(OMe)OAc$	94–96
Et_3SnOEt	82(11)	$(MeO)Bu_2SnOSnBu_2(OMe)$	176(0.1)
Bu_3SnOMe	90(0.1)		
		$MeSn(OMe)_3$	195
Ph_3SnOEt	112	$MeSn(OEt)_3$	110(0.1)
		$EtSn(OMe)_3$	165
$Me_2Sn(OMe)_2$	86–87	$BuSn(OMe)_3$	250
$Et_2Sn(OEt)_2$	78(0.1)	$PhSn(OMe)_3$	212
$Bu_2Sn(OBu)_2$	160(3)	$Bu^tSn(OBu^t)_3$	156(70)
$Ph_2Sn(OEt)_2$	95	$BuSn(OCH_2CH_2)_3N$	158–159dec

14.1.2 Structures and Properties

The ^{119}Sn NMR chemical shifts of triorganotin alkoxides vary little with concentration, suggesting that these compounds are essentially monomeric in solution. Coupling is apparent, at an appropriate temperature, between the tin and the OC*H* protons, with ^3J ca. 36 Hz for 1 M solutions in benzene, but this is lost if the solutions are heated, implying the rapid exchange of alkoxyl groups between different tin centres. For different tributyltin alkoxides, Bu_3SnOR, the temperature at which this occurs is (R, T/°C) Me, –20; Et, 40; $PhCH_2$, 90; $CHMe_2$, >160; CH_2CMe_3, >160. This would be compatible with a steric effect on the exchange occurring through an oxygen-bridged dimer.[4]



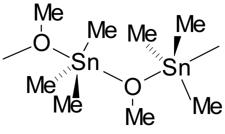
(14-25)

In the crystal, trimethyltin methoxide is a zig-zag polymer with trigonal bipyramidal tin (**14-1**), *r*SnO 220 and 226 pm, SnOSn 131.2°.[23] It readily decomposes into Me_4Sn and, presumably, other tin methoxides, $Me_nSn(OMe)_{4-n}$ ($n < 4$).[24]

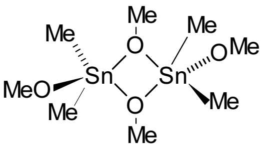
In solution, the dibutyltin dialkoxides and alkyltin trialkoxides are dimeric unless the alkoxyl groups are bulky, and the enthalpy of dissociation of the dialkoxide dimers is 60–100 kJ mol^{-1}.[3, 25] Dimethyltin dimethoxide shows a sharp ^{119}Sn NMR signal in solution at δ –162, consistent with five-coordinate tin, and in the crystal it has the structure **14-2**.[26] Dimethyltin diphenoxide similarly is an oxygen-bridged dimer in the crystal, and in solution is in equilibrium with the monomer.[27]

^{119}Sn NMR Spectroscopy over the range 25–50 °C shows that the degree of association of the monoalkyltin trialkoxides, $BuSn(OR)_3$, in solution depends on the size of the group R and on the temperature. When R = Et, Pr, or Bu, the compounds are 6-coordinate oligomers over the whole of the temperature range. $BuSn(OBu^i)_3$ Is 6-coordinate at room temperature, but 5-coordinate at 150 °C. When R = Pr^i, Bu^s, or CH_2Bu^t, the compounds are 5-coordinate at the low temperature and 4-coordinate at the high temperature, and $Bu^tSn(OBu^t)_3$ is monomeric over the whole temperature range.

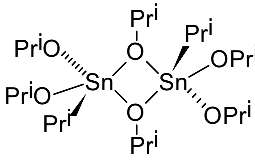
In the crystal, isopropyltin tri-isopropoxide is dimerised (**14-3**), but when it is dissolved, the value of δSn drops from –364 to –218, showing that the principal species in solution is the 4-coordinate monomer.[28]



(**14-1**)



(**14-2**)



(**14-3**)

14.1.3 Reactions

The Sn–OR′ bond in alkoxides and phenoxides shows the same types of substitution and addition reactions that are observed for the Sn–OSn bond in the distannoxanes.

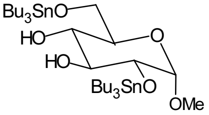
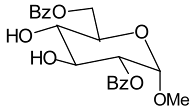
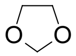
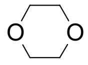
$$R_3Sn\text{-}OR' + N\text{-}E \longrightarrow R_3Sn\text{-}N + E\text{-}OR' \qquad (14\text{-}26)$$

$$R_3Sn\text{-}OR' + N{=}E \longrightarrow R_3SnN\text{-}EOR' \qquad (14\text{-}27)$$

They undergo nucleophilic substitution more readily than the corresponding oxides (but less readily than the amides $R_3SnNR'_2$), and are useful for the stannylation of nucleophiles. They are hydrolysed in air, and precautions have to be taken in handling them. Other protic reagents which can be stannylated by the alkoxides include alcohols, phenols, hydroperoxides, thiols, carboxylic and other acids, carboxamides, sulfonamides, and 1,3-diones. *O*-1,2,3-Triacetyl-,4,6-ethylidene-β–D-glucoside reacts with tributyltin methoxide to give *O*-1-tributylstannyl-2,3-diacetyl-4,6-ethylidene-α-D-glucoside, the structure of which was confirmed by X-ray crystallography.[29]

Examples of substitution reactions of tributyltin alkoxides are given in Table **14-2**.

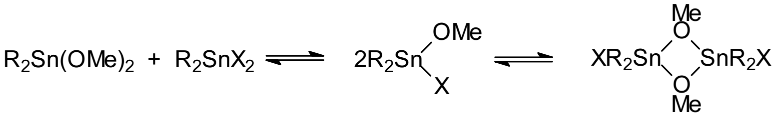
Table 14-2 Substitution reactions of tributyltin alkoxides.

Alkoxide	Co-reagent	Conditions	Product	Ref.
Bu_3SnOMe	Cl_2CHCH_2OH	50 °C	$Bu_3SnOCH_2CHCl_2$	30, 31
Bu_3SnOMe	9-DecalylOOH	Et_2O, RT	Bu_3SnOO-9-decalyl	32
Bu_3SnOEt	$MeCOCH_2COMe$	C_6H_6, 80 °C	$Bu_3SnOCMe{=}CHCOMe$	5
	PhCOCl	20 °C, 7 h		33
Et_3SnOMe	HCONHPh	160 °C, 10 min	$HCONPhSnEt_3$	34
$Bu_2Sn(OEt)_2$	$[MeSi(H)O]_\infty$	Vacuum distillation	Bu_2SnH_2	35
$(Bu_3SnOCH_2)_2$	CH_2Br_2	190 °C, 5 h		36
$(Bu_3SnOCH_2)_2$	$BrCH_2CH_2Br$	170 °C, 2 h		36
Bu_3SnOMe	$Pr^iCH{=}CMeOCOMe$	Boiling	$Pr^iCH{=}CMeOSnBu_3$	37

Exchange reactions also occur readily between alkoxyl groups and other electronegative groups bonded to tin. Triorganotin alkoxides, which are difficult to prepare by other methods, can often be made by exchange between a tin halide and an appropriate tin alkoxide.[38]

$$\text{4-ClC}_6\text{H}_4\text{SnMe}_2\text{Br} + \text{Bu}_3\text{SnOMe} \longrightarrow \text{4-ClC}_6\text{H}_4\text{SnMe}_2\text{OMe} + \text{Bu}_3\text{SnBr} \qquad (14\text{-}28)$$

The ^{119}Sn NMR spectra show that a similar exchange takes place between dialkyltin dimethoxides and dialkyltin dihalides; the principal species present in solution is the alkoxide halide **14-4**, which at high concentration forms the dimer **14-5**, which can be isolated as a crystalline solid.[39]

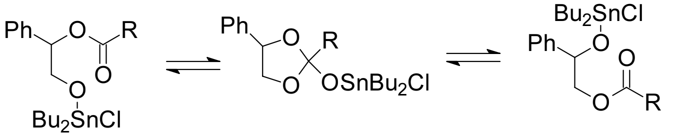

(14-29)

(**14-4**) (**14-5**)

Similar exchange reactions occur, immediately on mixing, between dialkyltin dialkoxides and other dialkyltin compounds R_2SnX_2 where X = NCS, $R''CO_2$, $R''SO_3$ etc., and the mixed-ligand compounds $R_2Sn(OR')X$ can be isolated.[40] A similar exchange reaction takes places between dialkyltin dialkoxides and dialkyltin oxides in boiling benzene to give the 1,3-dialkoxy-distannoxanes (e.g. **14-6**), which can also be obtained from the azeotropic dehydration of Bu_2SnO and the appropriate alcohol.[4]

$$\text{Bu}_2\text{Sn(OMe)}_2 + \text{Bu}_2\text{SnO} \longrightarrow \underset{(\mathbf{14\text{-}6})}{\text{(MeO)Bu}_2\text{SnOSnBu}_2\text{(OMe)}} \qquad (14\text{-}30)$$

Examples of addition reactions of tributyltin methoxide are given in Table 14-3. Most of these reactions are reversible; for example, the alkyl tin carbonate which is formed by the addition of a tin alkoxide to carbon dioxide eliminates CO_2 on heating to regenerate the tin alkoxide (equation 14-14). Again, the product of the reaction of an acyl halide with a dioxastannolane is involved in an exchange reaction in which the tin alkoxide adds reversibly to the carbonyl group (equation 14-31).[41]


(14-31)

These substitution and addition processes can be combined into useful synthetic sequences[48] and a few examples are given here.

Addition + substitution

$$\text{Sn-OR} \xrightarrow{\text{N=E}} \text{Sn-N-E-OR} \xrightarrow{\text{N'-E'}} \text{Sn-N'} + \text{E'-N-E-OR} \qquad (14\text{-}32)$$

The most important example of a combination of addition and substitution processes is the catalysis by organotin compounds of the formation of a urethane from an alcohol and isocyanate.[49] The mechanism which appears to be generally accepted[42] is that the

Table 14-3 Addition reactions of organotin methoxides

Alkoxide	Co-reagent	Product	Ref.
$MeN{=}CO$	Bu_3SnOMe	$Bu_3SnNMeCO_2Me$	42
$S{=}CNPh$	Bu_3SnOMe	$Bu_3SnSC(NPh)OMe$	43
$O{=}CO$	Bu_3SnOMe	$Bu_3SnOC(O)OMe$	43
$S{=}CS$	Bu_3SnOMe	$Bu_3SnSC(S)OMe$	43
$O{=}CHCCl_3$	Bu_3SnOMe	$Bu_3SnOCH(CCl_3)OMe$	44
$PhNC{=}NPh$	Bu_3SnOMe	$Bu_3SnNPhC({=}NPh)OMe$	43
$O{=}SO$	Bu_3SnOMe	$Bu_3SnOS(O)OMe$	43
$TolSO_2N{=}SO$	Bu_3SnOMe	$TolSO_2N(SnBu_3)SO_2Me$	45
$N{\equiv}CCCl_3$	Bu_3SnOMe	$Bu_3SnN{=}C(CCl_3)OMe$	43
$CH_2{=}CO$	Bu_3SnOMe	$Bu_3SnCH_2CO_2Me$	46
$PhN{=}CO$	$Bu_2Sn(OMe)_2$	$Bu_2Sn(OMe)NPhCO_2Me$	47
$O{=}CHMe$	$Bu_2Sn(OMe)_2$	$Bu_2Sn(OMe)CHMeOMe$	47
$EtN{=}CO$	$Bu_2Sn(Cl)OMe$	$Bu_2Sn(Cl)NEtCO_2Me$	47
$S{=}CS$	$Bu_2Sn(OAc)OMe$	$Bu_2Sn(OAc)SC(S)OMe$	47

organotin compound reacts with the alcohol to give an alkoxide.[50] The addition of the alkoxide to the isocyanate to give an *N*-stannylcarbamate (reaction 14-33), followed by acidolysis of the Sn-N bond by the alcohol to give the urethane with regeneration of the alkoxide (reaction 14-34), is then faster than the addition of the alcohol to the isocyanate. For example, 10 mol% of dibutyltin diacetate accelerates the reaction between butanol and phenyl isocyanate by a factor of 600,000. This process is used industrially for the synthesis of polyurethanes, where the catalyst used is commonly dibutyltin dilaurate or stannous "octoate" (2-ethylhexanoate) (Section 23.1).

$$Bu_3SnOR + R'N{=}CO \longrightarrow Bu_3SnNR'CO_2R \tag{14-33}$$

$$Bu_3SnNR'CO_2R + ROH \longrightarrow Bu_3SnOR + HNR'CO_2R \tag{14-34}$$

$$R'N{=}CO + ROH \xrightarrow{Bu_3SnOMe\ cat.} HNR'COOR \tag{14-35}$$

The tetraalkyldistannoxanes, $XR_2SnOSnR_2Y$, have been reported to be active as catalysts, particularly when X and/or Y is NCS, when a template effect may operate.[51] The tetraalkyldistannanes, $(R'CO_2)R_2SnSnR_2(O_2CR')$, can serve as latent catalysts; they are not themselves catalytic, and mixtures with the alcohol and isocyanate have a long pot life, but on exposure to air, aerobic oxidation gives the distannoxanes $(R'CO_2)R_2SnOSnR_2(O_2CR')$ which are catalytic.[52]

Attempts have been made to develop a "green" industrial route to dimethyl carbonate by the reaction of methanol with supercritical CO_2 in the presence of $Bu_2Sn(OMe)_2$ as catalyst.[53, 54] At 300 atm. and 180 °C, and removing the water by recirculating the solution through cooled molecular sieve, a yield of about 46% can be obtained in 24 h.[55–57] The mechanism shown in Scheme 14-2, which involves addition followed by an intramolecular substitution, appears to be compatible with the evidence.

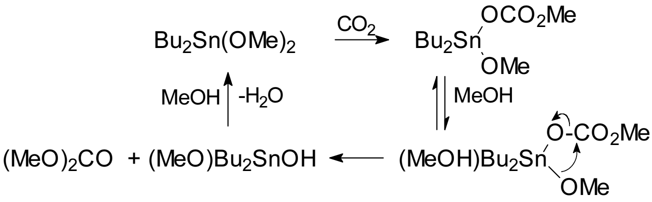
In a related process, methyl carbamate, H_2NCO_2Me, can be used as a CO_2 equivalent.[7]

Addition + addition

Addition of a tin alkoxide to chloral generates a stannylacetal in which the Sn-O bond has a similar reactivity to that of the initial alkoxide so that, with an excess of chloral, polychloral is formed.[58]

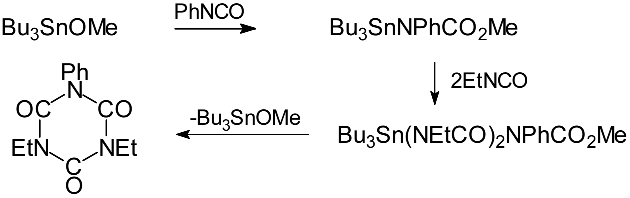
$$Bu_3SnOMe \xrightarrow{i} Bu_3SnOCH(CCl_3)OMe \xrightarrow{ii} Bu_3Sn[OCH(CCl_3)]_{n+1}OMe \tag{14-36}$$

i. $Cl_3CCH{=}O$ ii. $nCl_3CCH{=}O$



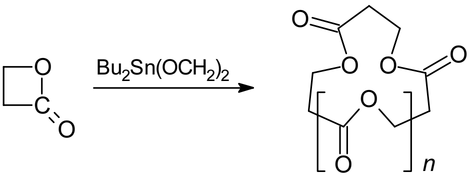
Scheme 14-2 Tin-catalysed formation of dimethyl carbonate.

Multiple addition also occurs with isocyanates. The carbamate which is first formed reacts with more isocyanate to give a 1:3 adduct, which then by cyclic elimination of the tin alkoxide gives an isocyanurate.



(14-37)

Similarly, if β-butyrolactone is treated with the cyclic alkoxide 2,2-dibutyl-1,3,2-dioxastannolane, the cyclic trimer and higher oligomers are formed.[59]

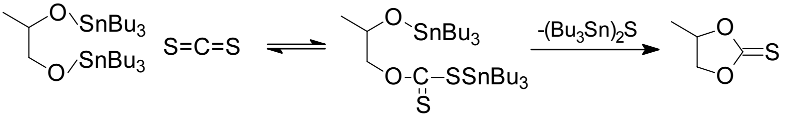


(14-38)

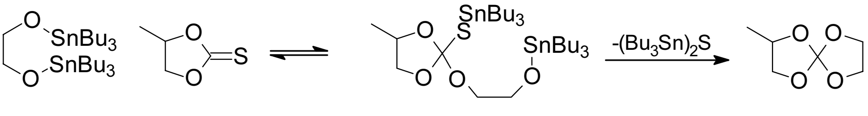
Addition + elimination

The reaction of tributyltin methoxide with hexachloroacetone to give tributyl(trichloromethyl)tin (Section 6.1) involves an addition followed by a 1,2-elimination reaction.

A combination of 1,2-addition and 1,5-elimination reactions between an organotin glycolate and carbon disulfide gives ethylene thionocarbonate, which by a similar sequence reacts with more glycolate to give a spiro-orthocarbonate.[60]



(14-39)



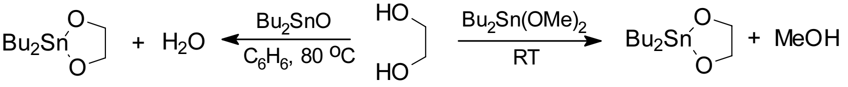
(14-40)

14.2 1,3,2-Dioxastannacycloalkanes

The cyclic diorganotin derivatives of 1,2-diols (the 5-membered ring 1,3,2-dioxastannolanes) are usually more readily available, and, once prepared, are more easy to handle than the acyclic organotin alkoxides, and they have attracted much attention because they can be used as intermediates in the regioselective reaction of the OH groups in, for example, carbohydrates. Relatively little work has been carried out on the 1,3,2-dioxastannacycloalkanes with larger rings, but they appear to have properties intermediate between those of the dioxastannolanes and the acyclic alkoxides.

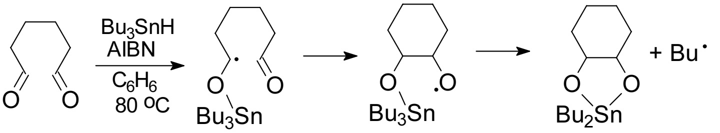
14.2.1 Formation

The 1,3,2-dioxastannacycloalkanes can be prepared by the usual routes to organotin alkoxides, but whereas simple alcohols react with diorganotin oxides only to the stage of the distannoxanes $(R'O)R_2SnOSnR_2(OR')$, 1,2-diols react further to give the dioxastannolanes (equation 14-41).[61, 62] The reactions proceed much more quickly (typically in 4 to 9 min) if the reactants are heated in a microwave oven.[63] Similar reactions can be carried out with dialkyltin dihalides[64] and, under milder conditions, with dialkyltin dialkoxides.[65-67]



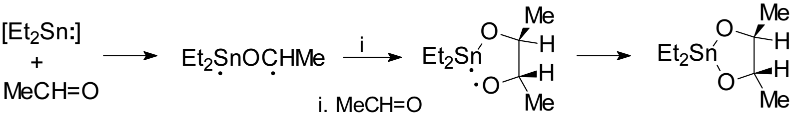
(14-41)

A different approach involves the intramolecular pinacol coupling of 1,5- or 1,6-dialdehydes or -ketoaldehydes with a tin hydride. The ring is closed by an S_H2 reaction of the oxyalkyl radical at the tin centre.[68]



(14-42)

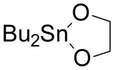
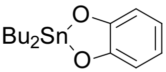
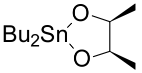
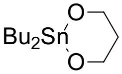
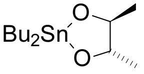
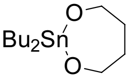
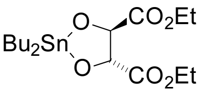
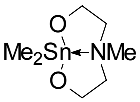
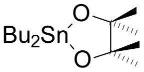
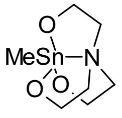
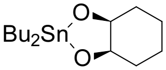
In a related reaction, a stannylene transfer reagent will bring about the intermolecular pinacol coupling of a carbonyl compound.[69]



(14-43)

Some examples of the cyclic dialkoxides are given in Table 14-4.

Table 14-4 1,3,2-Dioxastannacycloalkanes.

Compound	M.p./°C or b.p./°C(mm Hg)	Ref.	Compound	M.p./°C or b.p./°C (mm Hg)	Ref.
	215–220	61, 64, 65, 70		272	71
	124–126	61		200(1.5)	65
	134	72		160(0.2)	65
	140–145	73		68–70	74
	45	65		289–290	75
	164–165	61			

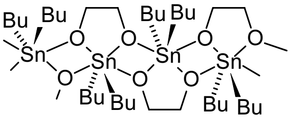
14.2.2 Structures and properties

Crystal structures of four dioxastannolanes[76] and one dioxastannanane have been determined. All four of the dioxastannolanes are associated, but the degree of association depends on the steric requirements of the 1,1-dialkyl groups and on the substituents on the methylene groups of the ring.

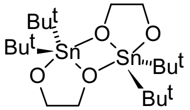
1,1-Dibutyl-1,3,2-dioxastannolane is a ribbon polymer (**14-7**) containing 6-coordinate tin in a highly distorted octahedral arrangement, with inter- and intra-monomer SnO bond lengths within the central 4-membered SnOSnO ring of 204(1) and 251(1) pm, respectively.[70] This corrects earlier conclusions, based on Mössbauer and IR spectroscopy, that the compound had the structure of a distannatetraoxacyclodecane. 1,1-Di-t-butyl-1,3,2-dioxastannolane, on the other hand, is a dimer with 5-coordinate tin with a highly distorted trigonal bipyramidal geometry (**14-8**), and SnO bond lengths within the central ring of 208.6(6) and 225.3(7) pm, and 204.9(7) and 218.8(7) pm respectively, in two independent molecules.[76]

2,3-Di-*O*-dibutylstannylene-4,6-di-*O*-benzylidene-α-D-glucopyranoside (**14-9**) forms a dimer with a structure analogous to that of (**14-8**), and the corresponding average SnO bond lengths are 207.3(25) and 223.7(13) pm.[77, 78] In 2,3-di-*O*-dibutylstannylene-4,6-di-*O*-benzylidene-α-D-mannopyranoside (**14-10**), on the other hand, intra-oligomer repulsion between the glucoside units is less severe, and the molecule exists in the crystal as a pentamer (**14-11**), with three 6-coordinate and two 5-coordinate tin atoms. In the formula (**14-11**), the mannoside unit is simplified for the sake of clarity.[79]

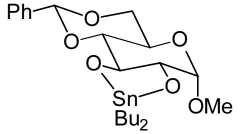
1,1-Dibutyl-1,3,2-dioxastannanane is a ribbon polymer (**14-12**) with *r*SnO 203.6(6) and 256.2(6) pm.[80]



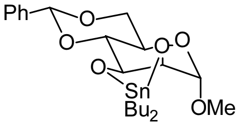
(**14-7**)



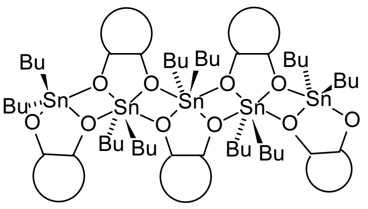
(**14-8**)



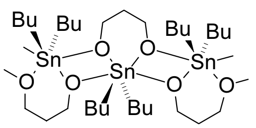
(**14-9**)



(**14-10**)



(**14-11**)



(**14-12**)

The 5- or 6-coordinate tin which is present in the solid dioxastannolanes and dioxastannananes shows high-field ^{119}Sn signals in the solid state NMR spectrum. For example, the dimer of the ethylidene equivalent of **14-9** shows signals at –126 and –129 ppm for the 5-coordinate tin (–125 in $CDCl_3$ solution), and the mannoside pentamer shows signals at –119 and –127 ppm for the two terminal 5-coordinate tin atoms, and –223 and –234 ppm for the inner 6-coordinate tin atoms.

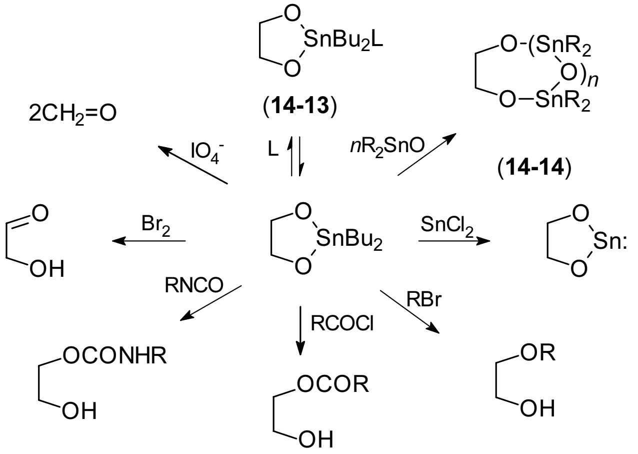
With most of the dioxastannolanes, the principal species present in solution in non-coordinating solvents (e.g. $CDCl_3$) appears to be the dimer; at higher concentration, and particularly at low temperature, higher oligomers can be detected, but there seems to be little evidence for the presence of monomers.

The ^{119}Sn chemical shifts for the oligomers of 2,2-di-n-butyl-1,3,2-dioxastannolane can be used to determine the equilibrium constants and thermodynamic parameters for the equilibria between the various oligomers. Thus in a 0.072 M solution in $CDCl_3$/$CHClF_2$ (3 : 1) at 300 K, the mole fractions of dimer, trimer, tetramer, and pentamer are 0.77, 0.20, 0.032 and 0.00002 respectively, but at 200 K, they are 0.14, 0.52, 0.29, and 0.058 respectively, and the value of $\Delta G°$ for the dimerisation of two molecules of dimer to give one of tetramer is -10.5 ± 0.4 kJ mol^{-1}.[72] For the dimer-tetramer equilibrium in 2,2-dibutyl-1,3,2-dioxastannanane, the corresponding value for $\Delta G°$ is –26.4 kJ mol^{-1}.[80]

The principal reactions of the dioxastannolanes are illustrated in Scheme 14-3. The fact that the stannolanes exist in solution as dimers or higher oligomers has an important effect on the course of some of these reactions.[81]

The OSnO angle in a monomeric dioxastannolane is about 80°, much less than the tetrahedral angle required for *sp*^{3} hybridisation. This strain will be relieved if a fifth ligand coordinates to the tin, so that the ring bridges the axial and equatorial positions in a trigonal bipyramid. This may account in part for the readiness with which the dioxastannolanes form oligomers, and in line with this, they also form rather unstable 1 : 1 complexes, $R_2Sn(OCH_2)_2 \cdot L$ (**14-13**, Scheme 14-3), with ligands such as pyridine, DMF, DMSO, THF, and sulfolane. The ligands can be removed under reduced pressure, and, in solution, the complexes appear to be extensively dissociated. No complex with water could be obtained, hydrolysis occurring to give, probably, $HOBu_2SnOSnBu_2OH$.[82]

Similar complexes are not known for the dioxastannananes or acyclic dialkyltin dialkoxides.

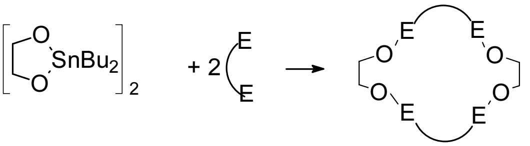


Scheme 14-3 Reactions of dioxastannolanes.

If the dioxastannolanes are heated with dibutyltin oxide in an inert solvent, the oxide dissolves and the telomers (**14-14**, Scheme 14-3; R = Bu) can be isolated usually as amorphous solids. The higher telomers (e.g. *n* = 10) can be used as a soluble source of dibutyltin oxide.[82] Tin(II) chloride reacts with **14-14** to give the corresponding tin(II) dioxastannolane and dibutyltin dichloride.[83] Cyclic oligomers of the type of **14-4** may be responsible for the unusual regioselectivity that occurs in the formation of benzoates when various glycosides are heated with an excess of Bu_2SnO, then treated with benzoyl chloride.[84]

Bromine reacts at room temperature to give the corresponding ketols[85] and the usual glycol-cleavage reagents [$Pb(OAc)_4$, $NaIO_4$, $PhI(OAc)_2$, and $Ph_3Bi(OAc)_2$] give the corresponding pair of carbonyl compounds.[86]

Electrophiles such as acyl halides or organic isocyanates react to give the 1-hydroxy-4-carboxylates or -carbamates, or 1,4-bis-carboxylates or -carbamates, depending on the ratio of reagents. Reactions with biselectrophiles such as bis(acyl halides) or bis-isocyanates give cyclic tetracarboxylates or tetracarbamates built up from two dioxastannolane units and two of the biselectrophile (equation 14-44). This may be a consequence of the (principally) dimeric structure of the dioxastannolanes in solution.[59, 87, 88]

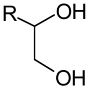
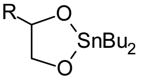


(14-44)

The acylation reactions can be carried out with the diol, acyl halide, triethylamine, and a catalytic amount of Bu_2SnO (0.2 molar equivalents)[89, 90] or of Me_2SnCl_2 (0.01–0.1 molar equivalents).[91] A kinetic resolution of diols RC*H(OH)CH_2OH has been achieved by use of a chiral diaryltin dibromide catalyst.[92]

A second apparent consequence of this dimeric structure is that reactions of substituted dioxastannolanes often show a regioselectivity towards electrophiles which is opposite to that shown by the parent diols, as illustrated in Table 14-5.[93]

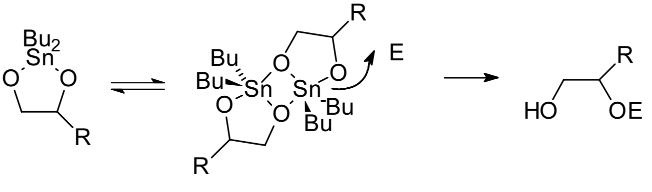
Table 14-5 Regioselective reactions of dioxastannolanes.

Reactant	R	Conditions	A : B
	Me	PhCOCl, py	91 : 9
	Ph		96 : 4
	Me	PhCOCl	15 : 85
	Ph		5 : 95

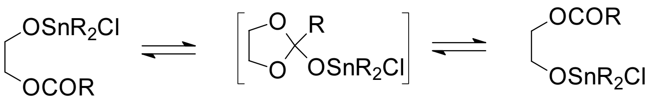
A = $PhCO_2CH_2CHROH$ B = $HOCH_2CHROCOPh$

These reactions are particularly useful in the regioselective acylation and alkylation of carbohydrates, when the selectivity depends on the nature of the solvent, and of the dimers or higher oligomers which are present.

The selectivity can sometimes be rationalised on the basis of the mechanism illustrated in equation 14-45. The less substituted diol moiety, which is more reactive towards electrophiles in the diol, is also more prone to donate to tin in forming the dimer of the dioxastannolane, leaving the unassociated more substituted oxygen centre as the stronger nucleophile. However, the acylation reactions are complicated by the equilibration of the two possible isomers by the reaction 14-46, and by a suitable choice of reaction conditions, regioselectivities of <99% can often be obtained.[41, 94–96]

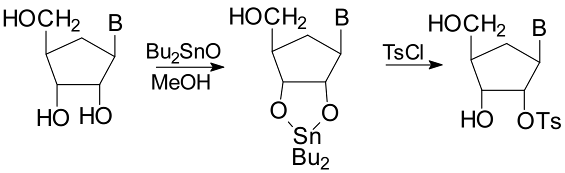


(14-45)



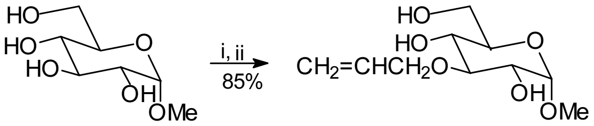
(14-46)

Tosylation gives the corresponding tosylates (equation 14-47).[97] Benzylation and allylation by the corresponding bromides is catalysed by quaternary ammonium salts[98] and the reactions can be carried out without isolating the dioxastannolane (equations 14-48,[98] and 14-49[67]).



(14-47)

(B = uracil, cytosine, adenine, hypoxanthine)



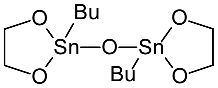
i. Bu_2SnO, C_6H_6, reflux. ii. CH_2=$CHCH_2Br$, Bu_4NI, 60 °C

(14-48)

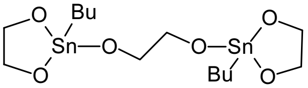
i. $Bu_2Sn(OEt)_2$, C_6H_6. ii. $PhCH_2Br$, Bu_4NI, 50 °C

(14-49)

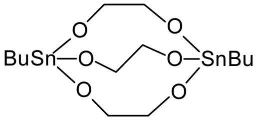
Less work has been carried out on the cyclic monoalkyltin glycollates. Azeotropic dehydration of a mixture of butylstannonic acid and ethane-1,2-diol gives products which are believed to have the structures **14-15**, and **14-16** or **14-17**.[99]



(**14-15**)



(**14-16**)



(**14-17**)

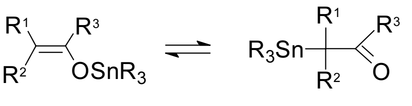
A similar reaction of a stannonic acid with triethanolamine, or of an alkyltin trihalide and triethanolamine in the presence of sodium methoxide (equation 14-50) gives stannatranes,[100] which have attracted some attention because of their interesting structures and their relation to the silatranes which have purported physiological properties.

$$BuSnCl_3 + N(CH_2CH_2OH)_3 \xrightarrow[90\%]{MeONa} BuSn(OCH_2CH_2)_3N \qquad (14\text{-}50)$$

Methylstannatrane hexahydrate, $MeSn(OCH_2CH_2)_3N \cdot 6\,H_2O$, in the crystal is a trimer containing one central 7-coordinate and two terminal 6-coordinate tin atoms, and this trimeric structure is preserved in solution.[75]

14.3 Acyclic Organotin Enolates

Organotin enolates (vinyloxystannanes) (**14-18**), containing an Sn–O bond, are in metallotropic equilibrium with the corresponding Sn–C bonded α-stannylcarbonyl compounds (**14-19**), providing a further example of the equivalent behaviour of hydrogen (prototropy) and metals (metallotropy) (Section 3.1.1.7).

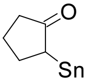
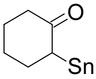


(**14-18**) (**14-19**)

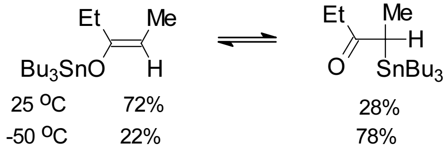
(14-51)

The position of the equilibrium has been shown by IR, and ^{1}H [37, 101] and ^{119}Sn NMR spectroscopy[102] to depend sensitively on the nature of the substituents, particularly their size, bulky groups favouring the less sterically congested enol form. Some typical results are shown in Table 14-6.

Table 14-6 Enol : keto proportions of stannyl enolates in $CDCl_3$ solution at room temperature.

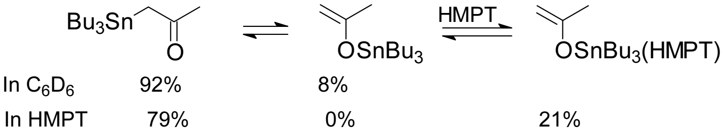
Compound (keto form)	% Enol **14-18**	% Keto **14-19**
$Bu_3SnCH_2COCH_3$	0	100
$Bu_3SnCHMeCOMe$	23	77
$Bu_3SnCHBu^tCOMe$	100	0
 R = Me or Ph R = Bu	0 57	100 43
 R = Me, Bu or Ph	100	0
$Bu_3SnCHEtCHO$	100	0
$Bu_3SnCHMeCOCMe_3$	>99	1
Bu_3SnCMe_2CHO	100	0

The reversible dependence of the keto/enol composition on temperature (e.g. equation 14-52) establishes that the two forms are in equilibrium. This structural mobility renders the reactions independent of the proportion of enol and keto form, and it is convenient to treat the compounds here together with the alkoxides, irrespective of the precise composition of the isomeric mixture.



(14-52)

In the presence of a good ligand (e.g. HMPT, Bu_3PO, or Bu_4NBr), the 5-coordinate enolate complex is formed; the equilibrium is shifted in favour of the enolate (equation 14-53)[103] and the enolate nucleophilicity is enhanced.



(14-53)

14.3.1 Preparation

A number of methods are now available for preparing the tin enolates, which are often not isolated, but are generated and caused to react further *in situ*. Tributyltin methoxide reacts exothermically with enol acetates without a solvent, to give the corresponding stannyl enolate, and methyl acetate which can be removed under reduced pressure or by slow distillation (b.p. 57 °C) (e.g. equation 14-54).[37, 104, 105]

$$Bu_3SnOMe + CH_2{=}CMe(OAc) \xrightarrow[70\%]{} CH_2{=}CMe(OSnBu_3) + MeOAc \qquad (14\text{-}54)$$

Lithium enolates react with organotin halides (e.g. equation 14-55),[106] and, in a mechanistically similar process, α-methoxyketones react with stannylamines,[107] or α-halogenoketones with stannylcarbamates.[108]

$$\mathrm{MeCOCH_2Me \xrightarrow{LDA} MeC(OLi){=}CHMe \xrightarrow[-76\ ^{o}C]{Ph_3SnCl} MeC(OSnPh_3){=}CHMe} \quad (14\text{-}55)$$

$$\mathrm{PhCOCH_2OMe + Bu_3SnNPr^i_2 \xrightarrow[30\ min]{0\ ^{o}C} PhC(OSnBu_3){=}CHOMe} \quad (14\text{-}56)$$

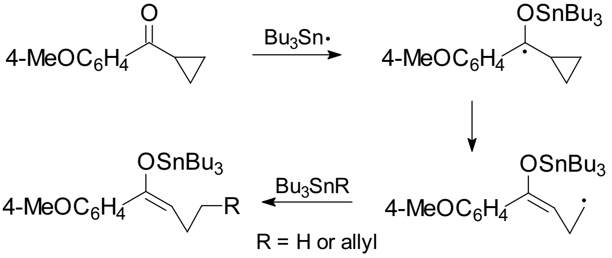
$$\mathrm{Me_3CCOCH_2Br + Bu_3SnNEtCO_2Me \longrightarrow Me_3CC(OSnBu_3){=}CHBr} \quad (14\text{-}57)$$

Stannyl enolates can also be prepared by hydrostannation of enones. The reagent Bu_2SnIH/Bu_3SnI (prepared by reducing Bu_2SnI_2 with Bu_3SnH) was found to be better than Bu_3SnH, Bu_2SnH_2, Bu_2SnIH, Bu_2SnClH/Bu_3SnCl, or Bu_2SnBrH/Bu_3SnBr for reducing chalcone. 1,2-Dinitrobenzene has little effect on the rate, and the reaction is thought to follow a polar rather than a radical mechanism.[109]

$$\mathrm{PhCOCH{=}CHPh + Bu_2SnHI/Bu_3SnI \xrightarrow[2\ h.\ 91\%]{0\ ^{o}C} PhC(OSnBu_2I){=}CHCH_2Ph} \quad (14\text{-}58)$$

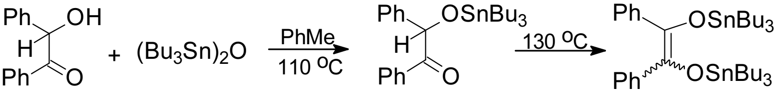
On the other hand, a homolytic mechanism is involved in the hydrostannation of methyl vinyl ketone in the presence of CuCl,[110] and in the reaction of tributyltin hydride or allyltributyltin with cyclopropyl ketones in the presence of AIBN.[14, 111]

$$\mathrm{MeCOCH{=}CH_2 + Bu_3SnH \xrightarrow[Et_2O,\ RT]{CuCl} MeC(OSnBu_3){=}CHCH_3} \quad (14\text{-}59)$$



(14-60)

Bis(tributyltin) enediolates can be prepared from the reaction of acyloins with bis(tributyltin) oxide or tributyltin methoxide (equation 14-61).[112]

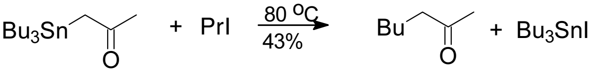


(14-61)

14.3.2 Reactions

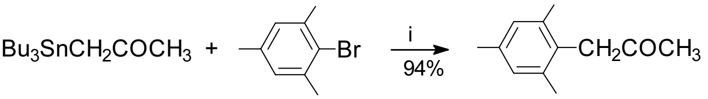
The tin enolates are useful in organic synthesis as a mild source of the nucleophilic enolate group in its reaction with alkyl or acyl halides, aldehydes or enones. The tin enolates are less basic than the lithium enolates, and more reactive though rather less easy to handle than the silicon enolates.[105, 113]

The reaction with halides such as methyl iodide, allyl bromide, benzyl bromide, bromomethyl acetate, or methoxymethyl chloride, to give the C-alkylated product, can be carried out in HMPT or without solvent.[114]



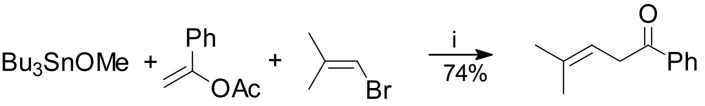
(14-62)

The reaction of less electrophilic halides, particularly aryl and vinyl halides, can be catalysed with a palladium compound (equations 14-63 and 14-64),[115] and the tin enolate can be prepared *in situ* from the enol acetate and tributyltin methoxide, or lithium enolate and tributyltin trifluoroacetate, or silyl enolate and tributyltin fluoride.



(14-63)

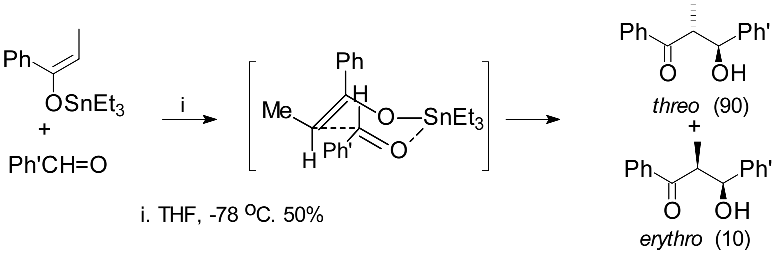
i. PhMe, PdCl$_2$[(*o*-MeC$_6$H$_4$)$_3$P]$_2$, 100 °C, 5 h



(14-64)

i. PhMe, PdCl$_2$[(*o*-C$_6$H$_4$)$_3$P]$_2$, 100 °C, 5 h

Aldol condensation of the tin enolates with aldehydes often takes place spontaneously at room temperature, but Lewis acids (e.g. $TiCl_4$, $BF_3.OEt_2$, $ZnCl_2$, $CuCl_2$) or $PdCl_2[(o\text{-}C_6H_4)_3P]_2$ can be used as catalysts, and enantioselective addition can be achieved with an (*R*)-BINAP-AgOTf catalyst.[101] The stereoselectivity is dependent on the presence of a cyclic transition state **14-20**.[104]

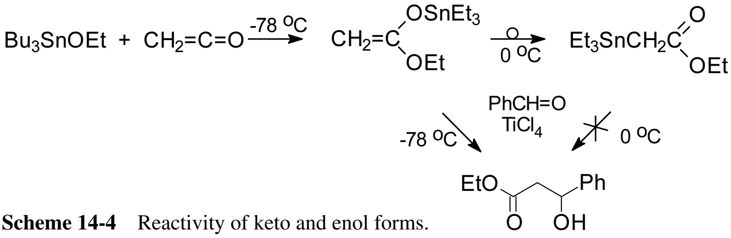


(14-65)

i. THF, -78 °C. 50%

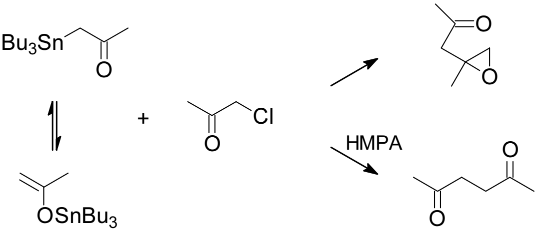
(**14-20**)

Evidence that the enol form is more reactive than the keto form is shown in Scheme 14-4. Tributyltin ethoxide reacts with ketene at –78 °C to give the ketene acetal, which at the same temperature adds to benzaldehyde to give the hydroxyester. However, if the enolate is allowed to stand at 0 °C for several hours before the aldehyde is added at that temperature, no reaction occurs.[116]



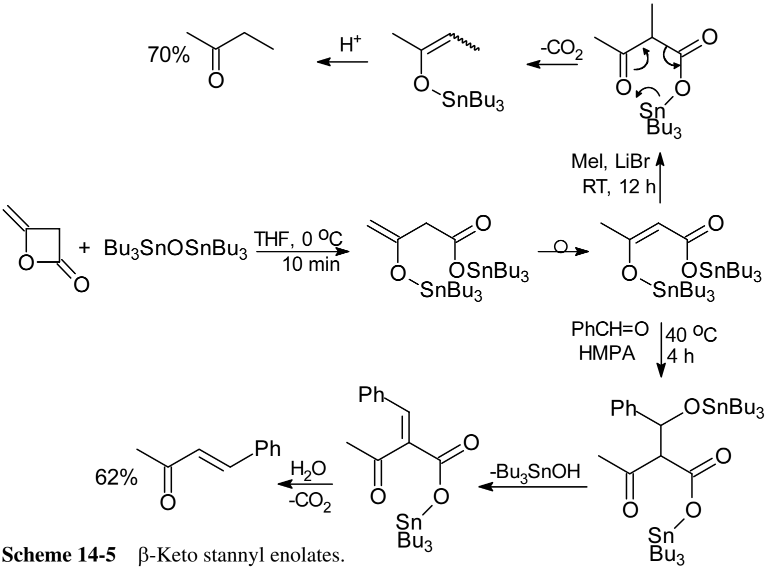
Scheme 14-4 Reactivity of keto and enol forms.

With α-halogenoketones, attack is principally at the carbonyl group to give an epoxide, but in the presence of a good ligand for the tin,[103, 117, 118] or of a Lewis acid catalyst,[119] coupling occurs with the displacement of halogen.



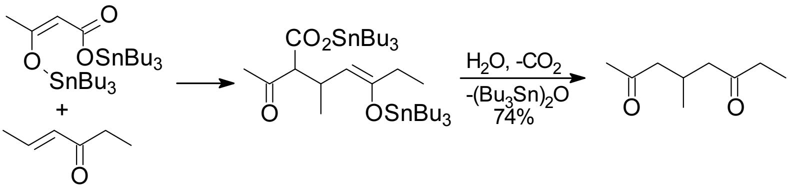
(14-66)

β-Keto stannylenolates can be prepared by the reaction of Sn−O or Sn−N bonded compounds with diketene, which can be regarded as a cyclic enol ester. The adducts formed from bis(tributyltin) oxide can undergo further reaction, with subsequent decarboxylation, to give the same products as those from the simple enolates. Alkylation with alkyl iodides or benzyl or allyl bromides is strongly catalysed by lithium bromide (e.g. Scheme 14-5). Double alkylation can be achieved with HMPA as solvent.[120] The product of alkylation before the final hydrolysis is itself a tin enolate, which can be used in reactions with further carbon electrophiles.



Scheme 14-5 β-Keto stannyl enolates.

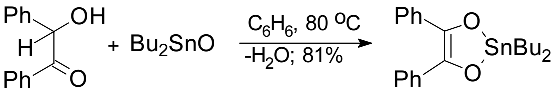
The β-keto stannyl enolates will give aldol reactions with aldehydes (Scheme 14-5),[121] and are more reactive than the simple enolates in that they also show Michael additions with unsaturated carbonyl compounds (equation 14-67).[122]



(14-67)

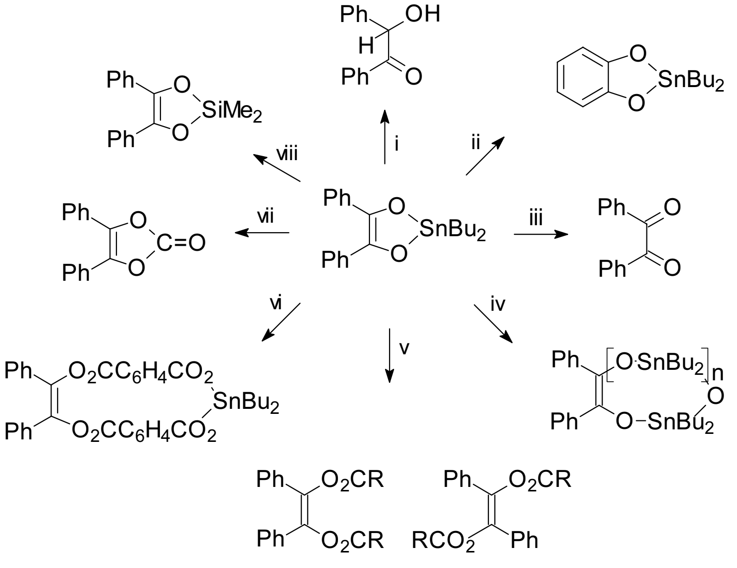
14.4 1,3,2-Dioxastannolenes

The dioxastannolenes are related to the acyclic enolates in the same way as the dioxastannolanes are related to the acyclic alkoxides, and similarly have special properties. They can readily be prepared by reaction of a diorganotin oxide with an acyloin or the cyclic carbonate of an ene-1,2-diol (e.g. equation 14-68).[112]



(14-68)

1,1-Dibutyl-3,4-diphenyl-1,3,2-dioxastannolene is a monomer in dilute solution in chloroform, and appears to be associated in the solid, though no X-ray structure has yet been reported. Its principal reactions are shown in Scheme 14-6.[112]



i, H_3O^+. ii, o-$C_6H_4(OH)_2$. iii, Br_2 or O_2. iv, Bu_2SnO. v, RCOCl or $(RCO)_2O$
vi, o-$C_6H_4(CO)_2O$. vii, $COCl_2$. viii, Me_2SiCl_2

Scheme 14-6 Reactions of 2,2-dibutyl-3,4-diphenyl-1,3,2-dioxastannolene.

These reactions are generally similar to those shown by the saturated dioxastannolanes. The stannolenes are less readily hydrolysed than the stannolanes, and the conjugation of the unshared electrons on oxygen in the dioxastannolenes appears to render them less nucleophilic. Thus 2,2-dibutyl-3,4-diphenyl-1,3,2-dioxastannolene does not react with organic isocyanates, whereas the stannolanes do react to give carbamates. Acetyl chloride reacts to give the *cis*-diacetate, but acetic anhydride gives mainly the *trans*-diester.

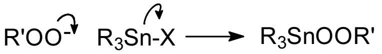
A distinguishing feature of the stannolenes is their sensitivity to oxygen, and in the air they are oxidised to the 1,2-diones and the telomer of the diorganotin oxide with the stannolene. A radical chain mechanism can be envisaged involving attack of a stannylperoxyl radical at the double bond, analogous to the reaction of acyclic tin enolates with carbon tetrachloride.[112]

14.5 Organotin Peroxides[123–125]

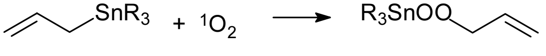
The organotin hydroperoxides (R_3SnOOH), peroxides ($R_3SnOOSnR_3$), and alkyl peroxides (R_3SnOOR'), have a heterolytic chemistry which is similar to that of the corresponding monoxy compounds (R_3SnOH, $R_3SnOSnR_3$, R_3SnOR', respectively), but the peroxides show also a characteristic homolytic chemistry. Like all organic peroxides, the organotin peroxides should be regarded as being potentially explosive, and when the peroxide content is high they should be handled only on a small scale, taking the appropriate precautions.

The two principal routes to the organotin peroxides involve substitution by a peroxide nucleophile at a tin centre (equations 14-69 and 14-70), or (pericyclic) reaction of an allyltin compound with singlet oxygen (equation 14-71). Distannyl peroxides have also been prepared by the (homolytic) reaction of distannanes with triplet oxygen (equation 14-72).

$$HOO^- \; R_3Sn\text{-}X \longrightarrow R_3SnOOH \xrightarrow{R_3Sn\text{-}X} R_3SnOOSnR_3 \qquad (14\text{-}69)$$



$$R'OO^- \; R_3Sn\text{-}X \longrightarrow R_3SnOOR' \qquad (14\text{-}70)$$



(14-71)

$$R_3SnSnR_3 + {}^3O_2 \longrightarrow R_3SnOOSnR_3 \qquad (14\text{-}72)$$

The hydroperoxides R_3SnOOH are rather unstable and have been little investigated. Trimethyl- and triphenyl-tin hydroperoxide are obtained when the corresponding hydroxide is treated with 98% H_2O_2 (Caution!) in ether or toluene at or below room temperature (e.g. equation 14-73).[126] In dioxane, Me_3SnOOH decomposes at room temperature to give Me_3SnOH, Me_2SnO, MeOH, and O_2, and Ph_3SnOOH explodes reproducibly at 75 °C. Triethyltin hydroperoxide is reported to form a complex $(Et_3SnOOH)_2.H_2O_2$ with hydrogen peroxide.

$$Me_3SnOH + HOOH \xrightarrow[0\ ^oC,\ 81\%]{Et_2O} Me_3SnOOH \qquad (14\text{-}73)$$

Similarly, few investigations have been made of the distannyl peroxides $R_3SnOOSnR_3$. They can be obtained by treating the corresponding trialkyltin methoxide with concentrated or anhydrous hydrogen peroxide (equation 14-74),[127, 128] or the bis(trialkyltin) oxide in ether with concentrated hydrogen peroxide in the presence of a mild desiccant (Na_2SO_4).[129] Bis(triphenyltin) peroxide has also been obtained by treating triphenyltin chloride with hydrogen peroxide in the presence of ammonia.[127] Like the hydroperoxides, the distannyl peroxides are thermally unstable. Bis(tributyltin) peroxide can be kept for about 1 day at –20 °C,[128] but is reported to decompose completely in 24 h at 0 °C.

$$Bu_3SnOMe + HOOH \xrightarrow[0\ ^{o}C,\ 1\ h]{Et_2O,\ H_2O_2} Bu_3SnOOSnBu_3 \qquad (14\text{-}74)$$

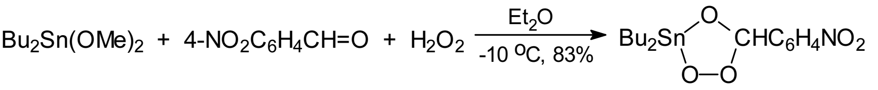
Some examples of stannyl hydroperoxides and peroxides are included in Table 14-7.

Stannyl hydroperoxides and distannyl peroxides are probably formed in homolytic chain reactions when triplet oxygen reacts with tin hydrides or distannanes, respectively, but the peroxide products are rapidly reduced by the reactants and these reactions are not useful preparatively.

Silyl and germyl hydrotrioxides, R_3MOOOH, have been characterised from the reaction of the corresponding hydrides with ozone at –78 °C. Under the same conditions, trialkyltin hydrides probably give the tin hydrotrioxides $R_3SnOOOH$, but only their decomposition products (e.g. Me_3SnOH, Me_2SnO, MeOH, and O_2, from Me_3SnH) have been observed.[130] Unstable distannyl trioxides, $R_3SnOOOSnR_3$, have also been reported to be formed from the ozonolysis of the distannanes R_3SnSnR_3.[131]

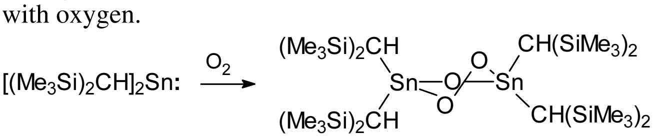
If dialkyltin dialkoxides are treated with 98% hydrogen peroxide in ether, insoluble cyclic or linear dialkyltin peroxides $(R_2SnOO)_n$ are formed. These are thermally more stable than the bistrialkyltin peroxides, $R_3SnOOSnR_3$, and lose about half their peroxide content in one month at room temperature. If the reactions are carried out in the presence of an aldehyde, 1,2,4-trioxa-3-stannolanes are formed, together perhaps with some oligomeric material.[132]

$$Et_2Sn(OMe)_2 + H_2O_2 \xrightarrow[-10\ ^{o}C,\ 68\%]{Et_2O} (Et_2SnOO)_n \qquad (14\text{-}75)$$



(14-76)

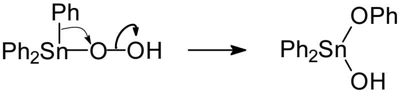
A unique 1,2,4-trioxa-3,5-distannolane (**14-21**) has been obtained from the reaction of bis[bis(trimethylsilyl)methyl]tin(II) with oxygen in the presence of $[Mo_2(OAc)_2(MeCN)_6][BF_4]$, and has been characterised by X-ray crystallography.[133] An analogous 1,2,4,5-tetraoxa-3,6-distannanane is obtained when $[(Me_3Si)_2N]_2Sn{:}$ is treated with oxygen.



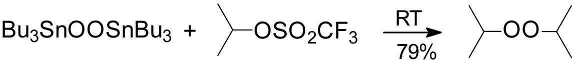
(14-77)

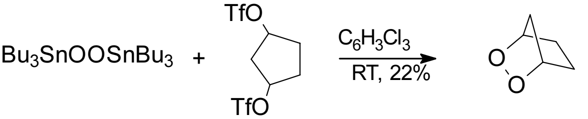
(**14-21**)

Little work has been carried out on the properties of these stannyl hydroperoxides and distannyl peroxides. Their thermal instability might suggest homolysis of the O–O bond, but the cleavage of the R–Sn bond which is observed might equally be regarded as resulting from a heterolytic mechanism similar to that which was invoked to account for the instability of the acylperoxysilicon compounds.[134]


(14-78)

Despite their thermal instability, the distannyl peroxides have found some application in organic synthesis as a source of nucleophilic peroxide. Secondary alkyl peroxides are difficult to prepare by nucleophilic substitution by alkaline hydrogen peroxide because the products are decomposed under the alkaline conditions, but they can be obtained in fair yield by treating alkyl triflates with bis(tributyltin) peroxide.[128, 135]

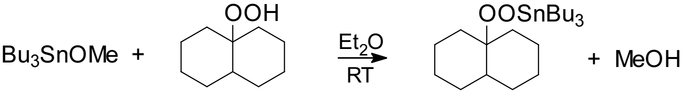

(14-79)


(14-80)

In contrast to these unstable stannyl hydroperoxides and distannyl peroxides, organoperoxytin compounds containing the moiety SnOOR are stable and well characterised.

Mono- and di-alkylperoxytin compounds can be prepared by treating the corresponding mono- or di-halides with the sodium salts of hydroperoxides[32, 127, 136] or with the hydroperoxides in the presence of ammonia[127] or an amine,[137] or from the reaction of the corresponding tin alkoxides with hydroperoxides.[32] Trialkyl(alkylperoxy)stannanes are also formed when the corresponding tin hydride is treated with two molar equivalents of a hydroperoxide; presumably the alkoxide is formed as an intermediate.[32] Again, by analogy with the preparation of alkoxides, the peroxides can be prepared by azeotropic dehydration of a mixture of the bistrialkyltin oxide and hydroperoxide.[137] Under these conditions, dialkyltin oxides react to give the tetraalkyldiperoxydistannoxanes, $(R'OO)R_2SnOSnR_2(OOR')$; $(Bu^tOO)Bu_2SnOSnBu_2(OOBu^t)$ is dimeric in benzene and doubtless has the tricyclic structure which has been established for other related distannoxanes (see Section 12.2). Some typical preparations of alkylperoxytin compounds by these reactions are shown in equations 14-81–14-84, and examples of the tin peroxides are given in Table 14-7.

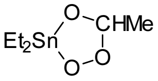
$$Et_3SnBr + Bu^tOONa \xrightarrow[MeONa]{Et_2O/MeOH} Et_3SnOOBu^t + NaBr \qquad (14\text{-}81)$$


(14-82)

$$Bu_3SnH + Bu^tOOH \xrightarrow[RT]{C_{10}H_{18}} H_2O + [Bu_3SnOBu^t] \xrightarrow{Bu^tOOH} Bu_3SnOOBu^t \qquad (14\text{-}83)$$

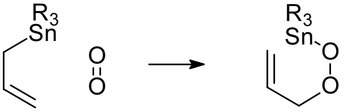
$$Bu_2SnO + Bu^tOOH \xrightarrow[-H_2O]{C_6H_6,\ boil} (Bu^tOO)Bu_2SnOSnBu_2(OOBu^t) \qquad (14\text{-}84)$$

Table 14-7 Organotin peroxides.

Peroxide	M.p. (°C) or b.p. (°C /mmHg)	Ref.	Peroxide	M.p. (°C) or b.p. (°C /mmHg)	Ref.
Me_3SnOOH	97 dec	126	$Bu_3SnOOBu^t$	87/0.04	32
Ph_3SnOOH	75 expl	126	$Bu_2Sn(OOBu^t)_2$	100/0.001	32
$(Et_2SnOO)_n$	97 expl	126	$[(Bu^tOO)Me_2Sn]_2O$	97–100	127
$Me_3SnOOBu^t$	56/12	127	$[(Bu^tOO)Bu_2Sn]_2O$	78–79	137
$Et_3SnOOCMe_2Ph$	86–87/0.04	127		123 dec	132

There are reports dating from the late 1970s, of the reaction of diorganotin porphyrins, $R_2Sn(Por)$, with oxygen under UV irradiation, to give the mono- and diperoxides $(ROO)(R)Sn(Por)$ and $(ROO)_2Sn(Por)$.[138–141] This work is described in Section 16.2.

The formation of allylperoxytin compounds by the ene reaction of an allyltin compound with singlet oxygen has been referred to in Section 9.1.3.4.



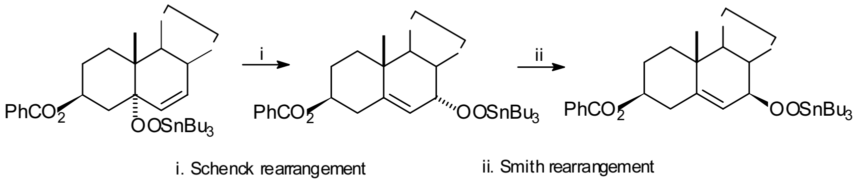
(14-85)

The singlet oxygen is generated by irradiating a solution containing a photosensitiser such as Rose Bengal (soluble in polar solvents) or tetraphenylporphine (soluble in non-polar solvents), with light from a sodium lamp. Oxygen is bubbled through the solution, or, on a small scale, the solution can be stirred under oxygen on a gas burette. The reactions are catalysed by high concentrations of lithium perchlorate.[142] The allyltin compounds are more reactive than the corresponding hydrocarbons, and the reactivity in the metalloene sense increases with increasing electronegativity of the ligands R on tin. When all three groups R are alkyl, an appreciable amount of the hydrogen-ene reaction, and of cyclisation and rearrangement to give the 4-stannyl-1,2-dioxolane, may accompany the metalloene reaction (see Section 9.1.3.4), but with at least one electronegative group on tin (e.g. Cl or OAc; equation 14-86), the metalloene reaction occurs exclusively. Tetraallyltin, however, gives only $Sn(OOCH_2CH{=}CH_2)_4$ and none of the byproducts.[143, 144] The M-ene pathway seems to be less significant for secondary allylstannanes $Bu_3SnCHRCH{=}CHR'$.[145]

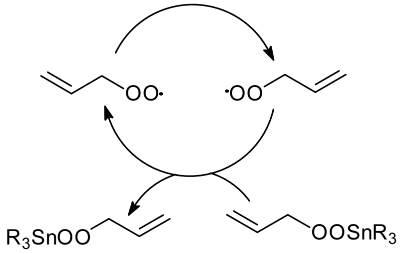
$$ClBu_2SnCH_2CH{=}CH_2 + O_2 \xrightarrow[\text{ca. }100\%]{\text{i}} ClBu_2SnOOCH_2CH{=}CH_2 \qquad (14\text{-}86)$$

i. CH_2Cl_2, tetraphenylporphine, sodium light

The allylperoxystannanes, like the allyl hydroperoxides, undergo the Schenck and Smith allylic rearrangements as illustrated in equation 14-87 for cholesterol derivatives.[146, 147] The rearrangements of the hydroperoxides are well established to be radical chain reactions;[148, 149] the rearrangements of the tin derivatives are inhibited by phenols, and it is assumed that they also proceed by a radical chain mechanism as illustrated for the Schenck rearrangement in Scheme 14-7.[150, 151] It will be noted that the mechanism assumes a bimolecular peroxyl-for-peroxyl radical substitution at the trialkyltin centre. The actual migration of the peroxyl group probably involves dissociation of the allylperoxyl radical into an allyl radical and triplet oxygen.



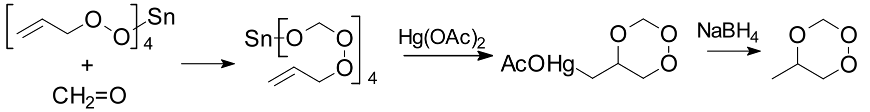
(14-87)



Scheme 14-7 Mechanism of the Schenck rearrangement.

The Sn–O bond in the alkylperoxytin compounds will in all probability show the same substitution and addition reactions as it does in alkoxytin compounds, but few studies of these reactions have been reported. In the air, hydrolysis occurs, and the stannyl peroxides, $ROOSnBu_3$, have been shown to react with electrophiles such as triphenylmethyl chloride, methoxymethyl chloride, t-butyldimethylsilyl triflate, and acyl halides or acid anhydrides to give the peroxides $ROOCPh_3$, $ROOCH_2OMe$, $ROOSiMe_2Bu^t$, and $ROOCOR'$, respectively. [137, 146]

The ease of addition of the Sn–O bond of a peroxide to a carbonyl group has been exploited in an improved route to the 1,2,4-trioxane antimalarials.[152]



(14-88)

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15 Organotin Hydrides[1, 2]

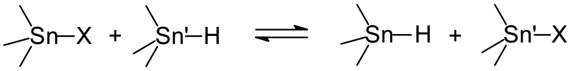
In recent years, the organotin hydrides have found extensive applications in organic syntheses which involve radical chain reactions in which the stannyl radical $R_3Sn^\bullet$ is a chain-carrying intermediate. Tributyltin hydride has been used most widely, and is commercially available.

15.1 Preparation

The organotin hydrides are usually prepared by reducing an organotin halide or other derivative R_nSnX_{4-n} with a metal hydride.

$$R_nSnX_{4-n} + 4\text{-}nMH \longrightarrow R_nSnH_{4-n} + 4\text{-}nMX \tag{15-1}$$

The exchange of the ligands H and X (X = halide, carboxylate etc.) between organotin compounds can be regarded as a special case of these reductions.



(15-2)

Two alternative routes, which have been little exploited, are the thermal decomposition of an organotin formate, or the hydrolysis of a stannylmetallic compound, and a promising different approach involves the alkylation of a lithium tin hydride.

$$R_3SnOCOH \xrightarrow{\Delta} R_3SnH + CO_2 \tag{15-3}$$

$$R_3SnM + H_2O \longrightarrow R_3SnH + MOH \tag{15-4}$$

$$R_2SnHLi + R'X \longrightarrow R'R_2SnH + LiX \tag{15-5}$$

15.1.1 Reductions with Metal Hydrides

The principal metal hydrides which have been used for the reductions are $LiAlH_4$, R_2AlH, $NaBH_4$, $NaBH_3CN$, B_2H_6, LiH, $(MeSiHO)_n$, Et_3SiH, and R_3SnH.[3]

Lithium aluminium hydride has been used most widely.[4] The halides R_nSnX_{4-n} are treated with $LiAlH_4$ in an ether solvent at room temperature, giving the hydrides R_nSnH_{4-n}, $n = 0-3$ which can be isolated by distillation (e.g. equation 15-6).[5]

$$Me_2SnCl_2 + LiAlH_4 \xrightarrow[72\%]{\text{dioxane}} Me_2SnH_2 \tag{15-6}$$

Dialkylaluminium hydrides similarly reduce the halides or alkoxides in good yields.[6, 7]

$$Me_3SnCl + Bu^i{}_2AlH \xrightarrow[66\%]{\text{i}} Me_3SnH \tag{15-7}$$

i. Bu_2O, -30 °C to RT

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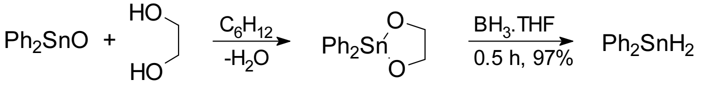
Sodium borohydride was reported to be unreactive towards organotin chlorides in diethyl ether or THF, but, in glyme or diglyme, trialkyltin chlorides and dialkyltin dichlorides are readily reduced to the corresponding hydrides (e.g. equation 15-8),[8] and ethanol is a convenient solvent for the reduction of bis(tributyltin) oxide [and of Bu_3SnCl, Bu_2SnCl_2, and Ph_3SnCl, but not Bu_2SnO or $(Ph_3Sn)_2O$].[9] The reactions can also be carried out with a suspension of sodium borohydride in toluene, using a crown ether as a phase-transfer catalyst.[10]

$$Me_2SnCl_2 + NaBH_4 \xrightarrow[96\%]{\text{diglyme}} Me_2SnH_2 \qquad (15\text{-}8)$$

Borane is an effective reducing agent for organotin alkoxides and amides,[11] and this has been exploited in the preparation of diorganotin dihydrides from the dioxastannolanes which can readily be obtained by azeotropic dehydration of a mixture of diorganotin oxide and 1,2-diol (e.g. equation 15-9).[12]



(15-9)

Organotin oxides and alkoxides can be reduced by silicon hydrides, and a very convenient route to tributyltin hydride is provided by the reduction of bis(tributyltin) oxide with poly(methylhydrosiloxane), [$(MeSiHO)_n$, PMHS], which is commercially available. Simple distillation under reduced pressure separates the stannane from the involatile polysiloxane reagent and product.[13] If aqueous KF is used to activate the PMHS, Bu_3SnCl in ether is reduced at room temperature in 3.5 h giving Bu_3SnH in excellent yield.[14, 15] Either of these two methods, or that using $NaBH_4$ in ethanol (see above), probably provide the best routes to tributyltin hydride, particularly on a large scale.

$$n(Bu_3Sn)_2O + 2(MeSiHO)_n \xrightarrow[79\%]{} 2nBu_3SnH + 2(MeSiO_{1.5})_n \qquad (15\text{-}10)$$

This technique works less well for preparing dibutyltin dihydride because of the insolubility of Bu_2SnO. This can be mitigated by heating the oxide first with butanol to give the more soluble distannoxane, $(BuO)Bu_2SnOSnBu_2(OBu)$,[16] or by working with a dialkoxide [e.g. $Bu_2Sn(OEt)_2$; 66% yield],[13] or probably with the dioxastannolane, $Bu_2Sn(OCH_2)_2$ (see above).[12] The amide Bu_3SnNMe_2 is reduced in excellent yield in one minute by $PhSiH_3$ in benzene at 25 °C.[17]

The trifluoromethyltin halides, $(CF_3)_nSnX_{4-n}$, react with trimethyl- or tributyl-tin hydride at –40 °C to give the trialkyltin halide and the corresponding trifluoromethyltin hydrides $(CF_3)_3SnH$, $(CF_3)_2SnH_2$, CF_3SnH_3, and $(CF_3)_2SnClH$ as liquids which are unstable at room temperature.[18]

The hydrides R_2SnHX (X = e.g. halide, carboxylate, sulphonate, alkoxyl) can be formed by the comproportionation between diorganotin dihydrides, R_2SnH_2, and the compounds R_2SnX_2.

$$R_2SnH_2 + R_2SnX_2 \rightleftharpoons 2R_2SnHX \qquad (15\text{-}11)$$

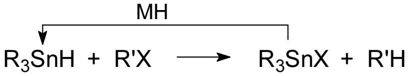
These reactions usually occur readily at room temperature, and can be followed by monitoring the SnH stretching band in the IR spectrum [e.g. ν(SnH) Bu_2SnH_2 1835,

Bu_2SnFH 1875, Bu_2SnClH 1853, Bu_2SnBrH 1847, Bu_2SnIH 1836 cm^{-1}] or the ^1H or ^{119}Sn chemical shift in the NMR spectrum [e.g. $\delta(Sn\mathit{H})$ Bu_2SnH_2 4.58, Bu_2SnFH 7.56, Bu_2SnClH 7.42, Bu_2SnBrH 7.09, Bu_2SnIH 6.08, $Bu_2Sn(OAc)H$ 7.6;[19, 20] $\delta(Sn)$ Bu_2SnH_2 –205.4, Bu_2SnClH –18.3].[21] The percentage yield of Bu_2SnHX in equilibrium with the reactants Bu_2SnH_2 and the various halides Bu_2SnX_2 is 93% (X = Cl), 87% (X = Br), and 85% (X = I).[21]

Similar more complex exchange reactions have been followed, for example between $PhSnCl_3$ and $Bu^i{}_3SnH$,[22] or Bu_3SnH and Bu_2SnCl_2.[23] The reagent Bu_2SnIH/Bu_3SnI, prepared by reducing Bu_2SnI_2 with Bu_3SnH, is more effective than Bu_2SnIH for reducing enones, perhaps because the Bu_3SnI acts as a Lewis acid catalyst.[24]

These hydrides with electronegative ligands on the tin, like the trifluoromethyltin hydrides above, are less stable than the simple tin hydrides. Distillation at reduced pressure usually gives back the dihydride as the most volatile of the components in equilibrium, but dibutyltin chloride hydride can be distilled under high vacuum. At room temperature these hydrides decompose at a rate depending on the nature of the groups X, to give principally the distannanes XR_2SnSnR_2X and hydrogen, or the oligostannanes $(R_2Sn)_n$.

When the tin hydride is to be used as a reagent in organic synthesis, it can often be prepared *in situ*, and when the reaction involves hydrostannolysis rather than hydrostannation, a catalytic amount of the precursor R_3SnX can often be used (equation 15-12),[25] reducing the cost and the problem of removing and disposing of organotin residues.



$$R_3SnH + R'X \longrightarrow R_3SnX + R'H \qquad (R_3SnX \xrightarrow{MH} R_3SnH) \tag{15-12}$$

For example, $NaBH_4$ (1.1 mol equiv.) and Bu_3SnCl (0.14 mol equiv.) in the presence of AIBN in toluene at 80 °C has been used on the pilot plant scale for reducing an aryl bromide.[26] The mixture $Bu_3SnCl/PMHS/KF_{(aq)}$ or $Bu_3SnF/PMHS/Bu_4SnF$ has been used in the presence of $(Ph_3P)_2PdCl_2$ for the hydrostannation of alkynes to give vinylstannanes, and systems of these types can be employed to bring about Stille reactions, or the hydrostannolysis of alkyl or aryl halides, or the reduction of alkynes, with a catalytic amount of trialkyltin oxide or halide.[14, 15, 27]

15.1.2 Decarboxylation of Stannyl Formates

If tripropyl- or tributyl-tin formate is heated at about 170 °C under reduced pressure, carbon dioxide is evolved and the corresponding tin hydride can be distilled off.[28] The reaction is reversible, and in THF at 150 °C, the same equilibrium mixture is obtained from either side in ca. 40 h.[29]

$$Bu_3SnOCOH \xrightarrow[60\%]{i} Bu_3SnH + CO_2 \tag{15-13}$$

i. 170-180 °C, 1 mmHg, 9 h.

If a bis(trialkyltin) oxide $(R_3Sn)_2O$ (R = Bu, Bu^i, or Oct) is heated with one molar equivalent of formic acid, the formate decarboxylates to give the hydride, which reduces *in situ* the excess oxide to give the corresponding distannane (Section 18.2.1.3).[30]

15.1.3 Hydrolysis of Stannylmetallic Compounds

Before lithium aluminium hydride was available as a reducing agent, the tin hydrides were prepared by treating the stannyl-lithium or stannyl-sodium compounds with ammonium halides in liquid ammonia.[31] More recently, stannyl-magnesium compounds have been used in the same way (equation 15-14).[32]

$$Ph_3SnSnPh_3 \xrightarrow[Mg]{THF} (Ph_3Sn)_2Mg \xrightarrow[NH_4Cl]{H_2O} 2Ph_3SnH \qquad (15\text{-}14)$$

With the advent of the metal hydrides as reducing agents, the hydrolysis of stannylmetallic compounds has been used principally for preparing isotopomeric hydrides (see below). For example, triethyltin deuteride has been prepared by treating hexaethyldistannane with sodium naphthalenide, then quenching the stannylsodium with D_2O (equation 15-15).[33] Similarly hydrolysis to give Bu_3SnD has been used for monitoring the formation of Bu_3SnMgX from the reaction of a Grignard reagent with Bu_3SnH.[34]

$$Et_3SnSnEt_3 + 2C_{10}H_8Na \longrightarrow 2Et_3SnNa \xrightarrow{D_2O} 2Et_3SnD \qquad (15\text{-}15)$$

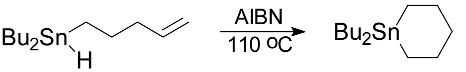
15.1.4 Alkylation of R_2SnHM

The availability of diorganotin dihydrides from the reduction of the corresponding dioxastannolanes[12] renders alkylation of a lithium tin hydride an attractive route to other organotin hydrides with mixed organic groups, $R_2R'SnH$.[35, 36]

The diorganotin dihydrides R_2SnH_2 can be monolithiated at –50 °C to give the compounds R_2SnHLi that are stable at low temperature but decompose at room temperature to give R_3SnH and $(R_2Sn)_n$.

Alkylation of Bu_2SnHLi with an alkyl halide at 0 °C gives a mixed trialkyltin hydride (e.g. equation 15-16), and 4-pentenyldibutylstannane, prepared by this method, undergoes homolytic 6-*endo* ring-closure to give 1,1-dibutylstannacyclohexane (equation 15-17). Reaction with functionally substituted alkyl halides gives the corresponding functionally substituted stannanes, for example $[MeO(CH_2CH_2O)_n(CH_2)_m]Bu_2SnH$ ($m = 4$, $n = 0$; $m = 4$, $n = 1$), and reaction with other electrophiles such as epoxides or aldehydes gives access to other types of functionality. Silylstannanes such as $Cy_2(^iPr_3Si)SnH$ are formed from the reaction of the lithiostannanes with the chlorosilanes.[36]

$$Bu_2SnH_2 \xrightarrow[-50\ ^oC,\ 30\ min]{LDA} Bu_2SnHLi \xrightarrow[0\ ^oC,\ 57\%]{PrCl} PrBu_2SnH \qquad (15\text{-}16)$$



(15-17)

Examples of some simple organotin hydrides are given in Table 15-1.

Table 15-1 Organotin hydrides

Hydride	m.p./°C or b.p./°C (mm Hg)	Ref.	Hydride	m.p./°C or b.p./°C (mm Hg)	Ref.
Me_3SnH	59(760)	4	Bu_2SnH_2	70(12)	5
Et_3SnH	39(12)	37	Cy_2SnH_2	$110(10^{-4})$	36
Vin_3SnH	−70(0.08)	38	Vin_2SnH_2	90(0.08)	38
Bu_3SnH	76−81(0.7)	37	Ph_2SnH_2	89−93(0.3)	5
Ph_3SnH	28	37	$MeSnH_3$	0−1.4(760)	4
Bu_2PrSnH	60(0.1)	36	$VinSnH_3$	−110(0.08)	38
Ph_2PrSnH	110(0.001)	36	$BuSnH_3$	98−100(760)	5
Me_2SnH_2	35(760)	4	$PhSnH_3$	57−64(106)	39

15.1.5 Special Hydrides[2]

Trialkyltin deuterides, R_3Sn^2H, have been made by the established routes to R_3SnH using deuteriated reagents (e.g. $Bu_3SnOSnBu_3$ + deuteriosilane, or $Bu_3SnMgX + D_2O$, or $Me_3SnBr + Bu_3SnD$),[40] and the tritiide Bu_3Sn^3H by the reduction of the chloride with Li^3H.[41]

$$^3H_2 + BuLi \longrightarrow Li^3H \xrightarrow[15\ min]{Bu_3SnCl} Bu_3Sn^3H \qquad (15\text{-}18)$$

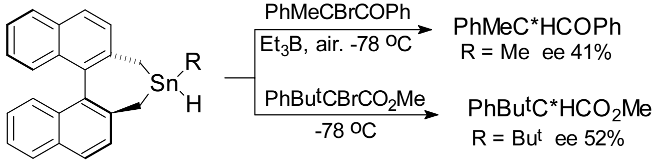
Although tributyltin hydride is used most widely in organic synthesis, it presents the problem of separating the required product from the organotin byproducts Bu_3SnX. The use of Bu_2SnClH reduces this problem as the compounds Bu_2SnX_2 are more readily separated, and a number of other tin hydrides have been developed with the aim of simplifying the work-up procedure and recovering the organotin compound. These hydrides are described in Section 22.3.

A number of organotin hydrides which carry a chiral group, usually menthyl or norbornyl, have been prepared for use in asymmetric synthesis.[42] An example is shown in equation 15-19; the enantioselectivity in this reaction is enhanced by the presence of a Lewis acid (e.g. BF_3 or Cp_2ZrCl_2), and ee values of up to about 80 have been achieved.[43] Force field and MO methods have been used to model the transition state for hydrogen transfer in such reactions.[44]

$$Men_2PhSnH + PhMeCBrCOPh \xrightarrow[-78\ ^oC]{9\text{-}BBN} PhMeC^*HCOPh \qquad (15\text{-}19)$$

Men = (1*S*,2*S*,5*R*)-Menthyl ee 16%

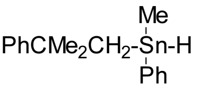
The binaphthyl stannepins **15-1**, where R = Me[45] or t-butyl[46] provide an interesting variant of this theme; the reaction with the bromoester can be carried out with $NaBH_3CN$ and a catalytic amount of the tin hydride, with no decrease in yield or enantioselectivity.[46]



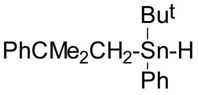
(15-20)

(**15-1**)

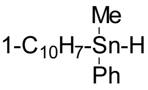
The optically active tin hydrides **15-2, 15-3**, and **15-4** with the asymmetry centred on the tin atom, have been prepared by reduction of the corresponding halides with a chiral aluminium hydride, or by reduction of the corresponding (–)-menthoxides with $LiAlH_4$.[47]


$\mathrm{PhCMe_2CH_2\text{-}\overset{Me}{\underset{Ph}{Sn}}\text{-}H}$

(**15-2**)


$\mathrm{PhCMe_2CH_2\text{-}\overset{Bu^t}{\underset{Ph}{Sn}}\text{-}H}$

(**15-3**)


$\mathrm{1\text{-}C_{10}H_7\text{-}\overset{Me}{\underset{Ph}{Sn}}\text{-}H}$

(**15-4**)

They are optically stable in solution at –30 °C, but **15-3** rapidly racemises at 80 °C in the presence of AIBN by a homolytic mechanism. Reaction with Pd/C gives the corresponding optically stable distannane. In CCl_4 solution, the optical rotation rapidly increases as the corresponding tin chloride is formed, then falls in a reaction which is inhibited by hydroquinone, with a half life of about 10 minutes, to give the racemic chloride. Diazomethane inserts the methylene unit into the Sn–H bond of **15-3** with retention of optical activity. Reaction of optically active **15-2** with $LiAlD_4$ gives the corresponding active deuteride, then the deuteride exchanges with an excess of Ph_3SnH to regenerate **15-2** with retention of configuration.[47]

15.2 Properties

Some examples of organotin hydrides are given in Table 15.1. Bond dissociation enthalpies are: $Me_3Sn{-}H$ 322.7(4.2), and $Et_3Sn{-}H$ 317.7(8.4) kJ mol^{-1}.[48, 49]

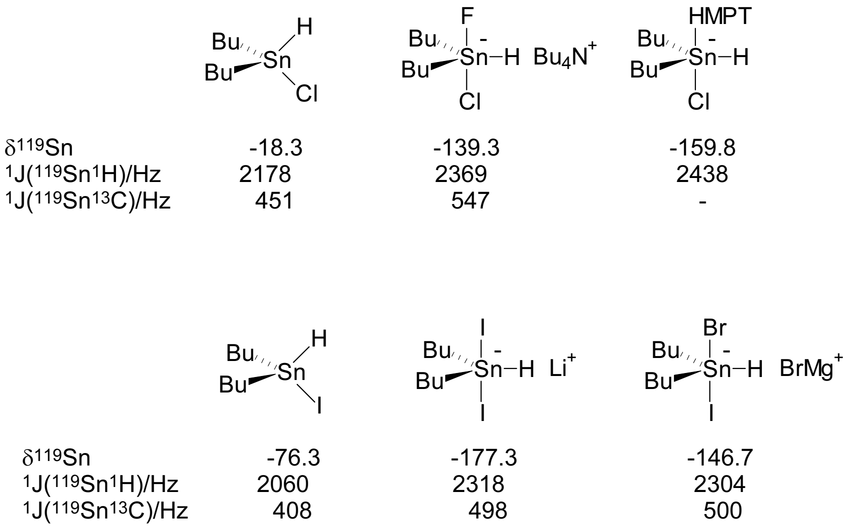
A microwave study of $MeSnH_3$ in 1951[50] gave, with some assumptions, the Sn–H bond length of 170.0(7.5) pm. By electron diffraction the values for *r*SnH in Me_3SnH and Me_2SnH_2 were found to be 170.5(6.7) pm and 168.0(1.5) pm respectively, with the structures approximately tetrahedral about tin.[51] Values that have been found by X-ray diffraction are 190(4) pm in $[(Me_3Si)_2CH]_3SnH$,[52] 190(4) pm in $[(Me_3Si)_2CH]_2Sn(OH)H$,[53] 179(4) and 178(4) pm in $Me_2Si(Bu^t{}_2SnH)_2$,[54] and an average of 160(7) pm in $Si(CH_2CH_2SnH_3)_4$. In t-butyl-8-(dimethylamino)-1-naphthyl-(–)menthyltin hydride, where there is some interaction between the nitrogen and the tin, *r*SnH is 152(5) and 165(5) pm.[55]

There is no evidence from Mössbauer, IR, or NMR spectroscopy for self-association of the hydrides in the solid or solution states, or for the interaction of Bu_3SnH with Lewis bases (e.g. Bu_3PO, HMPTA, F^-).

In t-butyl-8-dimethylamino-1-naphthyl-(–)menthyltin hydride (see above) the interaction between N and Sn is weak, and the structure about the tin atom remains near to tetrahedral. Such weak interaction as there may be in this compound,[55] and in 2-(2-pyridyl)ethyltin hydrides,[56] and, intermolecularly, between tin hydrides and Lewis bases,[57] is, nevertheless, apparently important in controlling their homolytic and heterolytic reactivity.

The halide hydrides R_2SnXH, on the other hand, do form identifiable complexes. Scheme **15-1** shows ^{119}Sn NMR chemical shifts and coupling constants for Bu_2SnClH and Bu_2SnIH.[58, 59] When halide ion or HMPT is added, the chemical shift moves upfield and the coupling constants increase, as the tetrahedral 4-coordinate precursor is converted into a trigonal bipyramidal 5-coordinate adduct.

If bipyridyl is added to a solution of Bu_2SnClH, the complex $Bu_2SnCl_2 \cdot bipy$ separates, by a reversal of the reaction by which Bu_2SnClH can be formed.



Scheme 15-1 ^{119}Sn NMR spectra of dialkyltin halide hydrides.

Addition of D_2O to Bu_2SnHLi gives a 1:2:1 mixture of Bu_2SnH_2, Bu_2SnHD, and Bu_2SnD_2.[36] Details of the NMR spectra of these compounds, and of the isotopomers of tributyltin hydride[41] are given in Table 15-2.

Table 15-2 NMR spectra of hydrogen isotopomers of Bu_3Sn^nH.

Compound	δ^nH	δSn	$^1J(^{117/119}Sn^nH)$/Hz
Bu_3Sn^1H	4.7	–89.2	1501/1575
Bu_3Sn^2H	4.7	–91.0	231/242
Bu_3Sn^3H	4.7	–91.9	1610/1685
$Bu_2Sn^1H_2$	4.58	–204.0	
$Bu_2Sn^1H^2H$		–205.2	
$Bu_2Sn^2H_2$		–206.4	

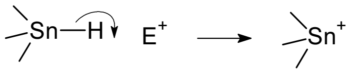
In the air, the hydrides are oxidised to the corresponding hydroxides or oxides, presumably by a radical chain mechanism. The thermal stability of the hydrides R_nSnH_{4-n} increases as the value of n increases. Trialkyltin hydrides can be kept for long periods in the absence of oxygen, but dibutyltin dihydride is not stable enough to be commercially available. Decomposition is more rapid in the presence of a good ligand for tin, and this has been exploited in the formation of Sn–Sn bonds (see Section 15.3.4).

Trialkyltin hydrides are stable to water. Some hydrides such as $(MeOCH_2CH_2OCH_2CH_2CH_2)_3SnH$ have been specially designed for reduction in homogeneous aqueous solution,[60] but halides[61] and aldehydes have also been reduced with Bu_3SnH in water,[62] sometimes in the presence of a phase-transfer agent.[61]

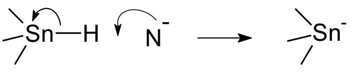
15.3 Reactions

The organotin hydrides can react at the hydrogen centre with electrophiles (equation 15-21), nucleophiles (equation 15-22), or free radicals (equation 15-23),[2] and also undergo reactions involving transition metals, through intermediates $H-M(L_n)-SnR_3$ (equation 15-24); all four processes are important in organic synthesis, but the recent chemistry of the hydrides has been dominated by the radical reactions which provide important procedures in synthetic organic chemistry.[63–66] The organotin hydrides, especially tributyltin hydride, have so monopolised free radical methods of organic synthesis involving the replacement by hydrogen of halogen, hydroxyl, amino, nitro, thiol, selenide carboxylate and other functional groups, the radical addition to alkenes, and alkynes, and the reductive formation of C–C bonds, particularly C–C ring closures, that this has been referred to as "the tyrrany of tin".[67]

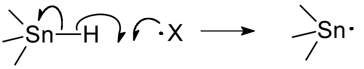
Sometimes homolytic and heterolytic reactions can proceed in parallel, sometimes giving different products, and there are some reactions where the mechanism is obscure.



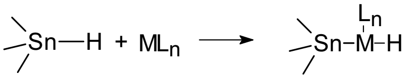
(15-21)



(15-22)



(15-23)



(15-24)

The mechanism that is followed depends on:

1. The structure of the hydride; for example Bu_2SnClH, and particularly Cl_3SnH, is more prone to give heterolytic reactions than is Bu_2SnH_2 or Bu_3SnH.

2. The structure of the substrate; for example protic acids attack electrophilically, and metal hydrides react nucleophilically, both reactions giving dihydrogen.

3. The solvent; for example polar methanol promotes heterolytic reactions.[68]

4. The presence of a Lewis base; by complexing with the hydride, this can promote, in different systems, either a homolytic or a heterolytic reaction, as discussed below.[68]

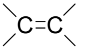
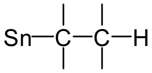
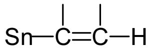
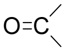
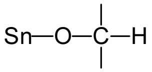
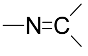
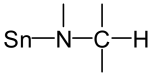
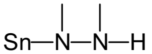
5. The presence of a Lewis acid; by associating with the substrate (e.g. a carbonyl compound) this can enhance its electrophilic character.

6. The presence of a radical initiator or inhibitor. For example, AIBN or UV light is used to promote radical addition of a tin hydride to a carbonyl compound, and galvinoxyl can suppress a homolytic reaction, and permit a heterolytic path to be followed.

7. The presence of a transition metal catalyst.[69, 70]

The principal addition reactions of tin hydrides to unsaturated systems are listed in Table 15-3. These reactions are discussed in the sections dealing with the products, as noted in Column 3.

Table 15-3 Addition reactions of organotin hydrides.

Reactant	Product	Section
 $>C=C<$	 $Sn-C-C-H$	4.4
$-C\equiv C-$	 $Sn-C=C-H$	4.4
 $O=C<$	 $Sn-O-C-H$	20.1.3
 $-N=C<$	 $Sn-N-C-H$	16.1.1.3
$-N=N-$	 $Sn-N-N-H$	16.1.1.3
O_2	$Sn-O-O-H$	14.5

Substitution reactions which follow the equation 15-25 are considered here.

$$R_nSnH_{4-n} + X\text{-}Y \longrightarrow R_nSnH_{3-n}X + HY \qquad (15\text{-}25)$$

15.3.1 Reactions with Protic Acids and Carbenium Ions.

The hydrides R_3SnH react with acids HX (e.g. HCl, carboxylic acids) to give R_3SnX and H_2, and the reactivity follows the sequence of acid strength ($CH_3CO_2H < ClCH_2CO_2H < Cl_2CHCO_2H < Cl_3CCO_2H$).[71]

$$R_nSnH_{4-n} + X\text{-}H \longrightarrow R_nSnH_{3-n}X + H_2 \qquad (15\text{-}26)$$

The hydrostannation of aliphatic and aromatic aldehydes and ketones is catalysed by tributyltin triflate, $Bu_3SnOSO_2CF_3$, acting as a Lewis acid, and this can be formed *in situ* from the reaction between triflic acid and tributyltin hydride.[72]

In FSO_3H at –78 °C, the methyltin hydrides $Me_{4-n}SnH_n$ react to give dihydrogen and the solvated cations $Me_{4-n}SnH_{n-1}^+$ which have been identified by NMR spectroscopy.[73] If the solutions are then frozen to 77 K, the Mössbauer spectra show the presence of the stannyl fluorosulphonates $Me_{4-n}SnH_{n-1}OSO_2F$.

The abstraction of hydride ion from R_3SnH by Ph_3C^+ has been used as one approach for preparing cations R_3Sn^+ (Section 7-2).[74–76]

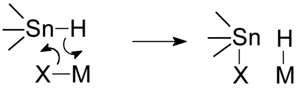
The rates of the reactions with carbenium ions have been used for comparing the nucleophilicity of the hydride donors R_3MH, M = C, Si, Ge, and Sn. Rate constants, with the ion $(4\text{-}MeOC_6H_4)PhCH^+$ as a reference standard, are given in Table 15-4.[77, 78]

Table 15-4 Rate constants ($M^{-1}\ s^{-1}$) for the reaction of $(4\text{-}MeOC_6H_4)PhCH^+$ with hydride donors in CH_2Cl_2 at –78 °C.

R	HCR_3	$HSiR_3$	$HGeR_3$	$HSnR_3$
Bu		3.9×10^2	2.8×10^4	2×10^6
Ph	2×10^7	8.3	1.1×10^2	5×10^3

15.3.2 Reactions with Metal Halides

In the reaction with halides of the less electropositive metals such as mercury,[79] arsenic,[80, 81] antimony,[82] and indium,[83] a stannane provides nucleophilic hydrogen and gives the new metal hydride (equation 15-27). Free radical inhibitors may be added to repress radical reaction of vinyl reactants. The preparation of vinylmercury hydride by this route involves the unusual use of tributyltin chloride as a solvent (equation 15-28).[79] On the other hand, in the reactions of tributyltin hydride with Grignard reagents, RMgX, the hydrogen behaves as an electrophile towards R, and the Sn–Mg bonded compounds are formed.[84]



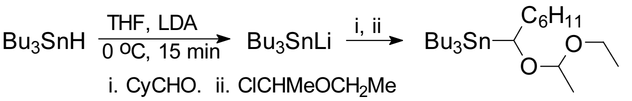
(15-27)

$$CH_2{=}CHHgCl + Bu_3SnH \xrightarrow[\text{Galvinoxyl inhibitor}]{Bu_3SnCl,\ 0\ ^{o}C} CH_2{=}CHHgH + Bu_3SnCl \qquad (15\text{-}28)$$

Halogeno-silanes[85] and -disilanes[86] and -oligosilanes[87, 88] are reduced by Bu_3SnH in the presence of a Lewis base to the corresponding hydrosilanes, the extent of reduction depending on the identity of the base. The reaction is suggested to involve the coordination of the base to the silane, followed by electron transfer from the tin hydride.

15.3.3 Reactions with Strong Bases

With strong bases (RLi, LDA, NaH, KH, RMgX), deprotonation occurs to give tin-metal bonded products which provide a useful source of nucleophilic tin (Section 19.1).[35, 89, 90]



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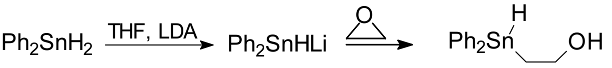


(15-30)

The neophyltin hydrides $Me_nNph_{3-n}SnH$ react with sodium hydride in DMSO to give the stannylsodium compound in 60–70% yield when $n = 1$ or 2, but when $n = 0$ only the distannane $Nph_3SnSnNph_3$ is formed.[91] No ate complexes $R_nSnH_{5-n}^{-}$ ($n < 5$), which would be analogous to the pentaorganostannates R_5Sn^-, have yet been detected.

15.3.4 Reactions Leading to the Formation of Sn–Sn Bonds

Tin hydrides can form tin-tin bonds by the two types of reaction shown in equations 15-31 and 15-32.

$$2R_3SnH \longrightarrow R_3SnSnR_3 + H_2 \qquad (15\text{-}31)$$

$$R_3SnH + R'_3SnX \longrightarrow R_3SnSnR'_3 + HX \qquad (15\text{-}32)$$

With the simple triorganotin hydrides, reaction 15-31 occurs only in the presence of a Lewis base such as an amine, or of a transition metal catalyst. The amine-catalysed reaction has been used for preparing catenary and cyclic oligostannanes (e.g. equations 15-33 and 15-34 and Section 18.2.1.3).[92]

$$\begin{tikzcd} Et_3SnSnEt_2NPhCHO \arrow[r, "Et_2SnH_2"] & Et_3SnSnEt_2SnEt_2H \arrow[d, "R_3N"', "-H_2"] \\ & Et_3Sn(SnEt_2)_4SnEt_3 \end{tikzcd} \qquad (15\text{-}33)$$

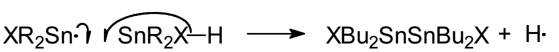
$$6Ph_2SnH_2 \xrightarrow{\text{pyridine}} (Ph_2Sn)_6 + 6H_2 \qquad (15\text{-}34)$$

The mechanism by which hydrogen is eliminated and the Sn–Sn bond is formed has been investigated in the case the hydrides R_2SnXH (equation 15-35).[93] The carboxylate hydrides, $Bu_2Sn(OCOR)H$, which are formed when Bu_2SnH_2 and $Bu_2Sn(OCOR)_2$ are mixed, decompose at room temperature in the absence of any catalyst to give hydrogen and the distannane $(RCO_2)Bu_2SnSnBu_2(OCOR)$, and the rate of the decomposition increases with the strength of the acid RCO_2H. Dibutyltin chloride hydride is more stable, but hydrogen is evolved as soon as pyridine is added.

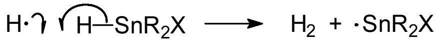
$$2Bu_2SnXH \xrightarrow{\text{pyridine}} XBu_2SnSnBu_2X + H_2 \qquad (15\text{-}35)$$

Both the catalysed and uncatalysed decompositions can be stopped by a radical inhibitor such as 2,6-di-t-butylphenol, but after a period the inhibitor is consumed and the decomposition recommences. If an alkyl halide or alkyne is added to the system, the evolution of hydrogen is quenched, and the substrates show the reactions which are characteristic of stannyl radicals.

It therefore appears that the decomposition to form an H–H and an Sn–Sn bond occurs by a radical chain mechanism, and the propagating steps 15-36 and 15-37 have been suggested.



$$XR_2Sn\cdot + SnR_2X{-}H \longrightarrow XBu_2SnSnBu_2X + H\cdot \qquad (15\text{-}36)$$



$$H\cdot + H{-}SnR_2X \longrightarrow H_2 + \cdot SnR_2X \qquad (15\text{-}37)$$

The second step of this chain is conventional, but the first step, which involves the S_H2 reaction of a tin radical at a tin centre to cleave an Sn–H bond is less readily accepted. The initiation step of the reaction, which with some compounds must be rapid as an inhibitor is quickly consumed, could occur via an electron-transfer process, or by molecule-induced homolysis.

Metal-catalysed dehydrogenative coupling of tin hydrides to give distannanes was originally established with Pd(II) complexes[94–97] (e.g. equation 15-38), but has since been found for a number of other transition metals[70] such as Au(II),[98] Ru(II),[99] Y(III), Ti(IV), Zr(IV),[98] Hf(IV),[98, 100] Cr(0), Mn(0), W(0),[98] and bimetallic (Fe-Pd) complexes;[70, 101, 102] the Au and the Fe-Pd complexes appear to be the most effective.

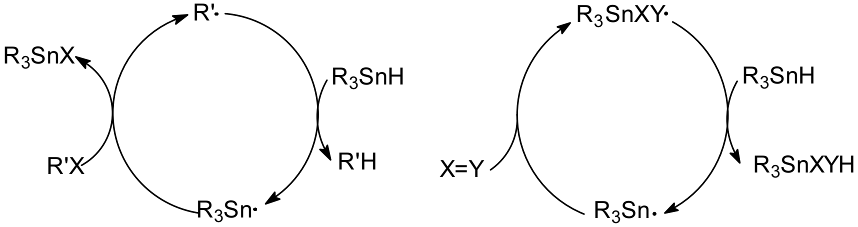
$$2R_2Sn(OAc)H \xrightarrow{PdCl_2(PPh_3)_2} (AcO)R_2SnSnR_2(OAc) \qquad (15\text{-}38)$$

The mechanisms of these reaction are usually thought to involve the formation of an M−SnR_3 complex which reacts directly, or via $HM(SnR_3)_2$ to give MH and R_3SnSnR_3, but the reaction of Cp*CpHfClH (Cp* = Me_5C_5, Mes = mesityl) with Mes_2SnH_2 is believed to proceed by the elimination of the stannylene Mes_2Sn**:** from Cp*CpHf(Cl)-$SnHMes_2$, followed by insertion of Mes_2Sn**:** into the SnH bond of Mes_2SnH_2.[100] If ketones are treated with Bu_2SnH_2 (but not Bu_3SnH) in the presence of $Pd(PPh_3)_4$, the corresponding alcohols are formed, usually in good yield. The mechanism again probably involves a Pd−Sn bonded complex.[103]

Similar dehydrogenative coupling reactions of the dihydrides R_2SnH_2 gives oligostannanes $(R_2Sn)_n$ (see Section 18.2.1.3 and 18.4).

15.3.5 Radical reactions

Organotin hydrides can bring about reductive hydrostannolysis or hydrostannation by radical chain mechanisms. Simple models of these two processes are shown in Scheme 15-2, but frequently further steps of substitution or addition involving the $R'^{\bullet}$ or $R_3SnXY^{\bullet}$ radicals, but not, directly, the tin radical or tin hydride, are interposed into the chain, resulting in an inter- or intra-molecular cascade process. These chains are preceded by some initiation process in which radicals are formed and introduced into the cycle from non-radical initiators, and they are terminated by removal of radicals from the cycle by radical-radical reactions. The overall kinetics of the reactions are not simple; they contain terms from the initiation, propagation, and termination steps, and it is important, in designing preparatively useful reactions to know the rate constant for each of these constitutent steps.



Scheme 15-2 Homolytic chain mechanisms of hydrostannolysis and hydrostannation.

In recent years, these reactions have found an important place in organic synthesis. We will consider in this chapter only the reactions of radicals with tin hydrides, and the basic hydrostannolysis processes that depend on these reactions. Hydrostannation reactions are covered in Section 4.4, and the reactions of stannyl radicals with substrates R′X in Section 20.1.3. The further use of organotin hydrides in organic synthesis, which depends largely on transformations of the radicals $R'^{\bullet}$ in hydrostannolysis reactions, or of the radicals $R_3SnXY^{\bullet}$ in hydrostannation reactions, are beyond the scope of this book, but have been extensively reviewed.[2, 64–66, 104–107]

The principal reactants R’X in Scheme 15-2 are R′Cl, R′Br, or R'I, R′OC(=S)Y (Y = H, Ph, imidazole, OPh, SPh, SePh), R′OC(O)SePh, R′SPh R′SePh, R′N=C:, $R'NO_2$, and the *O*-acyl derivatives of the thiohydroxamic acids (equation 15-48).

The sequence of reactivity of the various functional groups X towards the $Bu_3Sn^{\bullet}$ radical is Br > PhSe > Cl > *p*-NCC_6H_4S > PhS > *p*-MeC_6H_4S > MeS[108] (though this is not necessarily the same as the overall rate of reaction as the complete rate equation involves also the rates of initiation and termination). Whatever the nature of the group X, the reactivity usually decreases in the order R′ = benzyl ≈ allyl ≈ t-alkyl > s-alkyl > vinyl or aryl, reflecting the stability of the radical $R'^{\bullet}$ which is formed, and the reactivities of the various tin hydrides have been reported to be Bu_3SnH < Bu_2SnH_2 > Ph_3SnH > Ph_2SnH_2 and Bu_3SnH < Bu_2SnClH < $Bu_2Sn(OCOR)H$.

The reactions sometimes occur without imposed initiation, but most commonly initiation is brought about by AIBN at 75–85 °C in a solvent such as benzene or toluene, or by triethylborane in the presence of a trace of oxygen,[109, 110] or by irradiation with a sunlamp. Methods for removing organotin residues during the workup of the products of these reactions are discussed in Section 22.3.

15.3.5.1 Reactions of Radicals with Tin Hydrides[2]

The kinetics of many the reactions of radicals with tin hydrides have been studied because of their importance in organic synthesis. Examples are given in Table 15-5, and a more extensive list is given in a recent review by Chatgilialoglu and Newcomb.[111] The solvents are not quoted in the table, but in general they are non-polar (e.g. octane or benzene) and the rates are not sensitive to the nature of the solvent.

Table 15-5 Kinetics of the reaction $X^{\bullet} + Bu_3SnH \rightarrow XH + Bu_3Sn^{\bullet}$.

Radical $X^{\bullet}$	log *A*	*E*/kJmol^{-1}	*k*/M^{-1} s^{-1} at 293 K[a]	Ref.
$Me^{\bullet}$	9.39 ± 0.28	13.5 ± 1.4	9.6×10^{6}	112
$Bu^{\bullet}$	9.06 ± 0.31	15.3 ± 1.7	2.2×10^{6}	112
$c\text{-}C_6H_{11}^{\bullet}$	9.24 ± 0.78	16.6 ± 4.8	1.9×10^{6}	112
$Me_3C^{\bullet}$	8.43 ± 0.14	12.3 ± 0.79	1.7×10^{6}	112
$PhCH_2^{\bullet}$	8.65 ± 0.17	23.3 ± 1.0	3.0×10^{4}	113
$Me_2C{=}CH^{\bullet}$	9.7 ± 0.3	6.7 ± 0.2	3.2×10^{8}	114
$Ph^{\bullet}$			7.8×10^{8} [b]	115
$C_8F_{17}^{\bullet}$			2×10^{8} [b]	116
$(N{\equiv}C)RHC^{\bullet}$	6.8 ± 0.8	7.1 ± 3.8	3.4×10^{5}	117
$RC^{\bullet}({=}O)$	8.2	14.6	3.8×10^{5}	118
$ROC^{\bullet}({=}O)$			1.7×10^{5} [c]	119
$Me_3CO^{\bullet}$			2.0×10^{8} [d]	120
$PhMe_2COO^{\bullet}$			1.6×10^{3} [e]	121
$PhCO_2^{\bullet}$	10.0 ± 0.2	7.1 ± 1.3	5.4×10^{8}	114, 115
$R_2NO^{\bullet\bullet}$	333 K		2.5×10^{-2} [f]	122
$^3Me_2C{=}O^*$			5.4×10^{8} [g]	123
$^1Me_2C{=}O^*$			1.0×10^{9} [g]	123
$R_2N^{\bullet}$	9.11	19.5	4.3×10^{5}	124

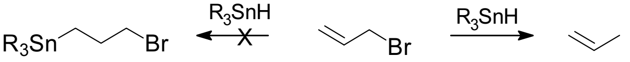
[a] $k = Ae^{-E/RT}$ [b] At 298 K. [c] At 275 K. [d] At 295 K. [e] At 345K. [f] At 333 K. [g] At room temperature.

It will be seen that the rates decrease in the sequence $Ph^{\bullet} > R_2C{=}CH^{\bullet} > Me_3CO^{\bullet} \approx RCF_2^{\bullet} > {}^3R_2C{=}O^{*} > RCH_2^{\bullet} > RC^{\bullet}({=}O) > R_2N^{\bullet} > ROO^{\bullet}$.

A temperature-dependent line-width effect on the NMR spectra of the hydrides and the ESR spectra of the radicals was ascribed to a rapid symmetrical exchange reaction, $R_3Sn^{\bullet} + R_3SnH \rightarrow R_3SnH + R_3Sn^{\bullet}$, but the measured activation energy (< ca. 8 kJ mol^{-1})[125] is much less than that calculated by empirical[126] or *ab initio*[127] methods (22.5–50 kJ mol^{-1}).

15.3.5.2 Reduction of Halides[107]

The hydrostannolysis of organic halides was discovered when an attempt at the hydrostannation of allyl bromide resulted instead in hydrodebromination.[37]



(15-39)

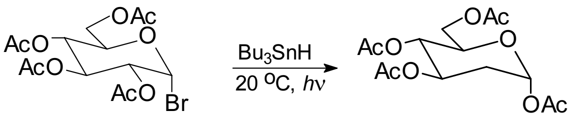
The reactions are accelerated by radical initiators or by UV light, and inhibited by radical scavengers,[128, 129] and, under suitable conditions, the reaction of stannyl radicals with alkyl halides to give the corresponding alkyl radicals can be observed by ESR spectroscopy.[130] Optically active alkyl halides react with racemisation,[129] but vinyl halides may show some retention of configuration at low temperature. The reactions are therefore accepted to follow the radical chain mechanism which is depicted in Scheme 15-2.

The reactivity follows the sequence X = I > Br > Cl; fluorides are much less reactive, though a few examples of the reduction of fluorides have been reported; rate constants are given in Table 20-2. Vinyl chlorides, bromides, and iodides can be used, but only aryl bromides or iodides. Geminal halides can be reduced stepwise, the removal of each successive halogen atom becoming progressively more difficult; $DCCl_3$ should not be used as a solvent for NMR studies of organotin hydrides, as it is reduced without initiator at room temperature to give $HDCCl_2$. The reactions are tolerant of a wide range of functional groups (C=C, C≡C, C=O, C≡N, SR, NO_2, S=O, SO_2, CO_2R etc.). Acyl chlorides, RCOCl are reduced in what appears to be a heterolytic process to a mixture of aldehyde RCHO, ester RCO_2CH_2R, and other products,[131] but in the presence of a palladium catalyst, good yields of the aldehyde can be obtained.[132]

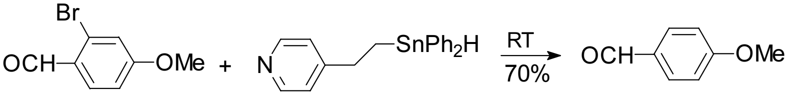
The reactions are commonly initiated with AIBN at ca. 80 °C in a solvent such as benzene or toluene, but alkyl halides have also been reduced at –60 °C with tributyltin hydride under sonication conditions.[133, 134] Some reductions of halides have been carried out by generating the tin hydride *in situ* from a molar equivalent of the reducing agent [lithium aluminium hydride, sodium borohydride, or poly(methylhydrosiloxane)] and a catalytic amount of organotin hydride, halide, or oxide. Reduction of halides has also been carried out under aqueous conditions, using 4,4′-azobis(4-cyanovaleric acid) (ACVA) as a water-soluble radical initiator.[60]

Examples of halide reductions are given in equations 15-40,[135] 15-41,[136] 15-42,[137] 15-43,[68] 15-44.[138] It will be noted that in reaction 15-41, an acetoxyl group is migrating in the intermediate radical.

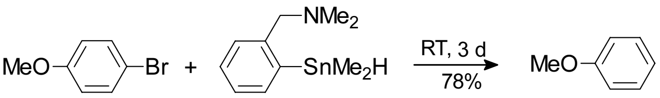
$$\mathrm{PhCCl_3} \xrightarrow[88\%]{\mathrm{Bu_3SnH}} \mathrm{PhCHCl_2} \xrightarrow[76\%]{} \mathrm{PhCH_2Cl} \xrightarrow[53\%]{} \mathrm{PhCH_3} \qquad (15\text{-}40)$$



(15-41)



(15-42)



(15-43)

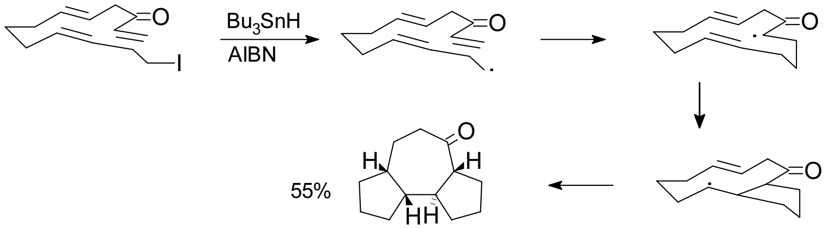
$$\mathrm{MeCHBr(CH_2)_2C{\equiv}N} \xrightarrow[\mathrm{(Bu_3Sn)_2O}]{\mathrm{(MeSiHO)}_n} \mathrm{Me(CH_2)_3C{\equiv}N} \qquad (15\text{-}44)$$

If halides RX are reduced in the presence of carbon monoxide, the free radical is carbonylated to the acyl radical, and the product is the aldehyde RCH=O (equation 15-45),[139-141] and if the reduction is carried out with $NaBH_3CN$ in the presence of a catalytic amount of the tin hydride, the alcohol RCH_2OH can be prepared directly.[142]

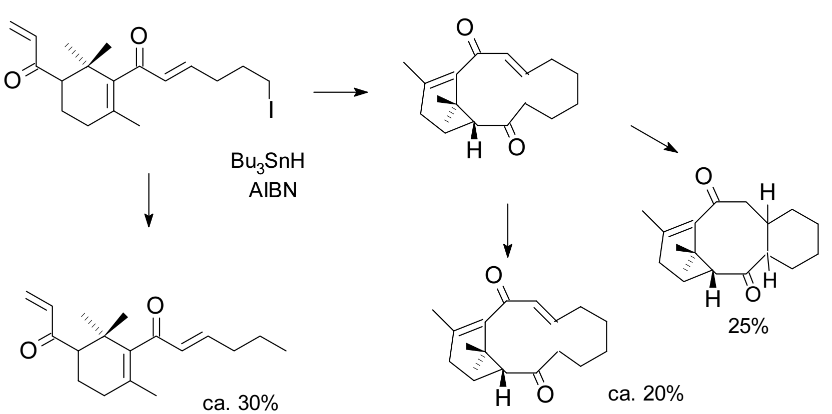
$$\mathrm{C_9H_{19}Br + CO + Bu_3SnH} \xrightarrow{\mathrm{i}} \mathrm{C_9H_{19}\dot{C}O} \longrightarrow \underset{84\%}{\mathrm{C_9H_{19}CH{=}O}} \qquad (15\text{-}45)$$

i. AIBN, C_6H_6, 80 °C. 80 Atm. CO

Reactions involving ring expansion and related annulations are reviewed in reference 143, and two examples of tandem macrocyclisation and transannulation are shown in Schemes 15-3[144] and 15-4. [145]



Scheme 15-3 Tandem macrocyclisation-transannulation induced by tributyltin hydride.

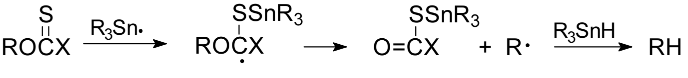


Scheme 15-4 Formation of the taxane ring system by tandem macrocyclisation-transannulation.

An interesting recent development is the demonstration that the reactivity of a stannyl radical can be controlled by amines that act intra- or inter-molecularly as ligands for the tin. Thus the stannyl radicals that are derived from dibutyl-2(2-pyridylethyl)tin hydride and butylbis-2(2-pyridylethyl)tin hydride show a reduced reactivity towards alkyl bromides and chlorides, and the presence of bipyridyl effectively suppresses the reduction of $C_{12}H_{25}Cl$ by Bu_3SnH.[56]

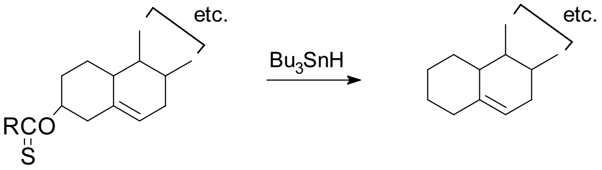
15.3.5.3 Reduction of Thiocarbonyl Compounds

A variety of thiocarbonyl derivatives of acids are reduced by organotin compounds by overall conjugate substitution involving addition and elimination, the reactivity depending on the formation of a strong C=O bond at the expense of a weak C=S bond.[146]



$$\mathrm{RO}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{X} \xrightarrow{\mathrm{R_3Sn\cdot}} \mathrm{RO}\underset{\bullet}{\overset{\overset{\mathrm{SSnR_3}}{|}}{\mathrm{C}}}\mathrm{X} \longrightarrow \mathrm{O{=}}\overset{\overset{\mathrm{SSnR_3}}{|}}{\mathrm{C}}\mathrm{X} + \mathrm{R\cdot} \xrightarrow{\mathrm{R_3SnH}} \mathrm{RH} \qquad (15\text{-}46)$$

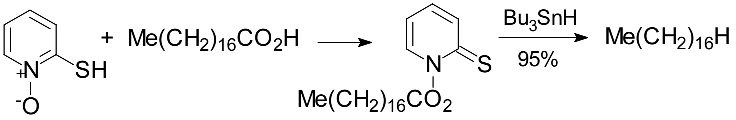
Thus secondary or tertiary alcohols ROH can be reduced to RH via their thiocarboxylates R′C(S)OR, or dithiocarbonates [xanthates, R′S(CS)OR; the Barton McCombie reaction];[147–149] for example cholesteryl thiobenzoate or *S*-methyl dithiocarbonate gives cholest-5-ene in 90% and 78% yield respectively (equation 15-47, R = Ph or MeS). The reaction works best for secondary alcohols; the *O*-t-alkyl xanthates are often rather unstable at room temperature, though the reactions can be carried out at low temperature with initiation by Et_3B/O_2. The primary alkyl xanthates undergo C–O fission only at higher temperatures, when other reactions may compete. The thiocarbonyl imidazolides provide a variant on this theme, and the cholesterol derivative (**15-5**, R = *N*-imidazole) reacts with tributyltin hydride to give an 18% yield of cholestene.[147]



(15-47)

(**15-5**)

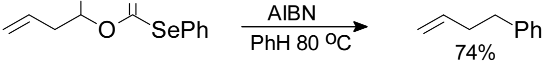
The reduction of the derivatives which carboxylic acids form with the thiohydroxamic acids (equation 15-48) provides a valuable alternative to the Hunsdiecker reaction for decarboxylating acids RCO_2H to RH.[107, 150, 151]



(15-48)

15.3.5.4 Reduction of Other Substrates

Selenoesters can be reduced with or without decarboxylation (equations 15-49 and 15-50).[152]



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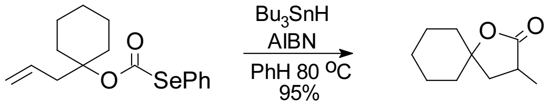
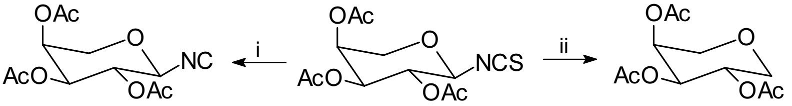


(15-50)

Isothiocyanates, RN=C=S, are reduced first to the isocyanides RNC:,[153, 154] and then the isocyanides are reduced to the compounds RH (equation 15-51).[155]



(15-51)

i. Bu$_3$SnH, AIBN, ether, 24 °C; 69% ii. Bu$_3$SnH, AIBN, PhMe, 110 °C; 85%

Secondary and tertiary nitroalkanes RNO$_2$ can be reduced to RH (equation 15-52 and 15-53).[156]

$$\mathrm{PhCH_2CH(NO_2)CHMeCO_2Me} \xrightarrow[\substack{110\ ^{\circ}\mathrm{C},\ 1\ \mathrm{h} \\ 53\%}]{\substack{\mathrm{Bu_3SnH} \\ \mathrm{AIBN}}} \mathrm{PhCH_2CH_2CHMeCO_2Me} \qquad (15\text{-}52)$$

$$\begin{tikzcd} & & \mathrm{PrCHDCOPr}\ \ 67\% \\ \mathrm{PrCH(NO_2)COPr} \arrow[r, "\mathrm{D_2O}", "\mathrm{NaOAc}"'] & \mathrm{PrCD(NO_2)COPr} \arrow[ur, "\mathrm{Bu_3SnH}"] \arrow[dr, "\mathrm{Bu_3SnD}"'] & \\ & & \mathrm{PrCD_2COPr} \end{tikzcd} \qquad (15\text{-}53)$$

Pattenden has described the reduction of a triene selenyl ester, RCOSeR′, by a cascade sequence to give a tetracyclic steroidal ketone,[157] and of an acyclic heptaene selenyl ester, by a seven-fold cascade of ring closures to give a heptacyclic system.[158]

References to Chapter 15

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16 Compounds with Sn–N Bonds[1, 2]

The principal compounds with an SnN covalent bond are the aminostannanes containing the structure Sn-NR_2 and the amidostannanes and sulfonamidostannanes containing the structures SnNRC(O)R′ or $SnNRS(O)_2R'$, respectively. A few compounds containing a tin-nitrogen double bond, Sn=NR, have also been identified.

16.1 Aminostannanes

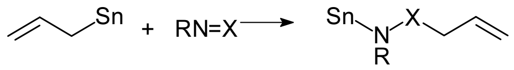
16.1.1 Preparation

The aminostannanes are usually prepared by transmetallation between an organotin compound such as a halide and an aminometallic compound by transamination of a stannylamine by addition of a tin reagent to a multiple bond to nitrogen, or by an ene reaction (equations 16-1–16-4). The Sn–N bond which is formed is very reactive towards moisture and carbon dioxide, and the reactions must be carried out in an inert atmosphere.

1. $SnX + MNR_2 \longrightarrow SnNR_2 + MX$ (16-1)

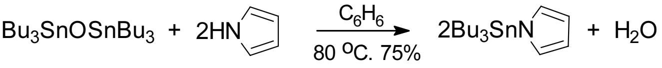
2. $SnNR_2 + HNR'_2 \longrightarrow SnNR'_2 + HNR_2$ (16-2)

3. $SnX + RN{=}Y \longrightarrow SnNRYX$ (16-3)

4. 
(16-4)

16.1.1.1 Transmetallation

Whereas alkoxystannanes can be prepared by azeotropic dehydration of a mixture of bis(tributyltin) oxide and an alcohol (pK_a ca. 16), aminotin compounds cannot normally be prepared from the oxide and an amine (pK_a ca. 35). The important exception to this rule is pyrrole which is a stronger acid (pK_a 15), and *N*-tributylstannylpyrrole can readily be prepared by the azeotropic dehydration of bis(tributyltin) oxide and pyrrole, or by heating together tributyltin methoxide and pyrrole.[3]


(16-5)

Other amines must first be converted into their more strongly nucleophilic metal derivatives which are then treated with tin halides. Examples of the transmetallation reactions which occur are given in equations 16-6,[4] 16-7,[5, 6] 16-8,[7] 16-9,[8] 16-10,[9] 16-11[10] 16-12,[11] and 16-13.[12] The metal is usually an alkali metal, most commonly lith-

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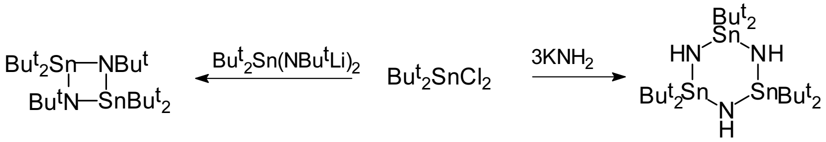
ium from the treatment of an amine with butyllithium, though aminomagnesium compounds and aminosilanes have also been used. In the product $R_nSn(NR'_2)_{4-n}$, n can have the value 0-4, and one to three tin atoms can be bonded to the nitrogen. The stability of the products from primary amines towards disproportionation appears to be sterically controlled. Thus, $Bu_3SnNHBu^t$ is stable, but $Me_3SnNHMe$ disproportionates to $(Me_3Sn)_2NMe$ and $MeNH_2$.[4, 13]

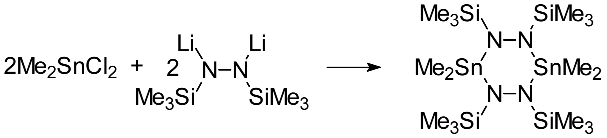
$$Me_3SnCl + LiNMe_2 \xrightarrow[3\text{ h. }91\%]{Et_2O,\text{ reflux}} Me_3SnNMe_2 \qquad (16\text{-}6)$$

$$3Me_3SnCl + Li_3N \longrightarrow (Me_3Sn)_3N \longleftarrow Me_3SnCl + NaN(SnMe_3)_2 \qquad (16\text{-}7)$$

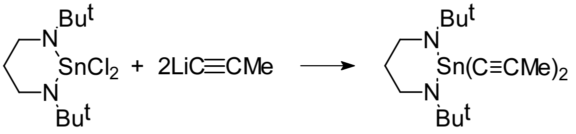
$$SnCl_4 + 4LiNEt_2 \longrightarrow Sn(NEt_2)_4 \xrightarrow{Bu^tLi} Bu^tSn(NEt_2)_3 \qquad (16\text{-}8)$$



(16-9)

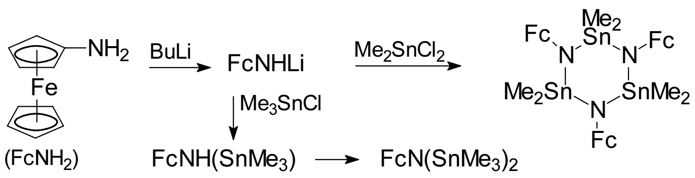


(16-10)



(16-11)

$$Me_2Pr^iSnNEt_2 \xrightarrow{2NaNH_2} (Me_2Pr^iSn)_2NNa \xrightarrow{Me_2Pr^iSnCl} (Me_2Pr^iSn)_3N \qquad (16\text{-}12)$$



(16-13)

16.1.1.2 Transamination

Transamination reactions are versatile processes which occur under mild conditions and in good yield. They are reversible and are usually driven to completion by distilling off the more volatile amine (e.g. equations 16-14, 16-15,[4] 16-16,[14] and 16-17[15])

$$2Me_3SnNMe_2 + EtNH_2 \longrightarrow (Me_3Sn)_2NEt \qquad (16\text{-}14)$$

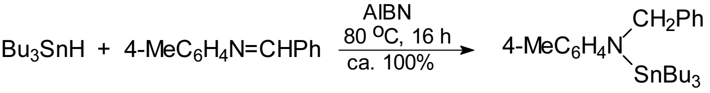
$$3Me_3SnNMe_2 + NH_3 \xrightarrow[distil]{petroleum} (Me_3Sn)_3N \qquad (16\text{-}15)$$

$$4Me_3SnNMe_2 + H_2NNH_2 \longrightarrow (Me_3Sn)_2NN(SnMe_3)_2 \qquad (16\text{-}16)$$

$$2Me_3SnNEt_2 + 2,6\text{-}Pr^i{}_2C_6H_3NH_2 \longrightarrow (Me_3Sn)_2NC_6H_3Pr^i{}_2\text{-}2,6 \qquad (16\text{-}17)$$

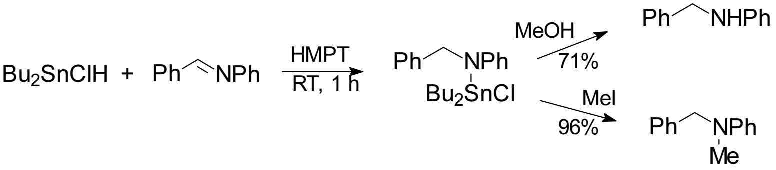
16.1.1.3 Addition to Multiple Bonds to Nitrogen

Included in this classification are the addition of a tin hydride to an imine RN=CR′$_2$ or azo compound RN=NR. Trialkyltin hydrides react with imines only in the presence of AIBN or of a Lewis acid catalyst such as zinc chloride.[16]



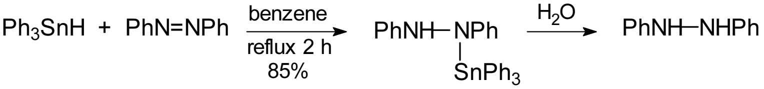
$$Bu_3SnH + 4\text{-}MeC_6H_4N{=}CHPh \xrightarrow[\text{ca. 100\%}]{\text{AIBN, 80 °C, 16 h}} 4\text{-}MeC_6H_4N(CH_2Ph)(SnBu_3) \qquad (16\text{-}18)$$

Dibutyltin chloride hydride is a more effective reagent for polar addition, particularly in the presence of a good ligand for tin such as HMPT. The reaction is now complete in one or two hours at room temperature, and the product can be hydrolysed to give a secondary amine, or alkylated with an alkyl bromide or iodide to give a tertiary amine (equation 16-19).[17] Unlike most other metal hydrides (LiAlH$_4$, DIBAL, or NaBH$_4$), it is chemoselective for the imino group in the presence of a carbonyl group.[18]



(16-19)

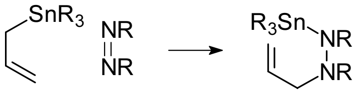
Triorganotin hydrides react with azoarenes to give, after hydrolysis, the hydrazoarenes in good yield.[19] In the presence of AIBN as catalyst, the reactions follow the usual radical chain mehanism, but when AIBN is absent, free stannyl radicals appear not to be involved, and it has been suggested that electron transfer gives the radical ion pair $Ar_2N_2^{\bullet-}$ $R_3SnH^{\bullet+}$, and that the products are formed by collapse of this ion pair.[20]



$$Ph_3SnH + PhN{=}NPh \xrightarrow[\text{reflux 2 h, 85\%}]{\text{benzene}} PhNH{-}N(SnPh_3)Ph \xrightarrow{H_2O} PhNH{-}NHPh \qquad (16\text{-}20)$$

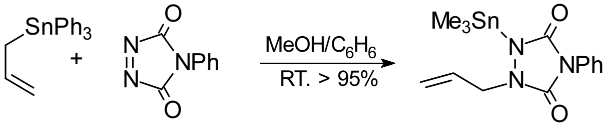
16.1.1.4 Ene Reactions

The ene reaction between an allylstannane and an azo compound is illustrated in equation 16-21. This reaction has already been referred to in the section on allylstannanes (Section 9.1.3.4).

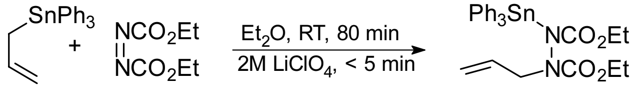


(16-21)

Any competing reactions involving hydrogen shift, or ring-closure with 1,2-migration of the stannyl group, are avoided if the tin carries electronegative substituents, and the reactions are strongly accelerated by high concentrations of lithium perchlorate. Two examples are given in equations 16-22 and 16-23.[21, 22]



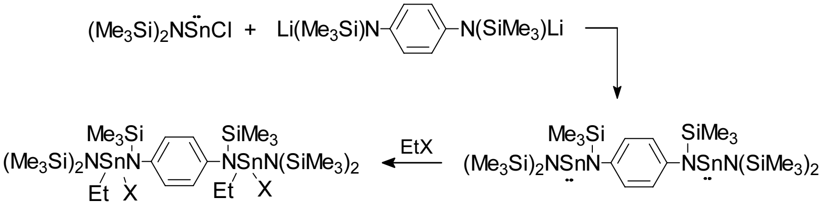
(16-22)



(16-23)

16.1.1.5 Miscellaneous Methods

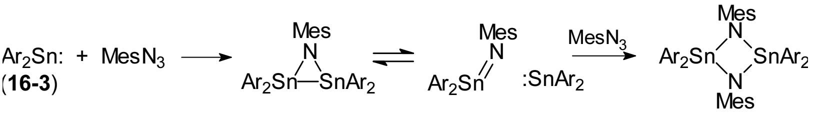
There are a few examples of the the formation of aminoorganotin(IV) compounds from diamino- or diorgano-tin(II) compounds. The tin(II) diamine (**16-1**) can be alkylated with ethyl bromide or iodide to give the ethyltin halide diamides (**16-2**).[23]



(16-24)

(**16-2**) (**16-1**)

The diarylstannylene (**16-3**) reacts with mesityl azide to give the distannaaziridine (**16-4**), which in solution is in equilibrium with the stannaimine (**16-5**) and stannylene, and this mixture reacts with further azide to give the distannaazetidine (**16-6**).[24]



(16-25)

(**16-3**)

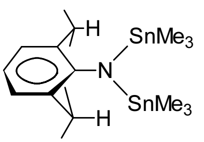
Ar = 2,4,6-$(CF_3)_3C_6H_2$
Mes = 2,4,6-$Me_3C_6H_2$

(**16-4**) (**16-5**) (**16-6**)

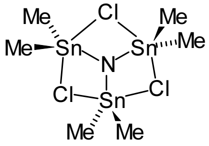
16.1.2 Structures

The structures of the stannylamines are interesting as they are a consequence of the interplay of steric effects, the electronegativities of the nitrogen ligands, and the possibility of π-bonding between nitrogen and tin. An electron diffraction study of $(Me_3Sn)_3N$ showed that the molecule is planar, with rSnN 203.8(3) pm.[25] In $(Bu^t{}_2SnNBu^t)_2$, the ring is planar and the coordination at nitrogen is almost planar with rSnN 205.2(6)–205.9(6) pm; in $(Bu^t{}_2SnNH)_3$ the ring is again planar, but the coordination at nitrogen is apparently that of a distorted pyramid.[8] The highly hindered aryldistannylamine **16-7** is planar at nitrogen with the plane containing the SnNSn group orthogonal to the plane of the ring, and the lone pair on nitrogen is in a p orbital.[15]

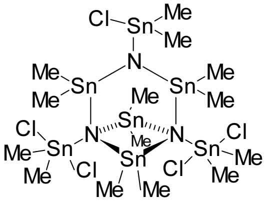
The reaction of tris(trimethylstannyl)amine with dimethyltin dichloride or dibromide gives $(XSnMe_2)_3N$. The compound $(ClSnMe_2)_3N$ has the structure **16-8** with a planar NSn_3Cl_3 group, and almost symmetrical (270–280 pm) bridges, and the structure of the corresponding bromide is similar.[11, 26] Pyridine abstracts two molecules of Me_2SnCl_2 from three of **16-8**, to leave the tetrastannatriazabicyclo[3.1.1]heptane **16-9**.[27]



(16-7)

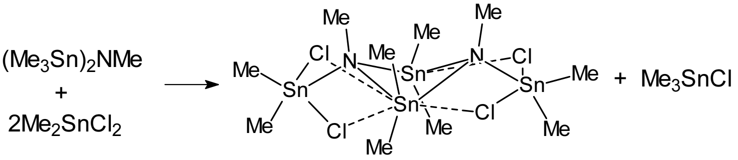


(16-8)



(16-9)

The compound $(ClMe_2Sn)_2NMe$ which can be obtained from a similar reaction of bis(trimethylstannyl)methylamine (equation 16-26) is interesting in that it is the nitrogen analogue of tetramethyldichlorodistannoxane $ClMe_2SnOSnMe_2Cl$ which is dimeric in the solid state and in solution (Section 12.2). It is similarly dimeric as shown in **16-10**, but the central Sn_2N_2 ring is non-planar, and the molecule can be regarded a diazadistannetidine coordinated to two *cis* Me_2SnCl_2 groups.[15]



(16-26)

(16-10)

The ^{15}N NMR parameters of organotin compounds have been reviewed by Wrackmeyer.[28]

16.1.3 Reactions

In most of the reactions of the stannylamines, the NR_2 group acts as a mild nucleophile in substitution or addition reactions.

$$\text{Sn-NR}_2 + \text{Nu-E} \longrightarrow \text{Sn-Nu} + \text{E-NR}_2 \qquad (16\text{-}27)$$

$$\text{Sn-NR}_2 + \text{Nu=E} \longrightarrow \text{Sn-Nu-E-NR}_2 \qquad (16\text{-}28)$$

When Nu-E is a protic acid (E = H), the substitution reactions provide a route to various new types of organotin compound. In the addition reactions, the heterocumulenes (CO_2, RN=C=O, RN=C=NR etc.) constitute an important group of acceptor molecules Nu-E. There are also a few reactions which involve homolytic cleavage of the Sn–N bond.

16.1.3.1 With Protic Acids[29]

Protic acids HX with pK_a less than about 25 cleave the Sn-N bond by reaction 16-29.

$$\text{SnNR}_2 + \text{HX} \longrightarrow \text{SnX} + \text{HNR}_2 \qquad (16\text{-}29)$$

These reactions occur more readily than with the Sn-OR or Sn-OSn bonds; they often provide useful syntheses under mild conditions of the products SnX, and these reactions are discussed in the sections dealing with those compounds.

Hydrolysis occurs very readily to give the organotin hydroxides or oxides, and the stannylamines must be prepared, stored and handled under dry, CO_2-free, conditions. The organotin derivatives of pyrrole are less sensitive, and their hydrolysis is reversible.[3] Alcoholysis of the aminostannanes provides a clean route under mild conditions to the alkoxides $R_nSn(OR')_{4-n}$, particularly when $n = 0–2$ (Section 14.1.1). Silanols similarly give stanna-siloxanes containing the group SnOSi. The transamination reaction with amines is discussed above as a route to other stannylamines (section 16.1.1.2); the *N*-stannylation of amides is described below (Section 16.3) but is less important as the reaction can usually be carried out more conveniently with bis(tributyltin) oxide or organotin alkoxides.

Terminal alkynes (Section 8.2), cyclopentadienes (Section 9.3), and diazocompounds (Section 6.2) are strong enough acids to undergo stannylation at room temperature. Chloroform brings about acidolysis reacts to give R_3SnCCl_3, and sealed NMR tubes containing $DCCl_3$ solutions of tin derivatives of volatile amines have been reported to explode in the probe.

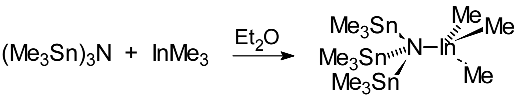
The reactions with hydrogen cyanide, hydrazoic acid, phosphines, and arsines (Section 16.5) have been used as routes to the organotin cyanides, azides, phosphines and arsines, respectively. Examples are given in the following equations.[29]

$$Me_3SnNMe_2 + Ph_2PH \xrightarrow[80\%]{20\ ^oC} Me_3SnPPh_2 + Me_2NH \qquad (16\text{-}30)$$

$$Et_3SnNMe_2 + Ph_2AsH \xrightarrow[80\%]{20\ ^oC} Et_3SnAsPh_2 + Me_2NH \qquad (16\text{-}31)$$

16.1.3.2 With Metal Derivatives

Tris(trimethylstannyl)amine reacts with Me_3M, M = Al, Ga, or In, to give the complexes $(Me_3Sn)_3N\text{-}MMe_3$ (e.g. equation 16-32). With Me_2InCl or Et_2InCl, complexation is followed by elimination of $Me_3Sn\text{-}Me$ to give $(Me_3Sn)_2N\text{-}InMeCl$ which exists as a centrosymmetic dimer.[30]



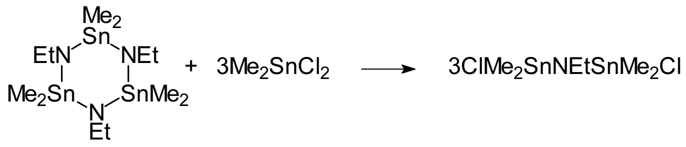
(16-32)

$$(Me_3Sn)_3N + InMe_2Cl \xrightarrow{Et_2O} [(Me_3Sn)_3N\text{-}InMe_2Cl] \xrightarrow{-Me_4Sn} [(Me_3Sn)_2N\text{—}InMeCl]_2 \qquad (16\text{-}33)$$

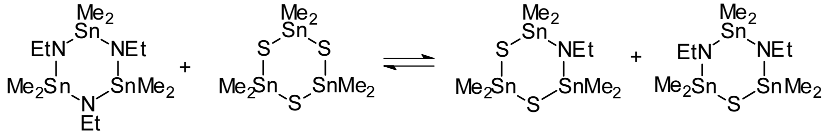
With other Lewis acids, exchange is usually observed between nitrogen on the tin and an electronegative ligand on the other metal. Some examples are shown in equations 16-34–16-36. The aminochlorostannanes (**16-11**) are rather unstable at room temperature and their detailed structures are not known. The tetraalkyldichlorodistannazanes (equation 16-35) are more stable, and the structure of one (**16-10**) is described above. The ^1H and ^{119}Sn NMR spectra show that a mixture of cyclotristannazane and a cyclotristannathiane is in equilibrium with the cyclotristannaazadithiane and cyclotristannadiazathiane (equation 16-36).[31]

$$Me_2Sn(NEt_2)_2 + Me_2SnCl_2 \longrightarrow 2Me_2Sn(NEt_2)Cl \qquad (16\text{-}34)$$

(**16-11**)



(16-35)

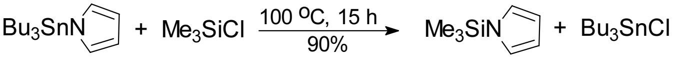


(16-36)

Analogous exchange reactions occur with derivatives of other metals. Some examples are shown in equations 16-37–16-39.[3, 32]

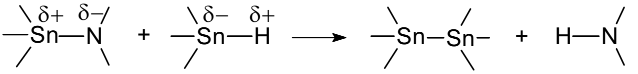
$$3Me_3SnNMe_2 + BF_3.OEt_2 \longrightarrow 3Me_3SnF + B(NMe_2)_3 + OEt_2 \tag{16-37}$$

$$3Me_3SnNMe_2 + B(OMe)_3 \longrightarrow 3Me_3SnOMe + B(NMe_2)_3 \tag{16-38}$$



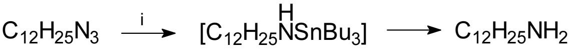
(16-39)

These are polar reactions with the components polarised in the sense $Sn^{\delta+}–N^{\delta-}$ and $M^{\delta+}–X^{\delta-}$. Different behaviour is observed in the reaction of the aminostannanes with tin hydrides in which the polarisation appears to be in the sense $Sn^{\delta-}–H^{\delta+}$ (equation 16-40), and the products are the distannane and amine. These hydrostannolysis reactions of amino- and amido-stannanes provide an important route to Sn-Sn bonded compounds, and are discussed in Section 18.2.1.3.



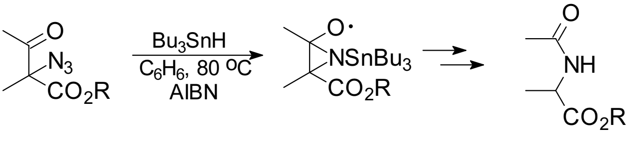
$$\overset{\delta+}{-Sn}-\overset{\delta-}{N} + \overset{\delta-}{-Sn}-\overset{\delta+}{H} \longrightarrow -Sn-Sn- + H-N \tag{16-40}$$

An aminostannane intermediate is involved in the homolytic reduction of an azide to the corresponding amine,[33] and in the conversion of α-azido-β-ketoesters into amides and lactams (equations 16-41 and 16-42).[34]



$$C_{12}H_{25}N_3 \xrightarrow{i} [C_{12}H_{25}\overset{H}{N}SnBu_3] \longrightarrow C_{12}H_{25}NH_2 \tag{16-41}$$

i. PHMS, 5 mol% $(Bu_3Sn)_2O$, PrOH, AIBN, 90 °C 95%

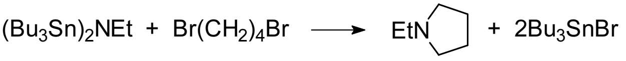


(16-42)

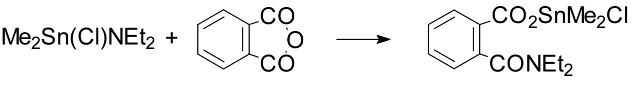
16.1.3.3 With Other Singly-bonded Electrophiles

Towards other singly-bonded electrophiles, the stannylamines behave as mild nucleophiles. The more reactive alkyl halides can be converted into the corresponding alkyl amines (equation 16-43 and 16-44)[35], and acid anhydrides (equation 16-45)[31] and acyl halides (equation 16-46)[36] give the amides.

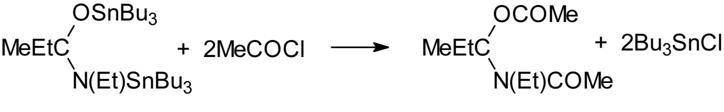
$$(Bu_3Sn)_2NEt + PhCH_2Cl \xrightarrow[70\%]{} Bu_3SnN(Et)CH_2Ph + Bu_3SnCl \tag{16-43}$$



(16-44)



(16-45)

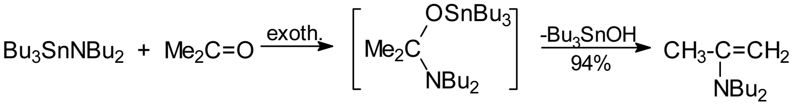


$$MeEtC\begin{cases}OSnBu_3\\N(Et)SnBu_3\end{cases} + 2MeCOCl \longrightarrow MeEtC\begin{cases}OCOMe\\N(Et)COMe\end{cases} + 2Bu_3SnCl \tag{16-46}$$

16.1.3.4 With Doubly-bonded Electrophiles [37]

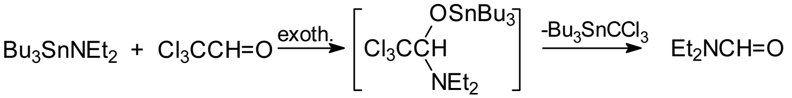
The aminotin compounds show the same type of addition reactions which are discussed for the alkoxytin compounds in Section 14.1.3.

The addition of dialkylaminostannanes to aldehydes and ketones often gives a mixture of tin-free products derived from addition and elimination reactions of the monomeric carbonyl compound and of its products of base-catalysed aldol condensation. With appropriate substituents, however, reasonable yields of the enamines can be isolated, for example:[38]



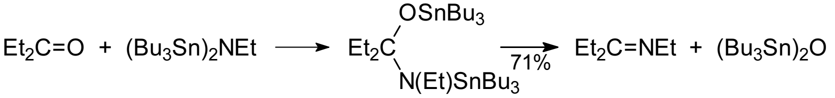
$$\mathrm{Bu_3SnNBu_2 + Me_2C{=}O \xrightarrow{exoth.} \left[Me_2C(OSnBu_3)(NBu_2) \right] \xrightarrow[94\%]{-Bu_3SnOH} CH_3\text{-}C(NBu_2){=}CH_2} \qquad (16\text{-}47)$$

In the reaction with chloral, Bu_3SnCCl_3 is eliminated, and diethylformamide is formed.[39]



$$\mathrm{Bu_3SnNEt_2 + Cl_3CCH{=}O \xrightarrow{exoth.} \left[Cl_3CCH(OSnBu_3)(NEt_2) \right] \xrightarrow{-Bu_3SnCCl_3} Et_2NCH{=}O} \qquad (16\text{-}48)$$

Distannazanes react with aldehydes and ketones to give the corresponding imines via addition to the carbonyl group, then elimination of bis(tributyltin) oxide (equation 16-49);[36] the intermediate can be identified by acetylation as shown in equation 16-46.

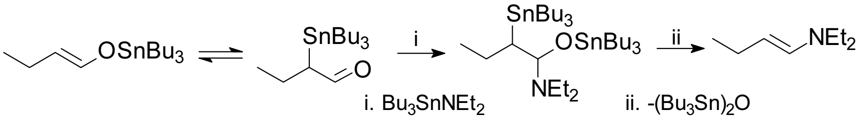


$$\mathrm{Et_2C{=}O + (Bu_3Sn)_2NEt \longrightarrow Et_2C(OSnBu_3)(N(Et)SnBu_3) \xrightarrow[71\%]{} Et_2C{=}NEt + (Bu_3Sn)_2O} \qquad (16\text{-}49)$$

α-Chloroketones containing the group O=C–C–Cl react with dialkylaminostannanes to give α-aminoketones, perhaps by way of addition, then elimination of Bu_3SnCl to give an α-epoxyamine which rearranges to the aminoketone.[40]

$$\mathrm{PhCOCH_2Cl + Bu_3SnNEt_2 \xrightarrow[48\%]{} PhCOCH_2NEt_2 + Bu_3SnCl} \qquad (16\text{-}50)$$

Enolates give enamines, again probably via addition and elimination (equation 16-51),[41] and benzonitrile undergoes addition on heating to give the stannylbenzamidine (equation 16-52).[42]



(16-51)

$$\mathrm{Me_3SnNMe_2 + N{\equiv}CPh \xrightarrow[60\%]{reflux\ 1.5\ h} Me_3SnN{=}C(Ph)NMe_2} \qquad (16\text{-}52)$$

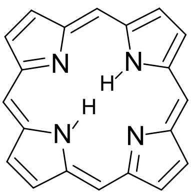
Addition reactions also occur with the same heterocumulenes which react with tin alkoxides. The reactivity of the Sn-N bond in this sense is usually greater than that of the Sn-O bond, and the reactions occur under mild conditions in essentially quantitative yield.[37, 42] Examples of the adducts formed by Me_3SnNMe_2 are given in Table 16-1.

Table 16-1 Reaction of Me_3SnNMe_2 with heterocumulenes.

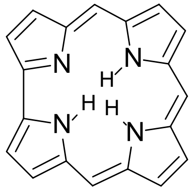
Acceptor	Adduct	Acceptor	Adduct
O=C=O	$Me_3SnOC(=O)NMe_2$	PhN=C=S	$Me_3SnNPhC(=S)NMe_2$
S=C=S	$Me_3SnSC(=S)NMe_2$	TolN=C=NTol	$Me_3SnNTolC(=NTol)NMe_2$
$CH_2=C=O$	$Me_3SnCH_2C(=O)NMe_2$	O=S=O	$Me_3SnOS(=O)NMe_2$
PhN=C=O	$Me_3SnNPhC(=O)NMe_2$	PhN=S=O	$Me_3SnNPhS(=O)NMe_2$

16.2 Stannyl Porphyrins and Corroles[43]

The diprotic porphyrins (**16-12**) and triprotic corroles (**16-13**) provide dianions and trianions which can form complexes with the R_2Sn^{2+} or $RXSn^{2+}$, and RSn^{3+} ions respectively.



(**16-12**)
Porphyrin $H_2(Por)$

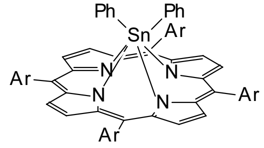


(**16-13**)
Corrole $H_3(Cor)$

The dialkylstannyl porphyrins $R_2Sn(Por)$, where Por represents a generalised porphyrin dianion, can be formed from the reaction of $Cl_2Sn(Por)$ with RMgX; they are rather unstable, and absorb oxygen in the presence of light to give the peroxides $R(ROO)Sn(Por)$, then, more slowly, $(ROO)_2Sn(Por)$.

The aryl- and alkynyl-tin derivatives are more stable. *cis*-Diphenylstannyl-*meso*-tetrakis(*p*-t-butylphenyl)porphyrin can be prepared from the corresponding $Li_2(Por)$ and Ph_2SnCl_2, and has the structure shown in **16-14**, in which the porphyrin ring is both ruffled and domed, and the tin atom is 111 pm out of the mean plane of the porphyrin.[44] *trans*-Diphenylstannyl-*meso*-tetrakisphenylporphyrin, **16-15**, made from $Cl_2Sn(Por)$ and Ph_2Mg, is centrosymmetric with a planar porphyrin unit.[44] The structure of the corresponding *trans*-di(phenylethynyl) derivative is similar.[45]

$L_2(Por) + Ph_2SnCl_2 \longrightarrow$

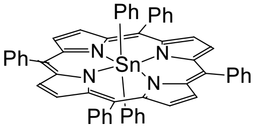


$Ar = 4\text{-}Bu^tC_6H_4$

(**16-14**)

(16-53)

$Cl_2(Por) + Ph_2Mg \longrightarrow$



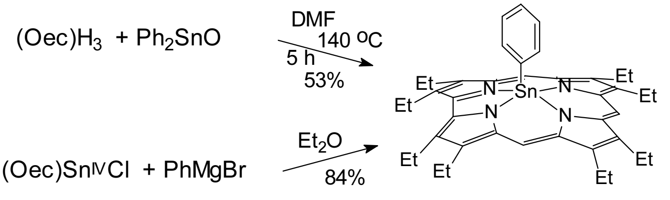
(**16-15**)

(16-54)

Exposure of either *cis*- or *trans*-diphenylstannyl-*meso*-tetrakisphenylporphyrin to light in $CHCl_3$ gives the corresponding *trans*-phenylchlorostannylporphyrin.[44] Methyliodostannylporphyrins can also be made by the oxidative addition ("direct reaction") of methyl iodide to tin(II) porphyrins.[46]

If bis(trimethylsilylmethyl)stannylporphyrin is photolysed in the presence of oxygen, one molecular equivalent of oxygen is absorbed rapidly, to give the monoperoxide $(Me_3SiCH_2)(Me_3SiCH_2OO)Sn(Por)$, then the second more slowly to give the diperoxide $(Me_3SiCH_2OO)_2Sn(Por)$.[47–50] This interesting reaction does not appear to have been investigated in recent years, and it deserves further attention.

Octaethylcorrole, $H_3(Oec)$ reacts with diphenyltin oxide to give PhSn(Oec), and the same product is formed from the phenylation of ClSn(Oec) with phenylmagnesium bromide (equation 16.55).[51] The corrole adopts a domed conformation (**16-16**), and the 5-coordinate tin atom is 72.2(3)pm above the average plane of the four nitrogen atoms, with *r*SnC 210.5 pm.



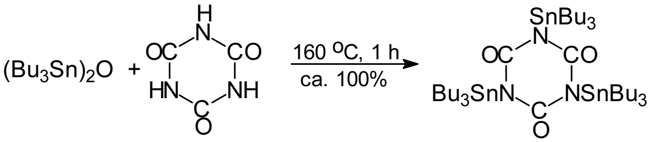
(**16-16**)

(16-55)

16.3 Amidostannanes

Amidostannanes containing the groups Sn-NC(=O)R or $Sn\text{-}NS(O)_2R$ are easier to prepare and to handle than are the aminostannanes. The acidity of the proton on nitrogen in the parent amide is now sufficient for reaction to occur with organotin hydroxides, oxides, and alkoxides (and aminotin compounds), and, once formed, the amidostannanes are less sensitive to moisture. A variety of amidostannanes is also available from the addition of Sn-O and Sn-N bonded compounds to nitrogen heterocumulenes.

Some examples of the *N*-stannyldeprotonation of amides are given in equations 16-56,[52] 16-57,[53] 16-58, and 16-59,[54] and 16-60.[55]



(16-56)

$$Et_3SnOMe + PhNHCH{=}O \xrightarrow[83\%]{10\ \text{min},\ 160\ ^{\circ}C} Et_3SnNPhCH{=}O \qquad (16\text{-}57)$$

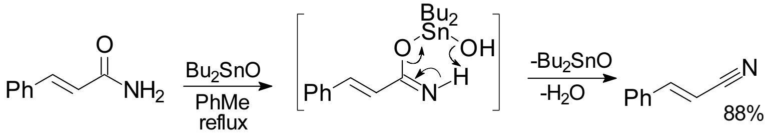
$$(Bu_3Sn)_2O + EtNHCO_2Me \xrightarrow{100\ ^{\circ}C} Bu_3SnNEtCO_2Me \qquad (16\text{-}58)$$

$$(Bu_3Sn)_2O + EtO_2CNHNHCO_2Et \xrightarrow{120\ ^{\circ}C} EtO_2CN(SnBu_3)N(SnBu_3)CO_2Et \qquad (16\text{-}59)$$

$$Me_3SnNMe_2 + MeCONH_2 \xrightarrow[24\ \text{h.}\ 89\%]{THF,\ 45\ ^{\circ}C} MeCON(SnMe_3)_2 \qquad (16\text{-}60)$$

If X in the reagent HN-C(=O)X is a more electronegative group, the secondary amides RNHCOX react with bis(tributyl)tin oxide to give ureas $\mathrm{Bu_3SnNRCONRSnBu_3}$, and primary amides $\mathrm{NH_2COX}$ give the isocyanate, $\mathrm{Bu_3SnNCO}$. These reactions can be understood in terms of initial stannyldeprotonation followed by elimination of $\mathrm{Bu_3SnX}$, and subsequent reactions.[54]

Dibutyltin oxide catalyses the dehydration of primary amides or thionoamides to nitriles under neutral conditions. The reaction can be represented as a cyclic elimination involving the *O*-stannyl (or *S*-stannyl) isomer.[56]



(16-61)

The formation of amidostannanes by the addition of organotin alkoxides or oxides to *N*-heterocumulenes such as isocyanates is discussed in Sections 12.1.2 and 14.1.3. The stannyl *N*-stannylcarbamates which are formed from bis(tributyltin) oxide and an isocyanate, decarboxylate on heating or on treatment with more isocyanate to give distannylureas, which can add to more isocyanate to give distannylbiurets, providing a route to mixed ureas and biurets. An example is shown in equation 16-62.[57]

$$\begin{tikzcd}
\mathrm{(Bu_3Sn)_2O} \arrow[r, "\mathrm{MeNCO}"] & \mathrm{Bu_3SnMeNCO_2SnBu_3} \arrow[r, "\mathrm{PhNCO}", "-\mathrm{CO_2}"'] & \mathrm{Bu_3SnMeNCONPhSnBu_3} \arrow[d, "\mathrm{NpNCO}"'] \\
& \mathrm{NpNHCONMeCONHPh} & \mathrm{Bu_3SnNpNCONMeCONPhSnBu_3} \arrow[l, "\mathrm{H_2O}"']
\end{tikzcd}$$

(16-62)

The reactivity of the Sn-N bond in additions of this type is greater than that of the Sn-O bond, and reaction of an aminostannane with an isocyanate provides an alternative route to stannylureas, for example equation 16-63.[42]

$$\mathrm{Me_3SnNMe_2} + \mathrm{PhN{=}C{=}O} \xrightarrow[95\%]{\mathrm{RT}} \mathrm{Me_3SnNPhCONMe_2} \tag{16-63}$$

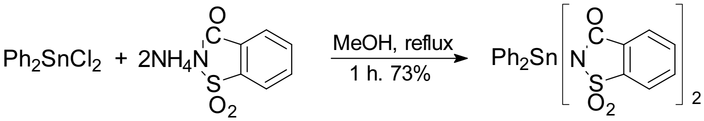
X-Ray diffraction confirms that, in the crystal, the compounds $\mathrm{MeCON(SnMe_3)Me}$ and $\mathrm{MeCON(SnMe_3)_2}$ have planar amide rather than imidate structures, and spectroscopic evidence suggests that this is the dominant structure also in solution; in the solid, the C=O and N-Sn bonds are *cis*, with a weak intramolecular O..Sn interaction, and a stronger intermolecular interaction.[55]

16.4 Sulfonamidostannanes

Sulfonamides, like carboxamides, can be *N*-stannylated by azeotropic dehydration in the presence of bis(tributyltin) oxide in a solvent such as benzene or toluene, and the products can usually be purified by distillation.[58]

$$\mathrm{(Bu_3Sn)_2O} + \mathrm{PrNHSO_2Ph} \xrightarrow[-\mathrm{H_2O}]{\mathrm{PhMe}} \mathrm{Bu_3SnNPrSO_2Ph} \tag{16-64}$$

Saccharin can be stannylated in an analogous way, or by treating an organotin chloride with a salt of saccharin (equation 16-65).[59] The triorganotin (e.g. $\mathrm{Me_3Sn}$ or $\mathrm{Ph_3Sn}$) derivatives readily form 5-coordinate complexes with water or with alcohols in which the structure is trigonal bipyramidal about the tin.[60]



(16-65)

The di(methylsulfonyl)amides, $Ph_3SnN(SO_2Me)_2$ and $Cy_3SnN(SO_2Me)_2$, form infinite chains consisting of alternate trigonal planar SnC_3 units and (α-O,ω-O)-bridging dimesylamide groups. $Ph_3SnN(SO_2Me)_2$ Forms a complex $Ph_3SnN(SO_2Me)_2 \cdot Ph_3SnOH \cdot 2MeCN$ which consists of an infinite chain in which Ph_3Sn groups are linked by alternating μ-O(H) and (α-O,ω-O)-bonded dimesylamide units; one MeCN is hydrogen bonded to the μ-O(H) group, and the second occupies a cavity in the crystal lattice between the chains.[61]

Stannylsulfonamides can also be prepared by the addition of the SnO bond to sulfodiimides (RN=S=NR) or sulfinylamines (RN=S=O); in these reactions, the bis(trialkyltin) oxides appear to be more reactive than the corresponding alkoxides.[62, 63] The weak sulfur-containing acceptors can then be displaced by more powerful acceptors such as isocyanates or chloral.

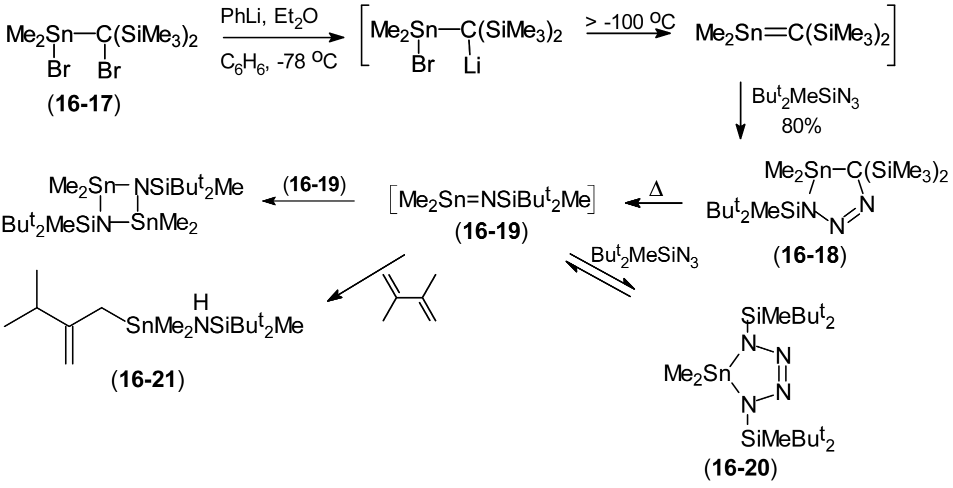
$$(Bu_3Sn)_2O + PhN{=}S{=}NPh \longrightarrow Bu_3SnNPhS(O)NPhSnBu_3 \qquad (16\text{-}66)$$

$$Bu_3SnOMe + TolSO_2N{=}S{=}O \longrightarrow TolSO_2N(SnBu_3)SO_2Me \qquad (16\text{-}67)$$

The stannylsulfonamides can react with singly or multiply bonded electrophiles by cleavage of, or insertion into, the Sn-N bond, but the reactivity appears to decrease in the sequence $R_3Sn\text{-}NR'_2 > R_3SnNR''COR' > R_3SnNR''SO_2R'$, in accord with the principle that the reactivity is dominated by the nucleophilicity of the nitrogen-containing group.

16.5 Stannaimines, $R_2Sn{=}NR'$

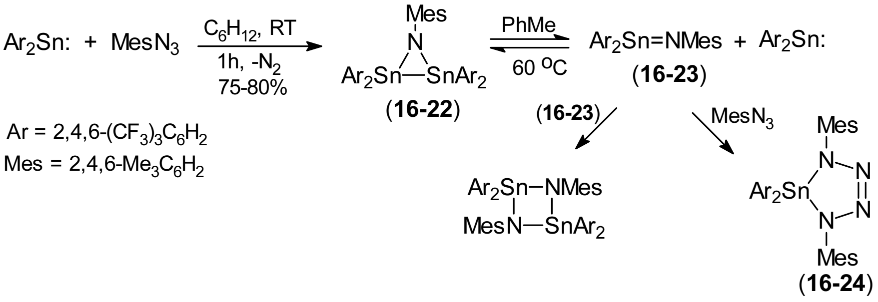
There has been evidence for some time for stannaimines as transient intermediates, and one example has been isolated and characterised by X-ray crystallography. If the



Scheme 16-1 Formation and reactions of a stannaimine (1).

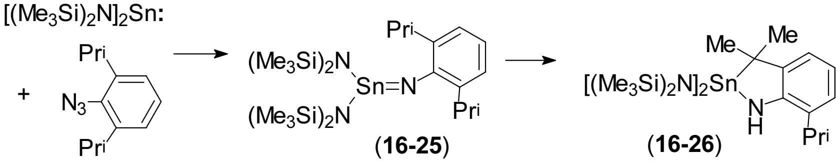
1-bromoalkyltin bromide **16-17** is treated with phenyllithium in the presence of di-t-butylmethylsilyl azide, (Scheme 16-1), the triazastannolene **16-18** is formed, and if this is warmed it gives the stannaimine **16-19** which, in the absence of any other reagent, dimerises to the diazadistannetane. If the reaction is carried out in the presence of di-t-butylmethylsilyl azide, the stannaimine is trapped to give the tetraazastannolene **16-20**, and, in the presence of 2,3-dimethylbuta-1,3-diene, it gives the aminostannane **16-21** by an ene reaction.[64]

An alternative route into similar chemistry is shown in Scheme 16-2. Bis[tris(trifluoromethyl)phenyl]stannylene reacts with mesityl azide to give the distannaaziridine (**16-22**), which dissociates at 60 °C into the stannylene and stannaimine (**16-23**). Again, the stannaimine dimerises to give the diazadistannetane, or it can be trapped by mesityl azide to give the tetraazastannolene (**16-24**).[65]



Scheme 16-2 Formation and reactions of a stannaimine (2).

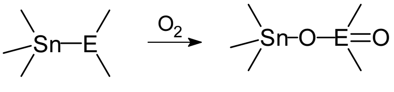
By stabilising the stannaimine by steric hindrance, and generating it at low temperature, **16-25** was isolated as dark red crystals. The three nitrogen atoms are coplanar about the tin, with *r*Sn-N 201.5(2) and 203.0(3) pm, and *r*Sn=N 192.1(2) pm, whereas the usual length of a Sn-N single bond is 205 pm. Below −30 °C, the imine is stable, but above −25 °C in hexane it rearranges to the stannazole **16-26**.[66]



(16-68)

16.6 Compounds with Sn–P Bonds[2]

The organotin derivatives of phosphorus, arsenic, antimony, and bismuth have much in common with the corresponding derivatives of nitrogen, the most obvious difference being that the nitrogen compounds are unreactive towards oxygen, whereas the others are oxidised in air:

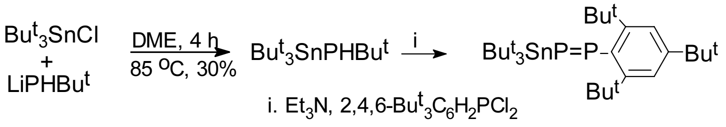


(E = P, As, Sb, or Bi)

(16-69)

Stannylphosphines can be prepared by treating an organotin halide with a metallophosphine, or with a hydridophosphine in the presence of a tertiary amine, or by acidolysis of a stannylamine with a phosphine. Some examples of these reactions are given in equations 16-70,[67] 16-71,[68] and 16-72.[69] Stannylphosphines containing a PH group, like the corresponding amines, disproportionate unless they are stabilised by steric hindrance.

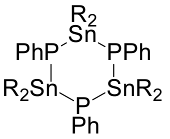
$$\mathrm{Bu_3SnBr} + \mathrm{NaPPh_2} \xrightarrow{\text{lqd. NH}_3} \mathrm{Bu_3SnPPh_2} \qquad (16\text{-}70)$$



(16-71)

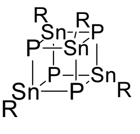
$$3\mathrm{Me_3SnCl} + \mathrm{PH_3} \xrightarrow{\mathrm{Et_3N}} \mathrm{(Me_3Sn)_3P} \qquad (16\text{-}72)$$

With di- or tri-functional reactants, these reactions can give cyclic oligomers, for example **16-27–16-29**.[70–72]

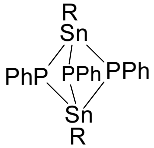


(R = Me, Bu, or Ph)

(**16-27**)



(**16-28**)



(R = Bu, or Ph)

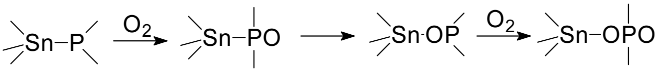
(**16-29**)

Acidolysis of an aminostannane with a phosphine or arsine provides a clean route to the stannyl-phosphines and -arsines (Section 16.1.3.1), and, under more forcing conditions, the phosphines can be prepared from bis(tributyltin) oxide.[73]

$$\mathrm{(Bu_3Sn)_2O} + \mathrm{Ph_2PH} \xrightarrow[80\ ^\circ\mathrm{C}]{\mathrm{C_6H_6,\ CaH_2}} \mathrm{Bu_3SnPPh_2} \qquad (16\text{-}73)$$

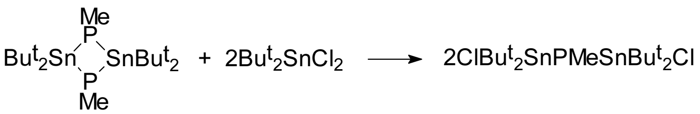
The Sn-P bond can also be formed by nucleophilic attack of tin on a phosphorus halide, though this reaction has not been widely exploited.

The autoxidation of the stannylphosphines appears to give first the phosphine oxides which then rearrange and are more rapidly oxidised to the phosphinates.[72]



(16-74)

The Sn-P bonds are readily cleaved by water and other protic acids, and enter into exchange reactions with tin halides (e.g. equation 16-75).[74]



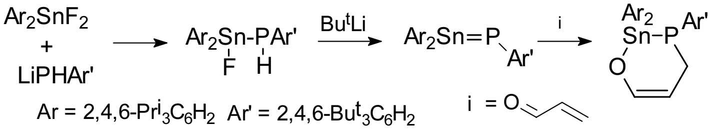
(16-75)

The Sn-P bond also adds to the same polar multiply-bonded acceptors (PhNCO, PhNCS, CS_2, and COS) to which Sn-O and Sn-N bonds add (Section 14.1.3 and 16.1.3.4) (e.g. equation 16-76); these reactions are thought to involve polar 4-centre processes.[75] Additions also occur to alkenes, alkynes, and allenes with much less polar multiple bonds (e.g. equation 16-77); these reactions are initiated by AIBN or by photolysis, and involve radical chain mechanisms similar to those of the addition of tin hydrides.[76-78]

$$Ph_3SnPPh_2 + PhNCO \xrightarrow[64\%]{C_6H_6,\ 80\ ^{o}C} Ph_3SnNPhCOPPh_2 \qquad (16\text{-}76)$$

$$Me_3SnPPh_2 + PhC{\equiv}CH \xrightarrow[59\%]{h\nu} \underset{Z/E\ 1/9}{Me_3SnCH{=}C(Ph)PPh_2} \qquad (16\text{-}77)$$

Compounds containing the Sn=P double bond (stannaphosphenes) have been characterised, where very bulky ligands prevent oligomerisation,[79-81] the double bond being introduced by the elimination of HF as shown in equation 16-78. The products are isolated as deep red solids; no crystal structure has yet been determined, but the NMR spectra are very characteristic. With 1,2-diones, *o*-quinones, or enones, [2+4]-cycloaddition occurs to give six-membered rings.



(16-78)

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17 Compounds with Sn–S Bonds[1, 2]

There are many parallels between the chemistry of compounds containing Sn–S bonds and those containing Sn–O bonds, and compounds of the structures R_3SnSR', $R_2Sn(SR')_2$, $RSn(SR')_3$, $(R_3Sn)_2S$, $(R_2SnS)_n$, and $(RSnS_{1.5})_n$ can be prepared by substitution at tin by a sulfur nucleophile. An important difference is that whereas the Sn–O bonded compounds often self-associate to give oligomers or polymers with 5-coordinate tin, the sulfur compounds show less tendency to associate. For example the compounds $(R_2SnX)_n$, and $(RSnX_{1.5})_n$, when X = O, are usually cross-linked insoluble polymers, whereas when X = S, they are usually unassociated, soluble, compounds, with n = 3 or 4 respectively, and with 4-coordinate tin. The Sn-S bonds are also less easily cleaved in substitution (e.g. hydrolysis) and addition reactions, and indeed the Sn-S bond is often formed in an elimination process.

The tin thiols, R_3SnSH, (like the hydroxides, R_3SnOH), are usually unstable and disproportionate to give the ditin sulfides and H_2S; the only known exception appears to be tri-t-butyltin hydrosulfide, which has been prepared by the reaction shown in equation 17-1. When it is sublimed at 200-210 °C/10^{-4} bar it is converted into the sulfide.[3]

$$\begin{tikzcd}
(Bu^t_2SnS)_2 + Bu^tLi \arrow[r] & Bu^t_3SnSLi \arrow[r, "H_2O"] \arrow[d, "Me_3SnCl"] & Bu^t_3SnSH \arrow[d, "\triangle"] \\
& Bu^t_3SnSSnMe_3 & (Bu^t_3Sn)_2S
\end{tikzcd} \qquad (17\text{-}1)$$

Some organotin thiolates and sulfides have found industrial application as stabilisers for poly(vinyl chloride). Much of the work on organotin compounds of sulfur has been directed towards this end, and much of it has been published only in the patent literature.

17.1 Organotin Sulfides

17.1.1 Preparation

The principal routes to the organotin sulfides are:

1. Nucleophilic substitution by H_2S or a metal sulfide at tin.
2. Reaction with a sulfur-transfer reagent via an addition-elimination or substitution-elimination sequence.
3. Reaction of an Sn-Sn bonded compound with elementary sulfur.

Some examples of the first method are shown in equations 17-2,[4] 17-3,[5] and 17-4.[5, 6]

$$Me_2Sn(OMe)Cl + H_2S \xrightarrow[94\%]{C_6H_6,\ RT} ClMe_2SnSSnMe_2Cl \qquad (17\text{-}2)$$

$$\underset{76\%}{(Mes_2SnS)_2} \xleftarrow[12\ h,\ 70\ ^{\circ}C]{Na_2S,\ EtOH/PhMe} Mes_2SnCl_2 \xrightarrow[\substack{4\ h,\ 70\ ^{\circ}C \\ 17\ h,\ 20^{\circ}C}]{Na_2S,\ EtOH} \underset{92\%}{(Mes_2SnS)_3} \qquad (17\text{-}3)$$

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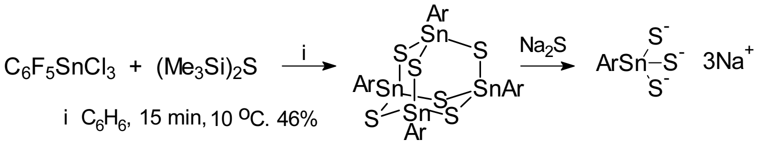
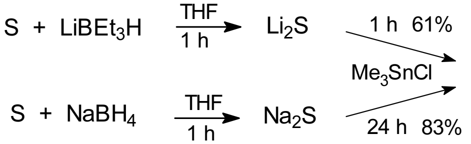


(17-4)

The metal sulfide can conveniently be prepared *in situ* by reducing sulfur with $LiBEt_3H$ or $NaBH_4$ in THF.[7]



$$\begin{array}{l} S + LiBEt_3H \xrightarrow[1\,h]{THF} Li_2S \xrightarrow[Me_3SnCl]{1\,h\ \ 61\%} (Me_3Sn)_2S \\ S + NaBH_4 \xrightarrow[1\,h]{THF} Na_2S \xrightarrow[24\,h\ \ 83\%]{Me_3SnCl} (Me_3Sn)_2S \end{array}$$

(17-5)

Sulfur-transfer reagents are compounds like thiourea or CS_2 which undergo stannylation by substitution or addition to give a compound with the structure SnABS, which then undergoes elimination to give SnS and A=B.[8]

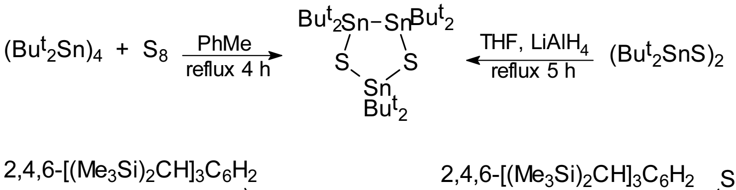
$$(Ph_3Sn)_2O + CS_2 \longrightarrow (Ph_3SnOCS_2SnPh_3) \longrightarrow (Ph_3Sn_2)_2S + COS \qquad (17\text{-}6)$$

$$\begin{array}{c} (Bu_3Sn)_2O \\ + \\ (PhNH)_2CS \end{array} \longrightarrow [Bu_3SnNPhC(=NPh)SSnBu_3] \longrightarrow \begin{array}{c} (Bu_3Sn)_2S \\ + \\ PhN{=}C{=}NPh \end{array} \qquad (17\text{-}7)$$

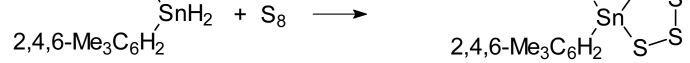
Elementary sulfur readily reacts with compounds containing an SnSn or SnH bond, to give the corresponding sulfides. The latter reaction may proceed via oxidation of SnH to SnSn, but even the broad details of the mechanisms of these reactions do not appear to have been studied. Some examples of the reactions are shown in equations 17-8,[9] 17-9,[10] 17-10,[11] and 17-11.[12]

$$Et_3SnSnEt_3 + S_8 \xrightarrow[67\%]{20\,^{\circ}C,\ 24\,h} Et_3SnSSnEt_3 \xleftarrow[64\%]{85\,^{\circ}C,\ 0.5\,h} Et_3SnH + S_8 \qquad (17\text{-}8)$$

$$(Ph_2Sn)_6 + S_8 \xrightarrow[reflux]{PhMe} (Ph_2SnS)_3 \qquad (17\text{-}9)$$



(17-10)



(17-11)

For the fabrication of semiconductor devices, tin chalcogenides are deposited by the thermal decomposition (MOCVD) of organotin chalcogenides R_3SnXR' (X = S, Se, or Te), which must be free of any contaminants which would detract from the performance of the semiconductors. These pure precursors can be prepared by the light-induced comproportionation of R_3SnSnR_3 and $R'XXR'$ (equation 17-12).[13] The obvious mechanism is a chain reaction involving the S_H2 reaction of $R_3Sn•$ radicals at X, and of $R'X•$ radicals at Sn.

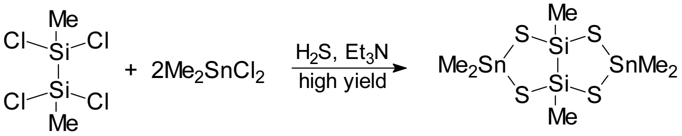
$$Me_3SnSnMe_3 + BuSSBu \xrightarrow[35\ ^oC,\ 1.5\ h]{40\ W\ lamp} 2Me_3SnSBu \qquad (17\text{-}12)$$

Examples of some simple organotin sulfides are given in Table 17-1.

Table 17-1 Organotin sulfides

Compound	M.p./°C or b.p./°C (mm Hg)	Compound	M.p./°C
$(Me_3Sn)_2S$	50 (0.5)	$(Bu_2SnS)_3$	64–6
$(Et_3Sn)_2S$	124–8 (0.1)	$(Ph_2SnS)_3$	185
$(Bu_3Sn)_2S$	140 (0.15)	$(MeSn)_4S_6$	250 dec
$(Ph_3Sn)_2S$	145–6	$(EtSn)_4S_6$	90 dec
$(Bz_3Sn)_2S$	85	$(BuSn)_4S_6$	150 dec
$(Me_2SnS)_3$	149	$(PhSn)_4S_6$	255 dec
$(Et_2SnS)_3$	25	$(Bu^t{}_2SnS)_2$	195

Silastannathianes containing the unit SiSSn can be prepared from the reaction of a mixture of tin halide and silicon halide with hydrogen sulfide in the presence of an amine, and the corresponding selenium and tellurium compounds from a similar reaction using lithium selenide or lithium telluride.[14]



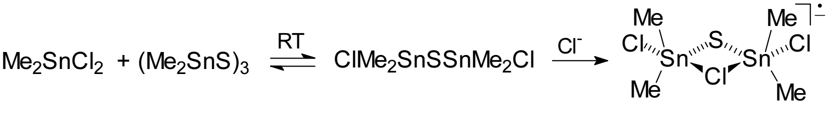
(17-13)

17.1.2 Structures

These compounds show little tendency towards self-association. Thus $(Ph_3Sn)_2S$ is a monomer in the crystal, with slightly distorted tetrahedral tin and rSnS 237 pm, SnSSn 107.4^0.[15] Hexabenzyldistannathiane, $[(PhCH_2)_3Sn]_2S$, is similarly bent [SnSSn 105.52(14)^0][16] (though the corresponding oxide is linear), but $(Bu^t{}_3Sn)_2S$, for steric reasons, is linear.[17] As in the oxides, the structure can be correlated with the $^2J(^{119}Sn-^{117}Sn)$ coupling.

Most dialkyltin sulfides are cyclic trimers, $(R_2SnS)_3$, with the structure of a twisted boat [e.g. $(Me_2SnS)_3$ [18, 19]], but the sterically congested di-t-butyltin sulfide is a dimer $(Bu^t{}_2SnS)_2$ with a planar ring.[20] The compounds $(Ph_2SnX)_3$ (X = S, Se, or Te) all have similar twisted boat structures, with average SnX bond lengths of 240.8, 252.6, and 273.2 pm, respectively.[21]

Whereas the compounds $ClR_2SnOSnR_2Cl$ are dimeric both in solution and in the solid state (see Section 12.2), with 5-coordinate tin, the corresponding sulfides $ClR_2SnSSnR_2Cl$ are monomeric in solution, with 4-coordinate tin, and are in equilibrium with $(R_2SnS)_3$ and R_2SnX_2. With chloride ion, they form the pentacoordinate dinuclear complexes as shown in equation 17-14.[4, 22]



(17-14)

The sesquisulfides and sesquiselenides, are tetramers, $(RSnX_{1.5})_4$, with adamantane-like structures.[5, 23, 24]

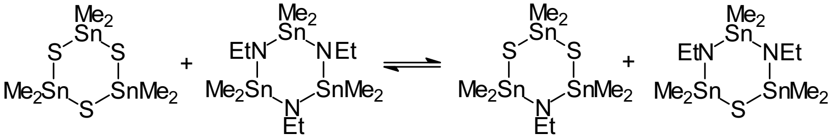
17.1.3 Reactions

The organotin sulfides are usually stable towards water and air, but react with acids such as HCl to liberate H_2S and give the corresponding tin halides. Bis(trimethyltin) sulfide (prepared *in situ* in THF as shown in equation 17-5) can be reduced with sodium, providing a convenient route to hexamethylditin (equation 18-14).[7]

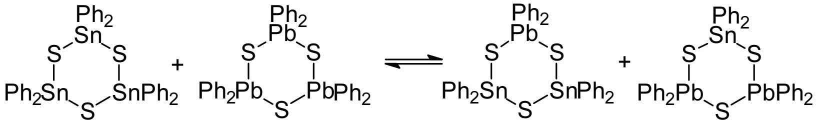
Exchange readily occurs between Sn–S and M–X, where M is tin or some other metal, and X is S or some other electronegative ligand. Thus, two simple bis(trialkyltin) sulfides $(R_3Sn)_2S$ and $(R'_3Sn)_2S$ react to give in equilibrium the mixed bis(trialkyltin) sulfide $R_3SnSSnR'_3$, and a bis(trialkyltin) sulfide reacts with a bis(trialkyltin) oxide to give in equilibrium the new simple oxide and sulfide, and the mixed oxide and sulfide (equation 17-15).[25] These compounds can be distinguished by the characteristic NMR values of $\delta^{119}Sn$ and $^2J(^{119}Sn\text{-}^{117}Sn)$. The only mixed sulfides which appear yet to have been isolated are $Bu^t_3SnSSnMe_3$ (equation 17-1) [3] and $Cy_3SnSSnPh_3$,[26] where exchange is slowed by steric hindrance.

$$(Ph_3Sn)_2S + (Bu_3Sn)_2O \xrightleftharpoons[\text{reflux 2 h}]{\text{PhMe}} \begin{array}{c} (Ph_3Sn)_2O + (Bu_3Sn)_2S \\ + \\ Bu_3SnSSnPh_3 + Bu_3SnOSnPh_3 \end{array} \qquad (17\text{-}15)$$

$(Ph_2SnS)_3$ And $(Me_2SnSe)_3$ react in solution to show the ^{119}Sn NMR spectra of 20 different interbred products.[27] Similar exchange occurs between cyclotrimeric dialkyltin sulfides and dialkylstannylalkylamines (equation 17-16),[28] and between diaryltin sulfides and diaryllead sulfides (equation 17-17),[28, 29] and again the components can readily be monitored by ^{119}Sn NMR spectroscopy.



(17-16)



(17-17)

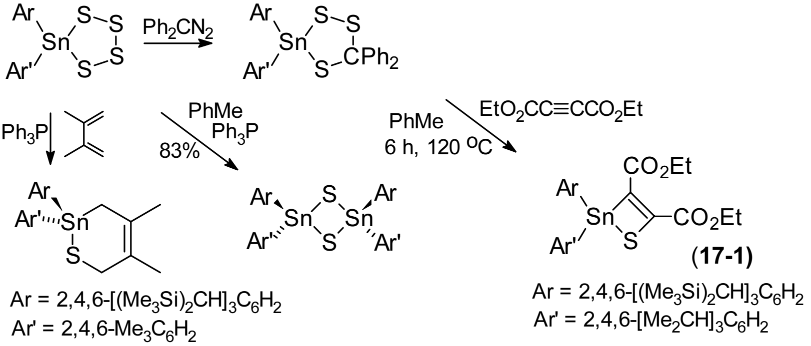
Exchange also occurs between the Sn-S bond in dialkyltin sulfides and the Sn-X bond in the organotin compounds R_2SnX_2 (X = halide, SCN, OMe, or carboxylate) to give functionally substituted distannathianes and tristannathianes, for example:[4]

$$(Bu_2SnS)_3 \xrightarrow{\text{i}} ClBu_2SnSSnBu_2Cl \xrightarrow{\text{ii}} ClBu_2SnSSnBu_2SSnBu_2Cl \qquad (17\text{-}18)$$

i. Bu_2SnCl_2, 40 °C, 5 min ii. $(Bu_2SnS)_3$, 69%

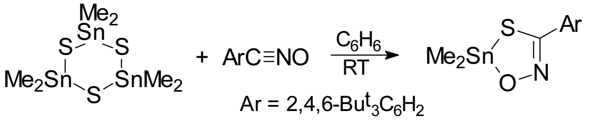
17.2 Stannathiones $R_2Sn{=}S$

No monomeric diorganotin sulfides, with an Sn=S double bond, have yet been isolated, but there is good evidence for their existence as reactive intermediates. If a tetrathiastannolane (from the diaryltin sulfide and sulfur) is heated with triphenylphosphine, the dimeric sulfide is formed, and in the presence of 2,3-dimethylbutadiene, the cycloadduct is formed (Scheme 17-1). If the trithiastannolane, prepared as shown in Scheme 17-1, is heated in toluene in the presence of diethyl acetylenedicarboxylate, the cycloadduct **17-1** is formed, presumably through the intermediate ArAr′Sn=S.[30]



Scheme 17-1 Reactions involving stannathione intermediates.

Similarly, if the dimeric $(Bu^t_2SnS)_2$ or trimeric $(Me_2SnS)_3$ or $(Me_2SnSe)_3$ is heated with a benzonitrile oxide, the corresponding oxathiaaza- or oxaselenaaza-stannolene is formed by a 1,3-dipolar cycloaddition (e.g. equation 17-19).[31, 32]



(17-19)

17.3 Organotin Thiolates $R_nSn(SR')_{4-n}$

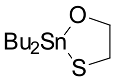
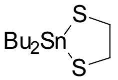
The organotin thiolates (mercaptides) are usually prepared by substitution by a sulfur nucleophile at a tin centre. Suitable pairs of reactants are (1) thiol and tin oxide, alkoxide, or amide, (2) thiol and tin halide in the presence of a base such as sodium hydroxide, sodium carbonate, ammonia, or triethylamine, or (3) metal thiolate and tin halide. Examples are shown in equations 17-20,[33] 17-21,[33] and 17-22,[34] and some of the common products are listed in Table 17-2.

$$Ph_3SnOH + HSCH_2CH_2OH \xrightarrow[-H_2O.\ 85\%]{C_6H_6,\ boil} Ph_3SnSCH_2CH_2OH \qquad (17\text{-}20)$$

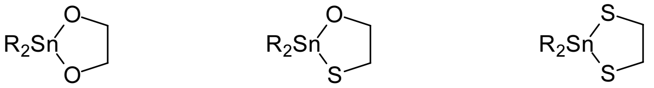
$$Bu_2SnO + 2BuSH \xrightarrow{-H_2O} Bu_2Sn(SBu)_2 \qquad (17\text{-}21)$$

$$Me_3SnCl + MeSH \xrightarrow[3\ h,\ 60\text{-}70\%]{H_2O,\ NaOH} Me_3SnSMe \qquad (17\text{-}22)$$

Table 17-2 Organotin thiolates.

Thiolate	M.p./°C or b.p./°C (mm Hg)	Thiolate	M.p./°C or b.p./°C (mm Hg)
Me_3SnSMe	163 (760)		158.5-159.5
Et_3SnPh	150 (1.7)		
Ph_3SPh	102-103		
$Me_2Sn(SMe)_2$	44 (0.05)		
$Et_2Sn(SEt)_2$	94/0.05		36
$Bu_2Sn(SBu)_2$	157-160 (0.7)		
$Bu_2Sn(SPh)_2$	179 (0.1)		
$MeSn(SEt)_3$	90 (0.05)		

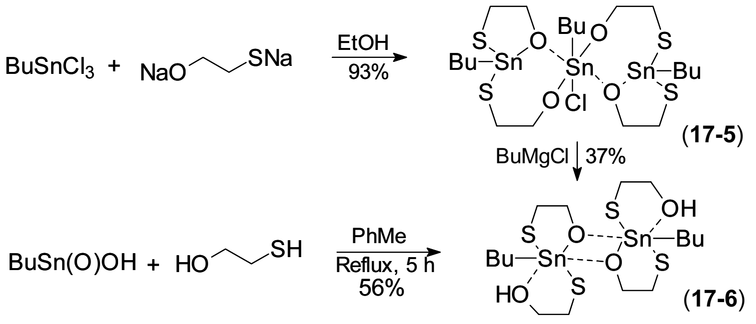
The tin thiolates are usually stable towards air and water, and, in general, the reactivity in both substitution and addition processes follows the sequence Sn–NR$_2$ > Sn–OR > Sn–SR. They are normally monomeric in solution and near to tetrahedral monomers in the crystal. The reduced tendency of the Sn–SR compounds to undergo self-association is illustrated (Scheme 17-2) by the dioxa-, oxathia-, and dithia-stannolanes, **17-2**, **17-3**, and **17-4**, where strain in the five-membered ring enhances the tendency for self-association to occur. The degree of self-association is reduced as sulfur is introduced in place of oxygen, and when bridging does occur in the oxathiastannolanes, it involves the oxygen rather than the sulfur.[35]



R	(**17-2**)	(**17-3**)	(**17-4**)
Bu solution	5-coord. dimer	5-coord. O-bridged dimer	4-coord. monomer
Bu solid	6-coord. polymer	5-coord. O-bridged polymer	weakly 6-coord. polymer
Bu^t solution	5-coord. dimer	4-coord. monomer	4-coord. monomer
Bu^t solid	5-coord. dimer	5-coord. O-bridged dimer	4-coord. monomer

Scheme 17-2 Structure of dioxa-, oxathia-, and dithia-stannolanes.

When butyltin trichloride is treated with an equimolar amount of the disodium salt of 2-mercaptoethanol, the trinuclear derivative **17-5** is formed, and this reacts with butylmagnesium chloride to give **17-6**, which can also be obtained from the reaction between butanestannonic acid and 2-mercaptoethanol (Scheme 17-3).[36] The reaction of butanestannonic acid with 2-mercaptoethanol and then with the sodium salt of a dithiocarbamate gives the compounds $BuSn(OCH_2CH_2S)S_2CNR_2$; in the crystal, the dithiocarbamate ligand is bidentate, and dimerisation occurs through oxygen, rendering the tin 6-coordinate, but the dimer dissociates in solution.[37]



Scheme 17-3 Butyl oxathiastannolanes

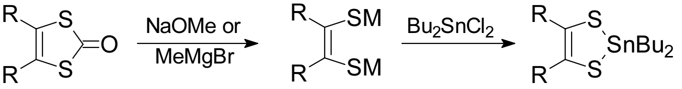
The Sn-SR bond is cleaved by protic acids (e.g. carboxylic acids) and by Lewis acids such as BCl_3, $HgCl_2$, and PCl_3, and bromine or iodine react quantitatively with R_3SnSR' to give R_3SnX and $R'SSR'$.[34] Their reactions with HCl and with tin halides are keys to their operation as stabilisers for PVC (Section 23.1).

$$3Me_3SnSBu + BCl_3 \longrightarrow 3Me_3SnCl + B(SBu)_3 \qquad (17\text{-}23)$$

Alkyl halides react to form the sulfonium salts (equation 17-24).[34]

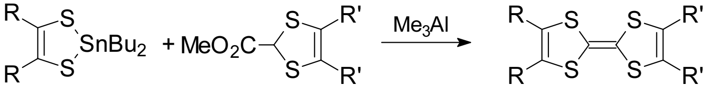
$$Me_3SnSMe + MeI \longrightarrow Me_3Sn\overset{+}{S}Me_2\ I^{-} \qquad (17\text{-}24)$$

The dithiastannoles **17-7** (the unsaturated equivalents of the dithiastannolanes that are mentioned above), have attracted attention because they can act as precursors for the tetrathiofulvalenes (**17-8**) which can show the properties of organic metals. The dithiastannoles can be prepared from the cyclic unsaturated dithiocarbonates as shown in equation 17-25, and then react with 1,3-dithiole-2-carboxylates in the presence of Me_3Al as catalyst to give the tetrathiofulvalenes (equation 17-26).[38-40] Diselenadithiofulvalenes can be prepared in a similar way.



(17-25)

(**17-7**)



(17-26)

(**17-8**)

The chemistry of the selenium and tellurium compounds is broadly similar to that of the sulfur compounds.

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18 Compounds with SnSn Bonds[1]

18.1 Introduction

The basic units of the distannanes R_3SnSnR_3 can be regarded as being the stannyl radical, $R_3Sn^{\bullet}$, and those of the oligostannanes $(R_2Sn)_n$ can be regarded as being the stannylene, $R_2Sn\mathbf{:}$ and the distannene, $R_2Sn{=}SnR_2$. All three moieties are indeed known (though only as reactive intermediates unless the groups R are specially selected), and these species are considered in Chapters 20 and 21.

The SnSn bond in distannanes and oligostannanes can be formed in a number of different reactions, and these compounds are sometimes isolated adventitiously as by-products from reactions aimed at other compounds. The principal ways of forming the SnSn bond are as follows.

1. From a stannylmetallic compound and a halide R_nSnX_{4-n}.
2. From an organotin compound R_nSnX_{4-n} and a metal or metal arene.
3. From an organotin hydride and a compound R_nSnX_{4-n}.
4. By elimination of dihydrogen from an organotin hydride.
5. By insertion of a stannylene $R_2Sn\mathbf{:}$ into an SnX bond.
6. By abstraction of a hydrogen atom from R_3SnH.
7. By cathodic reduction of R_3SnX.

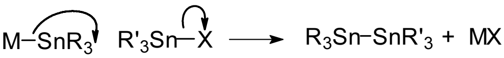
Sawyer[1] lists 20 different routes to hexaphenylditin, most of which can be understood in terms of these basic reactions. The detailed mechanisms of the reactions in which the Sn-Sn bond is formed, however, are often unclear, and even the broad distinction between homolytic and heterolytic mechanisms is sometimes in doubt.

18.2 Acyclic Distannanes

18.2.1 Formation

18.2.1.1 From a Stannylmetallic Compound and a Halide R_nSnX_{4-n}

These reactions probably involve nucleophilic attack of tin at a tin centre (equation 18-1) and two examples are shown in equations 18-2[2] and 18-3.[3]



$$M{-}SnR_3 \quad R'_3Sn{-}X \longrightarrow R_3Sn{-}SnR'_3 + MX \qquad (18\text{-}1)$$

$$p\text{-}Tol_3SnLi + p\text{-}Tol_3SnI \xrightarrow[\substack{3\text{ h, RT}\\ 65\%}]{Et_2O} p\text{-}Tol_3SnSn\,p\text{-}Tol_3 \qquad (18\text{-}2)$$

$$Me_3SnNa + Et_3SnBr \xrightarrow{NH_3} Me_3SnSnEt_3 \qquad (18\text{-}3)$$

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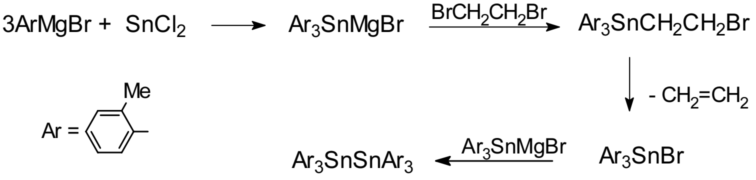
Neumann's synthesis of hexa(o-tolyl)distannane presumably involves a similar reaction of a stannylmetallic compound with a tin(IV) halide.[4]

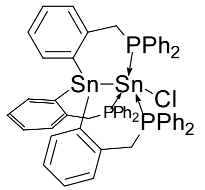


(18-4)

Five tin atoms can be assembled in a neopentane-like configuration by the reaction of triphenylstannyllithium with tin tetrachloride (reaction 18-5),[5] and the same compound can be prepared from Ph_3SnLi and $SnCl_2$, when $(Ph_3Sn)_3SnLi$ is an intermediate.

$$4Ph_3SnLi + SnCl_4 \longrightarrow (Ph_3Sn)_4Sn \qquad (18\text{-}5)$$

However, the reaction of $[o\text{-}(Ph_2PCH_2)C_6H_4]_3SnMgCl$ with $SnCl_2$ gives the $Sn^{IV}Sn^{II}$ compound **18-1**,[6] and the reaction of $(2\text{-pyridyl})(Me_3Si)_2CSn^{II}Cl$ with $(Me_3Si)_3SnLi$ gives **18-2** [*r*SnSn 268.9(5) pm];[7] in **18-1** and **18-2**, the Sn^{II} oxidation state is stabilised by ligation by phosphorus or nitrogen, respectively.



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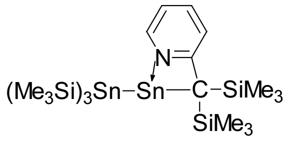
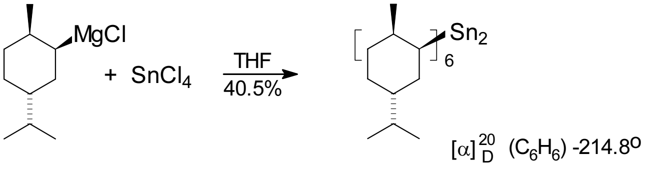


(18-2)

It is not uncommon for hexaorganodistannanes to be isolated also from the reaction of organometallic compounds with $SnCl_4$ or triorganotin halides, and sometimes yields are high enough to make this a preparatively-useful reaction (e.g. equation 18-6).[8] It is usually assumed that the R_3SnX which is formed reacts with the organometallic reagent RM to give R_3SnM (and RX) which in turn reacts with R_3SnX to form the SnSn bond.



(18-6)

18.2.1.2 From an Organotin Compound R_nSnX_{4-n} and a Metal

These reactions presumably occur by initial formation of the stannylmetallic compound by electron transfer, then nucleophilic substution by tin at tin, as above.

$$R_3SnX + M \longrightarrow R_3SnX^{\bullet-} + M^{+} \longrightarrow R_3Sn\cdot + X^{-} + M^{+} \qquad (18\text{-}7)$$

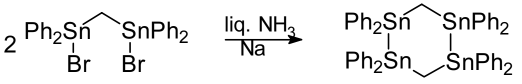
$$R_3Sn\cdot + M \longrightarrow R_3SnM \qquad (18\text{-}8)$$

$$R_3SnM + R_3SnX \longrightarrow R_3SnSnR_3 + MX \qquad (18\text{-}9)$$

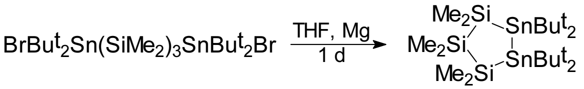
The group X may be halogen, oxygen, or sulfur, and the metal M may be an alkali metal, or magnesium, copper, or zinc. Some examples are given in equations 18-10,[9] 18-11,[10] 18-12,[11] 18-13,[12] 18-14,[13] 18-15,[14] and 18-16.[15]

$$2Me_3SnCl + 2\,Na \xrightarrow[80\%]{lqd\ NH_3} Me_3SnSnMe_3 + 2NaCl \qquad (18\text{-}10)$$

$$Bu^t{}_2MesSnCl + Na \xrightarrow[12\ h,\ 10\%]{PhMe,\ reflux} Bu^t{}_2MesSnSnMesBu^t{}_2 \qquad (18\text{-}11)$$



(18-12)



(18-13)

$$(Me_3Sn)_2S + 2Na \xrightarrow[24\ h.\ 45\text{-}50\%]{THF\ reflux} (Me_3Sn)_2 + Na_2S \qquad (18\text{-}14)$$

$$(Bu_3Sn)_2O + Mg \xrightarrow[24\ h.\ 45\text{-}50\%]{THF,\ reflux} (Bu_3Sn)_2 + MgO \qquad (18\text{-}15)$$

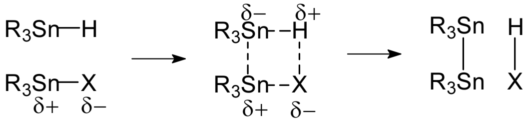
$$\underset{i.\ THF/H_2O,\ NH_4Cl,\ Zn\ dust,\ RT,\ 22\ h}{Pr_3SnCl + Bu_3SnCl} \xrightarrow{i} \underset{15\%}{Pr_6Sn_2} + \underset{28\%}{Pr_3SnSnBu_3} + \underset{13\%}{Bu_6Sn_2} \qquad (18\text{-}16)$$

Metal arene salts (e.g. naphthalene$^{\bullet -}$ Na$^+$ or anthracene^{2-} 2Li$^+$) can also be used,[16] when electron transfer takes place from the arene anion. An electron transfer process is also involved in the reduction of bis(tributyltin) oxide with samarium(II) iodide in THF/HMPT; a good yield of the distannane is obtained very quickly, but the reagent is expensive and toxic.[17]

$$(Bu_3Sn)_2O + SmI_2 \xrightarrow[20\ ^oC,\ 1\ min,\ 92\%]{THF/HMPT} Bu_3SnSnBu_3 \qquad (18\text{-}17)$$

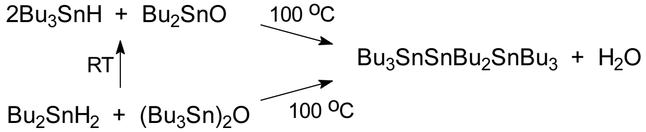
18.2.1.3 From an Organotin Hydride R_nSnH_{4-n} and a Compound R_nSnX_{4-n}

The reactivity follows the sequence X = $SeSnR_3 < SSnR_3 < OR \approx PR_2 < OSnR_3 < NRCHO < NR_2$, and a polar cyclic mechanism appears likely.[18]



(18-18)

The reaction is often accompanied by exchange of the groups X and H, for example:[1]



(18-19)

Decaorganotetrastannanes $\mathrm{RSn(SnMe_3)_3}$ have been obtained in good yields as colourless high-boiling oils from the reaction between $\mathrm{RSnH_3}$ and $\mathrm{Me_3SnNEt_2}$,[19] and hydrostannolysis reactions have been used extensively for preparing linear oligostannanes (Section 18.3).

The formation of a hexaalkyldistannane by heating together the hexaalkyldistannoxane and formic acid (equation 18-20, R = Bu, $\mathrm{Bu^i}$, Oct) similarly involves the reduction of SnX by SnH.[20] The stannyl formate is formed, and decarboxylates to give the tin hydride, which then reduces the distannoxane. Residual formate can be extracted into methanol, in which the distannanes (ca. 65–70% yields) are insoluble.

$$\mathrm{R_3SnOSnR_3 + HCO_2H \xrightarrow[200\ ^{o}C,\ 4\ h]{100\ ^{o}C,\ 4\ h} R_3SnSnR_3 + CO_2 + H_2O} \qquad (18\text{-}20)$$

18.2.1.4 By Elimination of Dihydrogen from an Organotin Hydride

The elimination of hydrogen may be induced by an amine or by a transition metal catalyst, or it may be spontaneous.[21]

$$\mathrm{2(PhCH_2)_3SnH \xrightarrow[24\ h.\ 85\%]{DMF} (PhCH_2)_3SnSn(CH_2Ph)_3 + H_2} \qquad (18\text{-}21)$$

The mechanisms of these reactions are not understood in detail, but the spontaneous or base-induced elimination of hydrogen from a variety of compounds $\mathrm{R_2SnXH}$ has been shown to involve a radical chain mechanism (see Section 15.3.4).

The reduction of bis(tributyltin) oxide with sodium borohydride in ethanol apparently falls into this group of reactions. After 5 min, the only tin compound present is tributyltin hydride, but, during 2 h, this is converted into hexabutylditin in good yield. The catalyst for the decomposition of the hydride appears to be the ethoxide ion which is generated from the $\mathrm{NaBH_4}$ and ethanol.[22]

$$\mathrm{(Bu_3Sn)_2O + NaBH_4 \xrightarrow[2\ h,\ 83\%]{EtOH,\ RT} Bu_3SnSnBu_3} \qquad (18\text{-}22)$$

Spontaneous evolution of hydrogen occurs with some dialkyltin hydrides, $\mathrm{R_2SnXH}$, where X is an electronegative group, particularly carboxylate. These reactions are discussed in Section 15.3.4. The compounds $\mathrm{R_2SnXH}$ can be formed (equation 18-23) by mixing $\mathrm{R_2SnH_2}$ and $\mathrm{R_2SnX_2}$; for example, if dibutyltin dihydride and dibutyltin diacetate are mixed, hydrogen is immediately evolved and the tetrabutyldiacetoxydistannane is formed by a radical chain reaction.[23] Dibutyltin chloride hydride is more stable, but hydrogen is readily evolved when pyridine is added, giving $\mathrm{ClBu_2SnSnBu_2Cl}$. Dimethyltin thiophenoxide hydride [from $\mathrm{Me_2SnH_2}$ and $\mathrm{Me_2Sn(SPh)_2}$] is less reactive, and, in the presence of pyridine, hydrogen is evolved during 3 days to give $\mathrm{PhSBu_2SnSnBu_2SPh}$.[24] These reactions provide a convenient route to the functionally-substituted distannanes $\mathrm{XR_2SnSnR_2X}$ in which the groups X can readily be exchanged for other ligands, including H.

$$\begin{array}{c}\mathrm{Bu_2SnH_2}\\ +\\ \mathrm{Bu_2Sn(OAc)_2}\end{array} \underset{}{\overset{\mathrm{RT}}{\rightleftharpoons}} \mathrm{2Bu_2Sn(OAc)H \longrightarrow (AcO)Bu_2SnSnBu_2(OAc) + H_2} \qquad (18\text{-}23)$$

The use of transition metal catalysts to induce the elimination of hydrogen is important and has the potential for considerable development.[25] The reaction of trialkyltin hydrides with a $\mathrm{Pd(PPh_3)_4}$ catalyst may provide the best method that is presently available for preparing hexaorganodistannanes, particularly on a large scale (> 200 g).[26, 27]

The yields are essentially quantitative and the distannanes can often be used without purification. When $\mathrm{Pd(PPh_3)_4}$ is added portionwise to trimethyltin hydride, the reaction is exothermic, and the hydride boils under reflux (equation 18-24). Tributyltin hydride reacts similarly, and the reaction of (solid) triphenyltin hydride can be carried out in benzene. The reaction with a 1:1 molar mixture of $\mathrm{Me_3SnH}$ and $\mathrm{Bu_3SnH}$ gives $\mathrm{Me_3SnSnMe_3}$, $\mathrm{Me_3SnSnBu_3}$, and $\mathrm{Bu_3SnSnBu_3}$ in the ratio of 1:2:1.

$$\mathrm{Me_3SnH} \xrightarrow[\text{RT, ca. 100\%}]{\mathrm{Pd(PPh_3)_4}} \mathrm{Me_3SnSnMe_3} + \mathrm{H_2} \qquad (18\text{-}24)$$

The most effective palladium catalysts are those in which a PdFe bimetallic compound carries a bridging diphosphine ligand, when the reaction is thought to occur at the palladium centre with the iron playing an important role.[25] Optically active methylphenylneophyltin hydride, [α] +28.9°, reacts with palladium on charcoal to give the optically active distannane, [α] +13.2°, which is optically stable for several weeks.[28]

The catalytic activity of the gold(I) complex, $\mathrm{AuCl(PPh_3)}$, is similar to that of the palladium complexes, and, for example, it reacts with trioctyltin hydride at room temperature in 13 h to give hexaoctyldistannane in 94% yield.[29] A number of other transition metals are catalytically active, and these are listed in Chapter 15.

18.2.1.5 By Insertion of a Stannylene $\mathrm{R_2Sn}$: into an SnM Bond

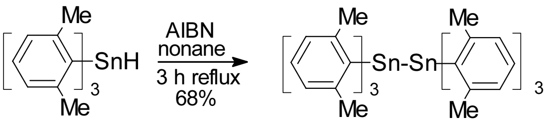
A number of reactions are known which appear to involve the formation of distannanes or oligostannanes (see below) by the insertion of stannylene units into a bond to tin, but the factors that control the regioselectivity between SnH, SnHalide, SnSn or SnM bonds is not understood, and these reactions have as yet a limited use in synthesis. An early example is provided by the reaction of triisopropyltin bromide with lithium; the triisopropyltinlithium generates diisopropylstannylene, which inserts into the SnLi bond to give pentaisopropyldistannyllithium.[30]

$$\mathrm{Pr^i{}_3SnBr} \xrightarrow[\text{THF}]{\text{Li}} \mathrm{Pr^i{}_3SnLi} \rightleftharpoons [\mathrm{Pr^iLi}] + \mathrm{Pr^i{}_2Sn{:}} \xrightarrow{\mathrm{Pr^i{}_3SnLi}} \mathrm{Pr^i{}_3SnPr^i{}_2SnLi} \qquad (18\text{-}25)$$

18.2.1.6 By Abstraction of a Hydrogen Atom from $\mathrm{R_3SnH}$

Hexaaryldistannanes with bulky *ortho*-substituted phenyl groups are in thermal equilibrium with the corresponding triarylstannyl radicals, which can be detected by ESR spectroscopy. These distannanes consequently can be prepared by abstracting hydrogen from the corresponding triarylstannanes (Section 18.2.3).[4]

$$\mathrm{Ar_3SnH} \xrightarrow{-\mathrm{H}\cdot} \mathrm{Ar_3Sn}\cdot \rightleftharpoons \mathrm{Ar_3SnSnAr_3} \qquad (18\text{-}26)$$



(18-27)

18.2.1.7 By Cathodic Reduction of $\mathrm{R_3SnX}$

Hexaorganodistannanes can also be prepared by electrochemical reduction of triorganotin salts, particularly the formates, in an undivided cell consisting simply of a beaker with a stainless steel cathode and carbon anode (equation 18-28).[31]

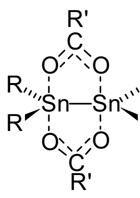
$$2Ph_3SnOCHO \xrightarrow[98\%]{DMA} Ph_3SnSnPh_3 \qquad (18\text{-}28)$$
$$100\ mA,\ 20\text{-}60\ V,\ 2.5\ F\ mol^{-1}\ R_3SnX$$

In a related reaction, hexakis(2-cyanoethyl)distannane, $(NCCH_2CH_2)_3SnSn(CH_2CH_2CN)_3$, can be prepared in 50% yield by the electrolysis of an aqueous alkaline solution of acrylonitrile with a sheet tin cathode and platinum gauze anode.[32, 33]

The emphasis of most other electrochemical studies, however, has been on the formation of polystannanes, $(R_2Sn)_n$, from difunctional compounds R_2SnX_2 (see below).

18.2.2 Structures

Bond lengths in the oligostannanes (see Table 18-1) increase with the steric demands of the organic groups.[21] Reaction of the dihalogenodistannanes, $ClMe_2SnSnMe_2Cl$, with the anions Y^- [$Y = RCO_2$, R_2NCS_2, or $(RO)_2PS_2$] gives the products $YMe_2SnSnMe_2Y$ in which Y acts as an isobidentate ligand.[34] For example, the dicarboxylates $(R'CO_2)R_2SnSnR_2(O_2CR')$ have symmetrically bridging carboxylate groups (**18-3**), and particularly short SnSn bonds (ca. 270 pm);[35] the structure of $AcOPh_2SnSnPh_2OAc$ [35] was shown on the cover of the first edition of this book. The longest $Sn^{IV}Sn^{IV}$ bond (303.4 pm) which seems to have been reported is that in compound **18-4**, which adopts a *syn* orientation with eclipsed groups.[36]



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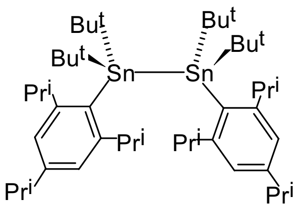


(18-4)

18.2.3 Properties

Examples of acyclic and cyclic oligostannanes are given in Table 18-1; some di- and tri-stannaferrocenophanes are described in Section 9.3.4

The SnSn bond is characterised in the Raman spectra by a stretching vibration at about 100-200 cm^{-1} (e.g. $Me_3SnSnMe_3$ 190 cm^{-1}, $Ph_3SnSnPh_3$ 138 cm^{-1}).[37] In the hexaaryldistannanes, this frequency is reduced as bulky substitutents are introduced, and the SnSn bond is weakened and undergoes reversible homolysis at elevated temperatures (equation 20-5).[4] Table 18-2 shows the values of $\nu(SnSn)$, the minimum temperatures at which the ESR signal of the radicals $Ar_3Sn^\bullet$ can be detected, and the enthalpy of dissociation of the SnSn bond as determined by ESR spectroscopy.[4] The SnSn bond dissociation energy in $Me_3SnSnMe_3$ is estimated to be between 209 and 243 kJ mol^{-1}.

^{119}Sn NMR Spectra of SnSn bonded compounds have been determined initially by heteronuclear magnetic resonance,[38] and subsequently by FT NMR.[20, 39, 40] Some values of $\delta(^{119}Sn)$ and $J(^{119}Sn^{119}Sn)$ are shown in Table 18-3. The oligostannanes have special optical properties (see below), and their ^{119}Sn NMR parameters have been studied as an aid to understanding their electronic configurations.

Table 18-1 Oligostannanes.

Compound	M.p./°CC or b.p./°C (mm Hg)	Av. *r*SnSn/pm
$Me_3SnSnMe_3$	23; 182(760)	
$Et_3SnSnEt_3$	162(23)	
$Bu_3SnSnBu_3$	158(0.02)	
$Bu^t{}_3SnSnBu^t{}_3$	200 dec	288.7
$Bn_3SnSnBn_3$	148	282.3
$Ph_3SnSnPh_3$	237	277.0
$ClMe_2SnSnMe_2Cl$		277.0
$ClBu_2SnSnBu_2Cl$	25–27	
$AcOPh_2SnSnPh_2OAc$	152	269.6
$Ph_3SnSnPh_2SnPh_3$	208–212	276.8–283.0
$MeSn(SnMe_3)_3$	108–112(0.005)	
$PeSn(SnMe_3)_3$	166(0.01)	
$(Ph_3Sn)_4Sn$	302–308	279.8
$[(2,6\text{-}Et_2C_6H_3)_2Sn]_3$	175 dec	286.0
$[(9\text{-}Phen)_2Sn]_3$ [a]	229–230dec	
$[(Me_3SiCH_2)_2Sn]_3$		283.6
$(Bu^t{}_2Sn)_4$	205 dec	288.7
$(Bz_2Sn)_4$	226–228	
$(Ph_2Sn)_5$	185 dec	
$(Ph_2Sn)_6$	270 dec	278.0

[a] 9-Phen = 9-phenanthranyl

Table 18-2 Hexaaryldistannanes $Ar_3SnSnAr_3$ in equilibrium with triarylstannyl radicals $Ar_3Sn^{\bullet}$.

Ar	ΔH/kJ mol^1	ESR signal/°C [a]	*g*	ν(SnSn)/cm^{-1}
Ph			2.0023	138
$2\text{-}MeC_6H_4$			2.0062	125
$2,3,4,5\text{-}Me_4C_6H$				1
$2,6\text{-}Me_2C_6H_3$	215.5 ± 8	170	2.0073	110
$2,4,6\text{-}Me_3C_6H_2$	205.0 ± 8	180	2.0073	102
$2,3,5,6\text{-}Me_4C_6H$	184.1 ± 8	180	2.0064	105
$2,3,4,5,6\text{-}Me_5C_6$	161.8 ± 8	130	2.0057	98
$2,4,6\text{-}Et_3C_6H_2$	111.3 ± 8	100	2.0076	92
$2,4,6\text{-}Pr^i{}_3C_6H_2$	35.6 ± 4	20	2.0079	

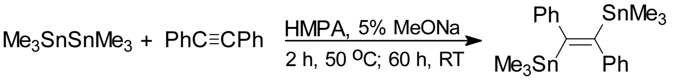
[a] Lowest temperature at which the ESR signal of the radical becomes apparent.

Table 18-3 ^{119}Sn NMR shifts and coupling constants in oligostannanes.

Compound	δ(^{119}Sn)	*J*(^{119}Sn^{119}Sn)/Hz
$Me_3SnSnMe_3$	108.7	^1J +4404
$Bu_3SnSnBu_3$	83.2	^1J 2748
$(AcO)Bu_2SnSnBu_2(OAc)$	126.8	^1J 11272
$Me_3Sn^1Sn^2Me_2SnMe_3$	99.5 (Sn^1)	^1J 2873
	261.7 (Sn^2)	^2J 763
$Me_3Sn^1Sn^2Me_2Sn^3Me_2Sn^4Me_2SnMe_3$	73.8 (Sn^1)	^1J 1368 (Sn^{1}Sn^2)
	199 (Sn^2)	^2J 261 (Sn^{1}Sn^3)
	210 (Sn^3)	^3J 220 (Sn^{1}Sn^4)

The simple hexaorganodistannanes are not in thermal equilibrium with their corresponding triorganostannyl radicals; thus, $Me_3SnSnEt_3$ can be distilled at 235 °C without disproportionation, and no exchange occurs between $Me_3SnSnMe_3$ and $Et_3SnSnEt_3$ at elevated temperatures.[18] However, the exchange can be induced by basic reagents such as HMPA, or NaOMe or MeMgBr in THF or acetonitrile (equation 18-29); under these conditions, the hexaalkyldistannanes will add trialkylstannyl units to alkynes such as phenylethyne, diphenylethyne, and 1,4-diphenylbuta-1,3-diyne (equation 18-30).[41] If hexaphenylditin is treated with potassium t-butoxide in *N,N*-dimethylpropyleneurea (DMPU) as solvent, the ^{13}C spectrum shows that Ph_3SnK is formed in good yield.[42]

$$Me_3SnSnMe_3 + Et_3SnSnEt_3 \xrightleftharpoons[< 1\ h]{HMPA} 2Me_3SnSnEt_3 \quad K\ 4.55 \tag{18-29}$$



(18-30)

No studies have been reported on the mechanisms of these interesting reactions. The addition of the R_3Sn fragments to alkynes and dienes might be seen as implying a radical mechanism, but the trialkylstannylmetallic compounds, which can be prepared from the distannanes and alkali metals or butyl lithium, are in rapid equilibrium in solution with the parent distannanes (equations 18-31–18-33), which might suggest a nucleophilic displacement by tin of tin at a tin centre. Under these conditions, the NMR spectra show a weighted average for the components, and similarly a mixture of Me_3SnLi and $Et_3SnSnEt_3$ shows the presence also of Et_3SnLi, $Me_3SnSnEt_3$, and $Me_3SnSnMe_3$.[43] These systems have also been studied electrochemically.[44]

$$Me_3SnSnMe_3 + 2Li \longrightarrow 2Me_3SnLi \tag{18-31}$$

$$Me_3SnSnMe_3 + BuLi \longrightarrow Me_3SnLi + BuSnMe_3 \tag{18-32}$$

$$Me_3SnLi + Me_3SnSnMe_3 \rightleftharpoons Me_3SnSnMe_3 + Me_3SnLi \tag{18-33}$$

Homolysis of the SnSn bond can be induced by irradiation with UV light, and the quantum yield can be increased by adding di-t-butyl peroxide or a ketone, when stannyl radicals are also produced by the S_H2 reaction of the t-butoxyl radical (equations 18-35 and 18-36) or ketone triplet (equation 18-37), respectively, at tin.[45, 46]

$$R_3SnSnR_3 \xrightarrow{h\nu} 2R_3Sn\cdot \tag{18-34}$$

$$Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO\cdot \tag{18-35}$$

$$Bu^tO\cdot + R_3SnSnR_3 \longrightarrow Bu^tOSnR_3 + R_3Sn\cdot \tag{18-36}$$

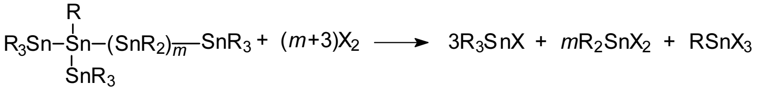
$$Ph_2C{=}O^* + Bu_3SnSnBu_3 \longrightarrow Ph_2\dot{C}OSnBu_3 + Bu_3Sn\cdot \tag{18-37}$$

Photolysis of tristannanes $Me_3SnSnR_2SnMe_3$ (R = Me or Et) similarly results in the formation of the radicals $Me_3SnSnR_2^{\bullet}$ and $Me_3Sn^{\bullet}$, which have been monitored by ESR and ^{119}Sn CIDNP spectroscopy.[47]

The hexaorganodistannanes are stable towards water and mild acids and alkalis. Hexamethyldistannane in methanol reacts with ca. 0.6 *M* HCl to give mainly Me_3SnCl by cleavage of the SnSn bond, together with about 18% cleavage of the SnC bond. The mechanism of the reaction is thought to be the reverse of the process by which an SnSn bond can be formed, as shown in equation 18-38.[48]

$$Me_3SnSnMe_3 \xrightarrow{HCl} Me_3SnCl + Me_3SnH \xrightarrow{HCl} 2Me_3SnCl + H_2 \qquad (18\text{-}38)$$

The SnSn bond is cleaved by halogens, and the nature of the products which are formed by titration with a halogen can be used to elucidate the structure of a branched oligostannane by the principle illustrated in equation 18-39.[49]



$$R_3Sn{-}\overset{\displaystyle R}{\underset{\displaystyle SnR_3}{Sn}}{-}(SnR_2)_m{-}SnR_3 + (m{+}3)X_2 \longrightarrow 3R_3SnX + mR_2SnX_2 + RSnX_3 \qquad (18\text{-}39)$$

In air, the distannanes are oxidised to the corresponding distannoxanes; presumably the peroxides, $R_3SnOOSnR_3$, are first formed in a radical chain process, then the peroxides are reduced by the distannanes to give the distannoxanes. Higher oligomers appear to be more sensitive to oxygen. Tetraalkylditin dicarboxylates, $(R'CO_2)R_2SnSnR_2(O_2CR')$, have been recommended as latent catalysts for the preparation of polyurethanes and the curing of silicone rubbers (Section 23.1).[50]

Sulfur and selenium can also be inserted into the SnSn bond.[51]

$$Ph_3SnSnPh_3 + S_8 \xrightarrow[2.5\text{ h, }83\%]{170\ ^{o}C} Ph_3SnSSnPh_3 \qquad (18\text{-}40)$$

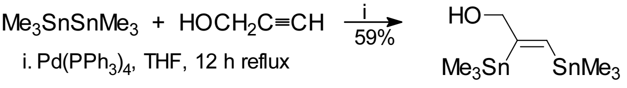
Cleavage of the SnSn bond can also be brought about by electron transfer reactions with reagents such as tetracyanoethylene (TCNE), tetracyanoquinodimethane, and tetrachloroquinone; for example, TCNE and Me_6Sn_2 gives the radical adduct $Me_3SnTCNE^{\bullet}$.[52]

In the presence of Pd^0 catalysts, hexaalkyldistannanes will react with aryl, heteroaryl, vinyl, or acyl halides to give the corresponding aryl-, heteroaryl-, vinyl-, or acylstannanes,[53] for example:[54]

$$Me_3SnSnMe_3 + PhCOCl \xrightarrow[80\%]{i} PhCOSnMe_3 + Me_3SnCl \qquad (18\text{-}41)$$

i. $Pd(PPh_3)_4$, THF, reflux 12 h

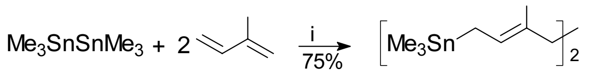
Palladium compounds will also catalyse the addition of hexamethylditin to terminal alkynes, or carbonyl-activated medial alkynes (e.g. equation 18-42),[27] and tris(trimethylstannyl)ethene can be prepared by the addition of hexamethylditin to trimethylethynyltin. Et_6Sn_2 And Bu_6Sn_2 do not react under these conditions, but reaction does occur under high pressure (750 to 1300 MPa, 7.5 × 10^3 to 1.3 × 10^4 atm).[55]



(18-42)

i. $Pd(PPh_3)_4$, THF, 12 h reflux

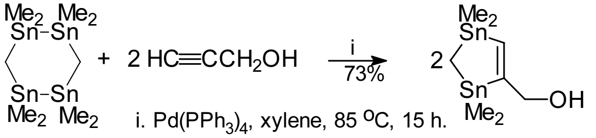
Hexamethylditin reacts with isoprene in the presence of palladium bis(dibenzylideneacetone) and triethylphosphite to give Z-$Me_3SnCH_2CMe{=}CHCH_2SnMe_3$ in 58% yield, but if $Pd(PPh_3)_4$ is used as the catalyst, the adduct of the dimer of the diene is formed (equation 18-43).[56]



(18-43)

i. $Pd(PPh_3)_4$, THF, 12 h reflux

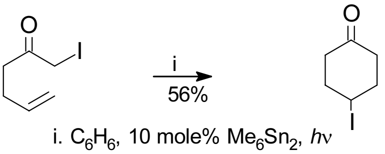
Under these conditions, the 1,2,4,5-tetraastannacyclohexanes do not give expanded rings by insertion of the alkyne into the Sn^1Sn^2 and Sn^4Sn^5 bonds, but instead add the alkyne across the Sn^1 and Sn^5 and the Sn^2 and Sn^4 positions to give a 3,5-distannacyclopent-1-ene.[57]



i. $Pd(PPh_3)_4$, xylene, 85 °C, 15 h.

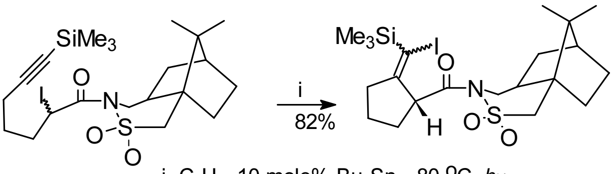
(18-44)

Hexaorganodistannanes are used in organic synthesis for bringing about free radical reactions where termination by hydrogen transfer from a trialkyltin hydride must be avoided. Typically, 5-10 mole% of the distannane is used, and the reactions are initiated by irradiation with a sun lamp. Examples are given in equations 18-45 and 18-46.[58, 59]



i. C_6H_6, 10 mole% Me_6Sn_2, *hν*

(18-45)



i. C_6H_6, 10 mole% Bu_6Sn_2, 80 °C, *hν*

(18-46)

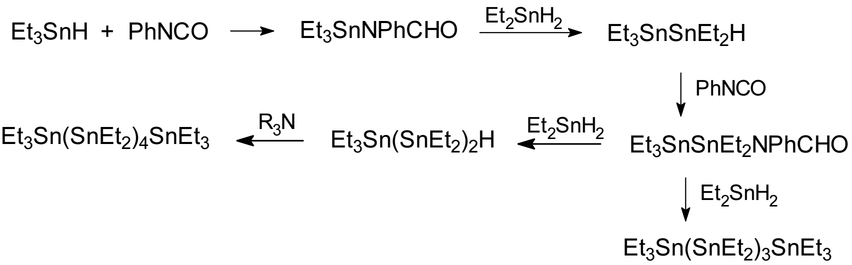
18.3 Linear Oligostannanes

Much of the interest in the oligostannanes stems from the fact that interaction between the Sn sp^3 orbitals in the chain gives rise to a delocalised electron structure that can be viewed as a linear combination of σ* Sn-Sn orbitals.[60, 61] This conjugated structure, as in conjugated polyenes, gives rise to a low energy absorption maximum which moves to the red as the chain length increases, and suggests possible applications in optical and electronic devices, and in microlithography.

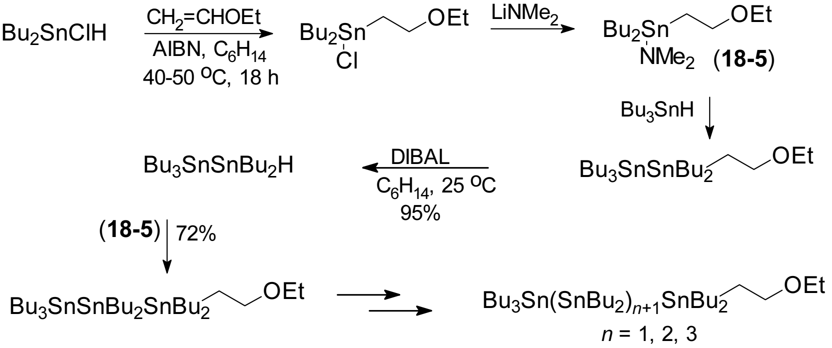
Most of the general methods for forming SnSn bonds that are listed at the beginning of this chapter can be used for the synthesis of oligostannanes. For example, the reaction of triphenylstannylsodium with diphenyltin dichloride gives octaphenyltristannane,[16] and dibutyltin dichloride reacts with sodium in anisole in presence of 15-crown-5 to give polydibutylstannane with M_n *ca.* 1×10^6.[62]

The hydrostannolysis technique has been used for preparing oligostannanes through reduction of the *N*-stannylformamides (Schemes 18-1[63] and 18-2[64]).

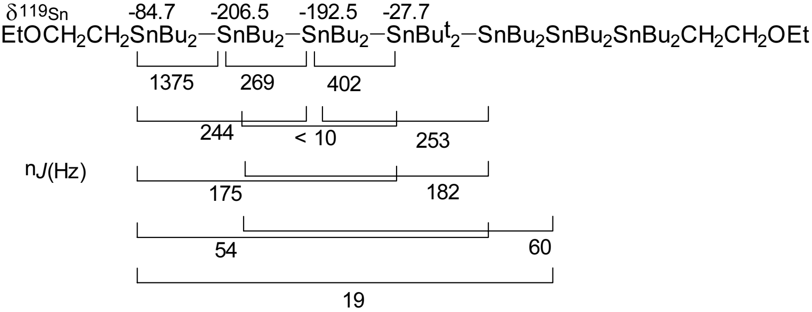
By the methodology of Scheme 18-2, but using $Bu^t_2SnH_2$ for the initial reaction, a series of oligostannanes with the structures $EtO(CH_2)_2(Bu_2Sn)_m(Bu^t_2Sn)(Bu_2Sn)_n(CH_2)_2OEt$ (m and n = 0–4), have been prepared, and have been used to determine the systematics of the electronic and NMR spectra in linear polystannanes.[65] Typical results for a heptastannane are shown in Scheme 18-3.



Scheme 18-1 Formation of oligostannanes by hydrostannolysis (1).



Scheme 18-2 Formation of oligostannanes by hydrostannolysis (2).

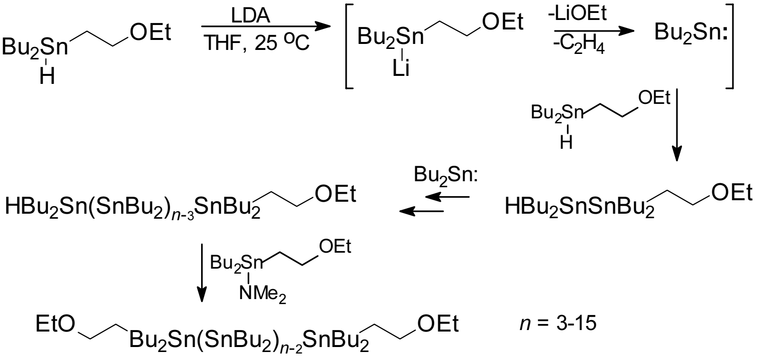


Scheme 18-3 ^{119}Sn Chemical shifts (top) and $^{n}J(^{119}Sn^{119}Sn)$ coupling constants (bottom; Hz) in a heptastannane.

If dibutyltin dihydride is treated with $(C_5H_5)(C_5Me_5)Zr(Me)[Si(SiMe_3)_3]$, hydrogen is evolved to give a dark red mixture, which solidifies. Extraction with MeOH gives a yellow oil (93%) which can be separated by gel permeation chromatography into two fractions. The first is tentatively identified as $(Bu_2Sn)_n$, where n_{av} = ca. 8.7, and the second as $H(Bu_2Sn)_nH$, where n = ca. 80.[66]

A number of reactions are known which appear to involve the formation of oligostannanes by the insertion of stannylene units into a bond to tin, but most of these have little preparative value. For example, hexamethylditin reacts with trimethyltin chloride or dimethyltin dichloride to give, amongst other products, oligodimethylstannanes, $(Me_2Sn)_n$, apparently by insertion of Me_2Sn: into SnSn or SnCl bonds.[67, 68]

A process which involves the formation of SnSn bonds by both the reduction of an SnX bond by SnH, and by stannylene insertion into SnH, is illustrated in equation 18-47. It is assumed that the terminal tin hydride is formed by repeated insertion of dibutylstannylene into SnH; this tin hydride is then coupled with the aminotin compound to give the symmetrical oligostannanes $EtOCH_2CH_2(Bu_2Sn)_nCH_2CH_2OEt$.[69]



(18-47)

The various oligomers can be separated by reverse phase HPLC; the main products have $n = 3$, 4, or 5, but higher oligomers with $n \geq 15$ can be separated. As n increases, the value of λ_{max} increases from λ_{max} 254 nm, ν 39,370 cm^{-1} when $n = 3$, to λ_{max} 362 nm, ν 27,548 cm^{-1} when $n = 15$. This is in accord with the predictions of the Sandorfy modification of the Hückel MO approximation which takes into account weak vicinal and strong geminal interactions between tin atoms, and implies that the electrons are highly delocalised along the σ backbone.[69]

Dialkyltin dichlorides, R_2SnCl_2 (R = Me, Et, or C_6H_{13}), react with samarium iodide or with magnesium or calcium vapour to give polystannanes with $M_W > 10^3$ and a narrow molecular weight distribution (e.g. equation 18-48).

$$Et_2SnCl_2 \xrightarrow[\text{HMPA/THF}]{\text{SmI}_2} (Et_2Sn)_n \text{ (74\%, MW 4820)} \qquad (18\text{-}48)$$

The polymers show UV absorption at 285–368 nm, and laser flash photolysis gives chain scission with the formation of the corresponding transient stannyl radicals with absorption at 400 nm (R = Me). They react with oxygen with a pseudo-first order rate constant of ca. 10^5 s^{-1}.[70]

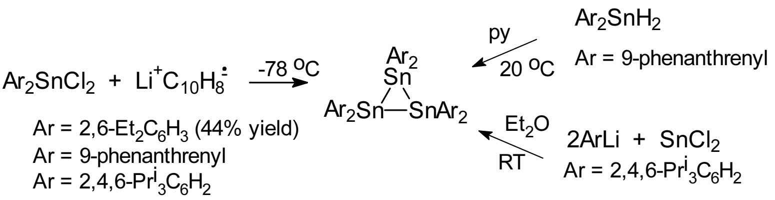
Poly(dialkylstannanes), $(Bu_2Sn)_n$ and $(Oct_2Sn)_n$, with M_W up to *ca.* 10,000,[71] and the corresponding Bu_2Sn/Bu_2Si and Bu_2Sn/Bu_2Ge copolymers,[72] have been prepared by electrolysis of the appropriate dichlorides in DME in a one-compartment cell fitted with a Pt cathode and Ag anode. The polystannanes appear to be stable to oxygen, but sensitive to moisture in the air, and the sensitivity of the Sn/Si or Sn/Ge copolymers increases with increase in the content of tin.

18.4 Cyclic Oligostannanes

The older literature contains references to long-lived simple monomeric diorganotin species, R_2Sn:. Subsequent work has shown that, unless the groups R are cyclopentadienyl or are very bulky (see Chapter 21), these stannylenes exist only as transient intermediates, and that the compounds are in fact cyclic oligomers, $(R_2Sn)_n$. Some examples are included in Table 18-1.

They can be prepared by the first four of the general methods for forming an SnSn bond which are listed above, and some examples are given in the equations which follow. As is usually observed, bulky ligands tend to result in the formation of smaller rings. Sometimes a slight change in the reaction conditions can affect the ring size. The reaction of R_2SnH_2 in the presence of an amine proceeds more rapidly and cleanly in the presence of a trace of R_2SnCl_2, when the reaction probably takes place through R_2SnClH which is formed by exchange.

Cyclotristannanes[73] have been identified only when the groups Ar in $(Ar_2Sn)_3$ are bulky aromatic rings, namely Ar = 2,6-$Et_2C_6H_3$,[9, 74, 75] 2,4,6-$Pr^i_3C_6H_2$,[76] and 9-phenanthrenyl (Scheme 18-4).[77]

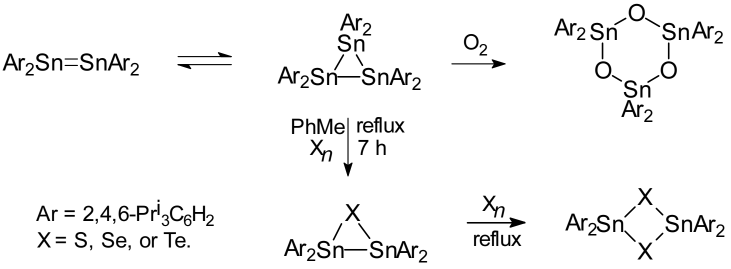


Scheme 18-4 Formation of cyclotristannanes.

All three cyclotristannanes have been isolated as yellow or orange solids. When R = 2,6-$Et_2C_6H_3$, the Sn_3 ring forms an isosceles triangle [*r*SnSn 285.4(1), 285.6(1), and 287.0(1) pm] , but, when Ar = 2,4,6-$Pr^i_3C_6H_2$, it is less regular (*r*SnSn 291.6, 294.7, and 296.3 pm). The compound $[(2,6\text{-}Et_2C_6H_3)_2Sn]_3$ can be reduced with potassium, when it shows an ESR spectrum consisting of a singlet with *g* 2.024, *a* $^{117/119}$Sn 15.2 mT. The relative intensity of the doublet satellites and the central signal implies that the species contains only one tin atom, and the spectrum has been ascribed to the anionic species $[R_2Sn{:}\bullet]^-$.[78]

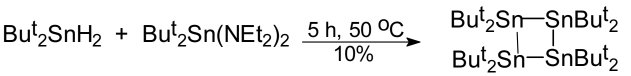
The crystals show little reactivity to air, but in solution, oxidation gives the cyclotristannoxanes $(Ar_2SnO)_3$.

At room temperature, the tristannane, $(Ar_2Sn)_3$, Ar = 2,4,6-$Pr^i_3C_6H_2$, is in thermal equilibrium with the distannene, $Ar_2Sn{=}SnAr_2$, and, in boiling toluene, it reacts with sulfur, selenium, or tellurium to give first the heterodistannirane, and then the 1,3-diheterodistannetane.[79] In the telluradistannirane, the two Ar ligands and the attached Sn are almost coplanar about the tin.



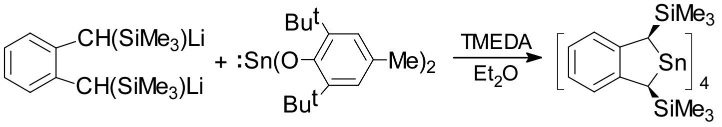
Scheme 18-5 Reactions of cyclotristannanes.

Some examples of the formation of cyclotetrastannanes are shown in equations 18-49–18-52.[18, 78]



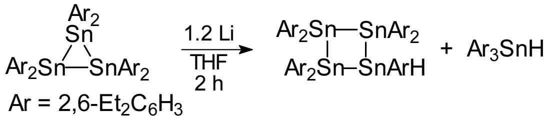
(18-49)

(18-50)



(**18-6**)

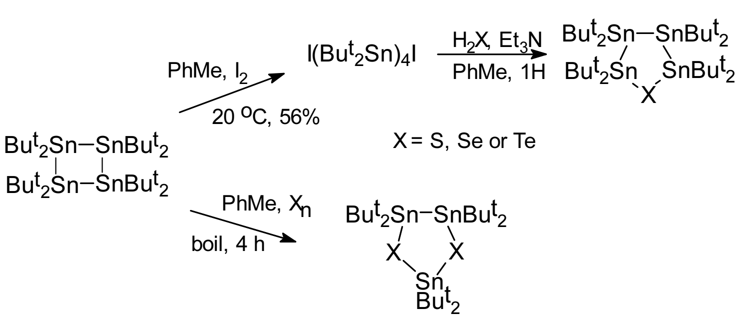
(18-51)



(18-52)

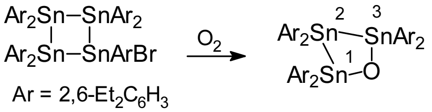
In $(Bu^t_2Sn)_4$ the ring is planar (SnSn 288.7 pm), but in $(Pe^t_2Sn)_4$ it is puckered (*r*SnSn 291.5–292.4 pm).[80] In the more complex tetrakis(stannadihydroindane) **18-6**, *r*SnSn is 285.2(3) pm,[81] the long bonds presumably reflecting the steric congestion.

The cyclotetrastannanes react with halogens with ring opening to give the 1,4-dihalogenotetrastannanes, $X(SnR_2)_4X$, and ultimately the diorganotin dihalides, R_2SnX_2. Cyclotetra(di-t-butylstannane) with one molar equivalent of iodine gives the 1,4-diiodotetrastannane, which reacts in turn with the hydrogen chalcogenides H_2X to give the cyclic compounds $(Bu^t_2Sn)_4X$, with almost planar Sn_4X rings.[82] When the cyclostannane is heated with the chalcogenides themselves, the 1,2,4-tristanna-3,5-dichalcogenacyclopentanes are formed; the rings containing sulfur or selenium are planar, but that in the tellurium derivative is puckered (Scheme 18-6).[83]



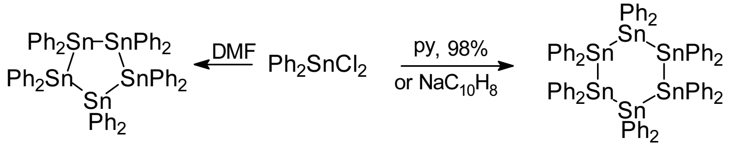
Scheme 18-6 Reactions of octa-t-butylcyclotetrastannane.

In contrast, air oxidation of the cyclotetrastannane $(Ar_2Sn)_3SnArBr$ (Ar = 2,6-$Et_2C_6H_3$) gives the oxatristannacyclobutane shown in equation 18-53; the Sn_3O ring is shaped like an arrowhead, with *r*Sn^1Sn^2 291.8(5), *r*Sn^2Sn^3 296.2(5) pm, $Sn^1Sn^2Sn^3$ 67.9(0)° and Sn^1OSn^3 113.5(7)°.[84]

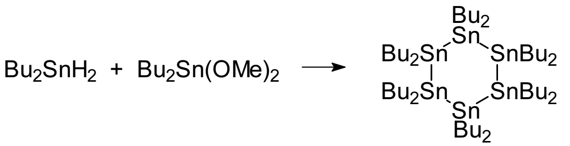


(18-53)

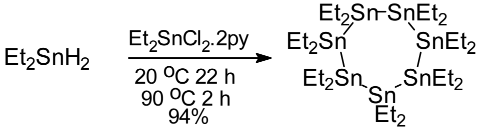
Examples of cyclopenta-, cyclohexa-, and cyclohepta-stannanes are shown in equations 18-54, 18-55, and 18-56. Both $(Ph_2Sn)_6$ and $[(PhCH_2)_2Sn]_6$. DMF have rings with a chair conformation, with average SnSn bond lengths of 278.0 pm and 280.1 pm, respectively.[85]



(18-54)

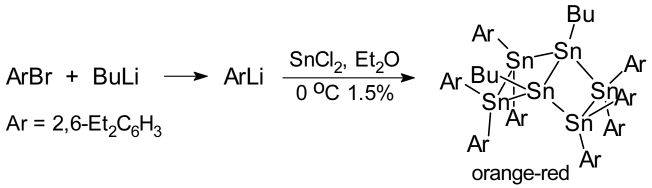


(18-55)



(18-56)

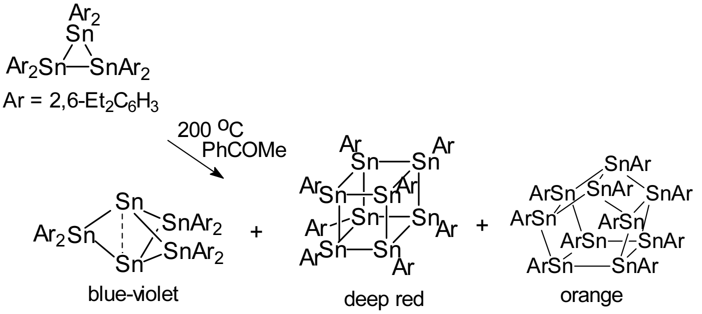
Most of the polycyclic oligostannanes that have been characterised contain a highly sterically hindered (2,6-dialkylphenyl)stannyl group. The first to be obtained was the [2.2.0]bicyclohexastannane (**18-7**), which was isolated from the reaction of 2,6-diethylphenyllithium with $SnCl_2$. With THF as the solvent for the reaction, the hexaaryltristannane was obtained in 50–55% yield (Scheme 18.4, above), but with ether as the solvent, a red oil was formed from which **18-7** was isolated in 1.5% yield. The butyl groups originate in the butyllithium from the first stage of the reaction. The two rings are puckered, and the angle between the mean planes is 131.9°; the shortest SnSn bond is the bridge bond, with *r*SnSn 281.8 pm. The compound is thermochromic, being pale yellow at 196 °C, and orange red at room temperature.



(**18-7**)

(18-57)

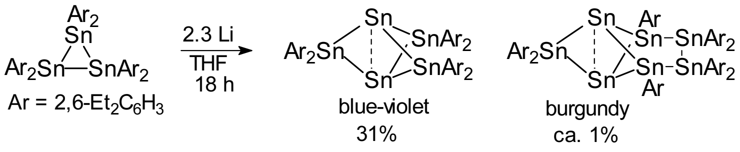
Some remarkable polycyclic oligostannanes have been obtained containing the $2,6\text{-}Et_2C_6H_3$ group.[86] If the cyclotristannane $[(2,6\text{-}Et_2C_6H_3)_2Sn]_3$ is heated in benzophenone, the pentastannapropellane **18-8**, the octastannacubane **18-9**, and the decastannaprismane **18-10**, can be isolated, along with the hexaaryldistannane.[75, 87, 88] It is suggested that initial dissociation gives the stannylene Ar_2Sn:, which disproportionates into ArSn:• and Ar_3Sn•, which are the major building blocks for the polycyclic structures. In the propellane, the outer SnSn bonds are in the range 282.1 to 287.1 pm, and the bridge bond is 336.7 pm, well above the normal length.



(**18-8**) (**18-9**) (**18-10**)

(18-58)

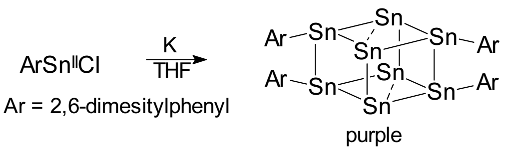
A second perstannapropellane, **18-11**, with a bridge bond length of 334.8 pm, is formed when the cyclotristannane is treated with lithium in THF for a prolonged period.[78] When **18.11** was reduced with potassium, it showed an ESR spectrum with *g* 1.95, $a(2\,^{117/119}\mathrm{Sn})$ 5.0 mT, $a(2\,^{117/119}\mathrm{Sn})$ 2.2 mT, $a(3\,^{117/119}\mathrm{Sn})$ 6.5 mT, which is ascribed its radical ion.



(**18-8**) (**18-11**)

(18-59)

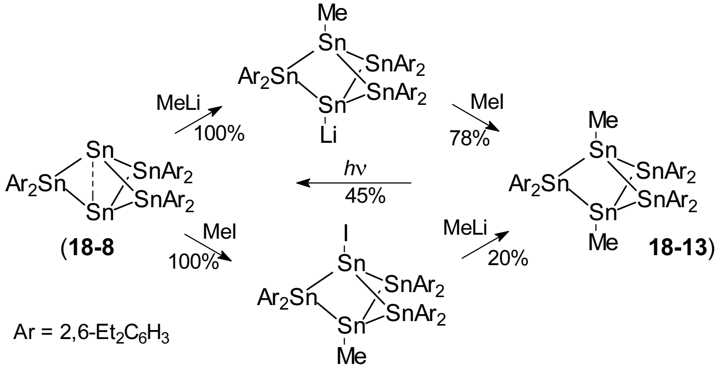
A tetraarylcubane has recently been reported. 2,6-Dimesitylphenyltin(II) chloride reacts with potassium to give, not the expected tetrahedral cluster $(\mathrm{ArSn})_4$ but the highly distorted cubane **18-12** with D_{2h} symmetry. The edges of the "cube" have *r*SnSn in the range of 285.3(2)–302.3(2) pm, but the diagonal bonds shown have *r* 310.7(2) pm.[89]



(**18-12**)

(18-60)

Some reactions of the perstannapropellane **18-8** have been established with reagents that are small enough to avoid the steric shielding by the aryl groups (Scheme 18-7). Reaction with methyl iodide and then with methyllithium, or reaction in the reverse sequence, gives the 1,3-dimethylbicyclo[1.1.1]pentastannane propellane **18-13**, and this can be photolysed to regenerate the propellane **18-8**.[90]



Scheme 18-7 Reactions of hexaarylpentastanna[1.1.1]propellane **18-8**.

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19 Compounds with Tin–metal Bonds[1–7, 8]

The early work on compounds containing an organotin group bonded to a different metal was largely limited to derivatives of the alkali metals (which were used as reaction intermediates) and of the other metals of Group 14 (Si, Ge, and Pb), but in recent years compounds containing an organotin group bonded to a transition metal have been investigated extensively. A review in 1968 listed compounds in which organotin was bonded to one of the metals Ti, Zr, V, Ta, Cr, W, Mn, Re, Fe, Ru, Co, Rh, Ir, or Pt,[1] and Glockling's 1998 review covers some 50 metals which include 13 transition metals, seven lanthanides (Pr, Nd, Gd, Er, Yb, Ho, and Lu) and one actinide (U), though the chemistry of many of these stannylmetallic compounds has been little developed.[5] Further compounds with an Sn–M bond, where the tin is not also bonded to carbon, are known for many metals, but these are not our concern here.

This chapter deals with the organotin compounds of the Main Group metals that have usually been studied more thoroughly, and of those transition metals that have attracted more attention because the compounds find some application in organic synthesis. A more comprehensive account is given in Glockling's review.[5]

19.1 Alkali Metals[9]

Organotin compounds in which tin is bonded to an alkali metal are important reagents in synthesis, when they are usually prepared and used *in situ* in solution. Compounds R_3SnM are known for all the alkali metals, and X-ray structures for some of the compounds Ar_3SnM have been determined.[10] There is also good evidence, mainly from NMR spectroscopy, for the existence in solution of 5-coordinate stannate species such as $Me_5Sn^-Li^+$.

19.1.1 Formation

The principal reactions by which the SnM bond can be formed are shown in equations 19-1–19-5.

$$R_3SnX + 2M \longrightarrow R_3SnM + MX \qquad (19\text{-}1)$$

$$R_3SnSnR_3 + 2M \longrightarrow 2R_3SnM \qquad (19\text{-}2)$$

$$R_3SnH + R'M \longrightarrow R_3SnM + R'H \qquad (19\text{-}3)$$

$$R_3SnSnR_3 + R'M \longrightarrow R_3SnM + R_3SnR' \qquad (19\text{-}4)$$

$$SnCl_2 + 3RM \longrightarrow R_3SnM + 2MCl \qquad (19\text{-}5)$$

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The reactions involving the metals are usually carried out in liquid ammonia or an ether such as THF as solvent (equations 19-6[11] and 19-7[12]), and can be accelerated by sonication. They involve electron transfer processes, and can also be accomplished with a metal-arene complex $M^+ArH^{\bullet -}$, or with the metal and a trace of an arene as catalyst. The composition of the product can be determined by adding an excess of bromobenzene and analysing for PhBr and R_3SnPh by GLC.[12]

$$2R_3SnCl + 2Na \xrightarrow{\text{lqd } NH_3} R_3SnNa + 2NaCl \qquad (19\text{-}6)$$

R = Me or Ph

$$R_3SnSnR_3 + 2NaC_{10}H_8 \xrightarrow{\text{tetraglyme}} 2R_3SnNa + C_{10}H_8 \qquad (19\text{-}7)$$

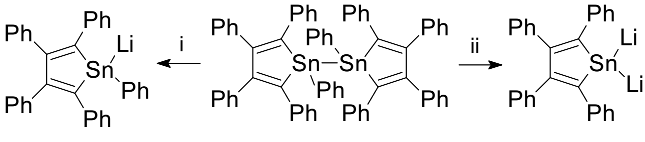
R = Me, Et, Bu, or vinyl

The reagent R′M in reactions 19-3 and 19-4 can be an organolithium compound such as butyllithium, or it can be sodium or potassium hydride[13] (but the quality of the hydride appears to be crucial[14, 15]), lithium diisopropylamide,[16] or potassium t-butoxide.[17] Some examples are given in equations 19-8,[13] 19-9,[14, 16] and 19-10.[18] Lithium pentaphenylstannole and dilithium tetraphenylstannole can be prepared from the bis(pentaphenylstannole) (equation 19-11).[19]

$$Bu_3SnH + NaH \xrightarrow[\text{30 min. quant.}]{Et_2O,\ RT} Bu_3SnNa + H_2 \qquad (19\text{-}8)$$

$$Ph_3SnSnPh_3 + 2KH \xrightarrow[RT]{DME} 2Ph_3SnK + H_2 \qquad (19\text{-}9)$$

$$Ph_3SnSnPh_3 + Me_3COK \xrightarrow[\text{0.5 h. 85 \%}]{\text{DMPU, 0 }^oC} Ph_3SnK + Ph_3SnOCMe_3 \qquad (19\text{-}10)$$



i. Li, THF, reflux ii. BuLi or Li, -80 °C or RT

(19-11)

The compounds Bu_3SnK and Bu_3SnCs have been obtained by treating Bu_3SnH with $Pr^i{}_2NK/Bu^tOLi$ or $Pr^i{}_2NCs/Bu^tOLi$, respectively.[14]

In the reaction of an organometallic compound with tin(II) chloride (e.g. equation 19-12), presumably R_2Sn is formed as an intermediate, which then undergoes oxidative addition of RM.[20]

$$3BuLi + SnCl_2 \longrightarrow Bu_3SnLi + 2LiCl \qquad (19\text{-}12)$$

A comparison of the efficiency of the production of R_3SnLi as determined by quenching with MeI is given in Table 19-1, which shows the reaction of Bu_3SnH with LDA, and the reaction of Me_6Sn_2 with MeLi to be most efficient.[21]

Table 19-1 Preparation of tributylstannyllithium

Conditions	Yield (%) R_3SnMe	Byproducts (Yield %)
$SnCl_2$, 3BuLi, THF, 0 °C, 15 min	33	Bu_4Sn (45) Bu_3SnCl (15)
Bu_3SnCl, Li wire, THF, 0 °C, 24 h	48	Bu_6Sn_2 (30) Bu_4Sn (30) Bu_3SnCl (4)
Me_3SnCl, Li dispn., THF, 0 °C, 8 h	70	Me_6Sn_2 (30)
Bu_3SnH, BuLi, THF, 0 °C, 15 min	4	
Bu_3SnH, LDA, THF, –30 °C, 15 min	90	Bu_6Sn_2
Me_6Sn_2, MeLi, THF, –40 °C, 20 min	80	

19.1.2 Properties

The stannyl-alkali metal compounds are very reactive towards oxygen and moisture and must be handled under an inert atmosphere in dry solvents. A mixture of R_3SnLi and R_3SnSnR_3 shows a single ^{119}Sn NMR signal at a position depending linearly on the ratio of the two compounds, as a result of rapid exchange through nucleophilic attack of tin on tin.[22] This exchange might involve a stannate intermediate, $(R_3Sn)_2SnR_3^-$, but this has not been detected as yet. The presence of R_3SnSnR_3 reduces the stability of the R_3SnLi, and, in about one day, decomposition occurs to give a mixture of R_4Sn, R_3SnSnR_2Li, $(R_3Sn)_3SnLi$, and organotin polymers. It is suggested that the R_3SnLi dissociates partially into R_2Sn: and RLi, then the R_2Sn: inserts into the SnLi bond;[23] this dissociation is the reverse of the formation of R_3SnLi by the reaction of RLi with $SnCl_2$.

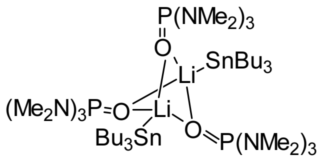
19.1.3 Structures

Me_3SnLi is monomeric in ether. If HMPA is added to a THF solution of Bu_3SnLi, the NMR spectra show that it forms first $Bu_3SnLi(HMPA)(THF)_2$, then $(Bu_3SnLi)_2(HMPA)_3$, and then solvent-separated ion pairs, Bu_3Sn^- II $Li(HMPA)_3^+$ and Bu_3Sn^- II $Li(HMPA)_4^+$.[24] The structure of $(Bu_3SnLi)_2(HMPA)_3$ is shown in **19-1**.

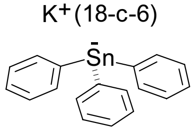
The ^{13}C NMR spectrum of Ph_3SnM shows that the negative charge is built up on the *meta* and particularly the *para* position of the ring, suggesting an inductive polarisation of the π-cloud, in contrast to the conjugative polarisation in Ph_3CM which places the negative charge particularly on the *ortho* and *para* positions.[17, 18, 25] The ^{119}Sn chemical shifts for Ph_3SnLi are –116.2 in 2-methyltetrahydrofuran (MTHF) and –106.7 in THF, and for Ph_3SnK are –114.7 in MTHF and –108.4 in THF; the downfield shift in THF is interpreted as reflecting the transition from a contact to a solvent-separated ion pair.[26, 27]

In the crystal, the molecule Ph_3SnK(18-crown-6) (**19-2**) consists of a pyramidal Ph_3Sn anion separated by more than 600 pm from a caged potassium cation which is sandwiched between two phenyl rings located on different Ph_3Sn units. The average Sn-C bond length is 222.4 pm which is 10 pm less than it is in Ph_4Sn, and the average CSnC bond angle is 96.9°.[28] Similarly, tri(2-furyl)tinlithium (**19-3**) does not contain an SnLi bond, but has a lithium cation which is octahedrally coordinated by the six oxygen atoms of two pyramidal trifurylstannyl anions, with a second, separate, solvated lithium cation.[29]

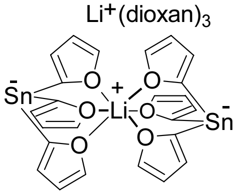
The first stannyl-alkali metal compound with a covalent Sn–M bond to be identified crystallographically was the pentamethyldiethylenetriamine (PMDETA) complex of Ph_3SnLi (**19-4**), with *r*SnLi av. 281.7 pm, slightly greater than the sum of the two covalent radii (274 pm), and CSnC 96.1(2)°.[30] This structure is preserved in solution, and, at –90 °C, the ^7Li NMR spectrum shows $^1J(SnLi) = 412$ Hz. Similarly the toluene complex



(**19-1**)

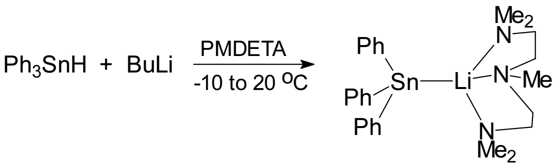


(**19-2**)



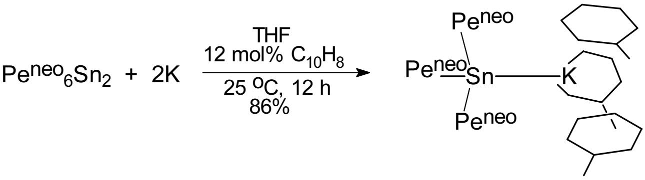
(**19-3**)

of $Pe^{neo}{}_3SnK$ (**19-5**) has a pyramidal R_3Sn group with CSnC 91.7°, and *r*SnK 354.8 pm, and the solid state ^{119}Sn NMR spectrum shows δ –221, with Sn–K coupling, ^1J 289 Hz.[31]



(19-13)

(**19-4**)



(19-14)

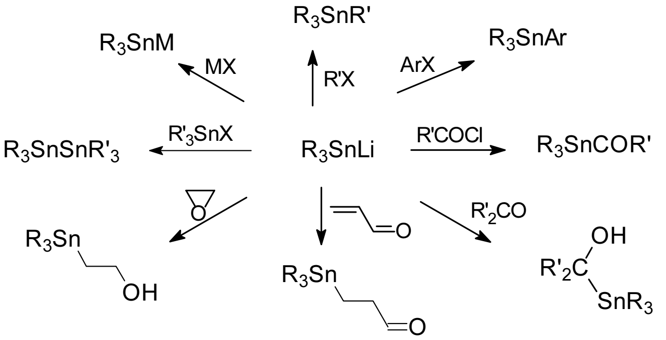
(**19-5**)

19.1.4 Reactions[32]

Applications of the stannylalkali metal compounds in synthesis are based on their provision of nucleophilic R_3Sn^- for reaction with electrophiles. Kinetic and mechanistic studies have been carried out only where the electrophile is an alkyl or aryl halide, when the behaviour of R_3SnM has been referred to as that of a supernucleophile, and a variety of detailed mechanisms have been identified by which overall substitution can be achieved (see Section 4.2).

The principal electrophiles which have been used in the reactions are shown in Scheme 19-1. These reactions are discussed in the relevant sections as follows.

$R_3SnX \rightarrow R_3SnSnR_3$	Section 18.2.1.1
$MX \rightarrow R_3SnM$	Chapter 19
$R'X \rightarrow R_3SnR'$	Section 4.2
Enones → saturated ketones	Section 4.2
$ArX \rightarrow R_3SnAr$	Section 4.2
Aldehydes and ketones → α-stannylalcohols	Section 6.2
$R'COX \rightarrow R_3SnCOR'$	Section 6.2
Epoxides → β-stannylalcohols	Section 6.3

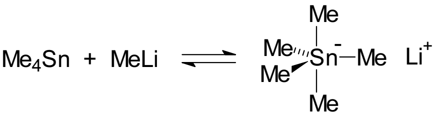


Scheme 19-1 Reactions of stannyllithium compounds with electrophiles.

19.1.5 Pentaorganostannates $R_5Sn^-Li^+$

There is good evidence from NMR spectroscopy, though not yet from X-ray crystallography, that compounds R_4Sn can react with organolithium reagents RLi to give the 5-coordinate stannate salts R_5Sn^- Li^+.[33] The reversibility of the process results in Sn/Li transmetallation which is important in organic synthesis, and this aspect is considered in Section 22.1. Grignard reagents will likewise bring about Sn/Mg transmetallation, and the reactions can be catalysed by BuLi;[34] presumably these reactions similarly involve pentaorganostannate intermediates, but these have not been detected spectroscopically.

A mixture of Me_4Sn and MeLi in THF shows a single ^{119}Sn NMR signal at δ 0. If HMPA is progressively added, a second signal develops at δ −277, and eventually replaces the first. At low temperature, the mixture shows dynamic ^1H, ^{13}C, and ^{119}Sn NMR behaviour. The high field ^{119}Sn signal can be resolved into a 16-line multiplet through coupling with 15 protons with $^2J(Sn{-}H)$ 39 Hz, and it is assigned to the Me_5Sn^- anion in which the methyl groups are in rapid positional exchange (equation 19-15).[35]



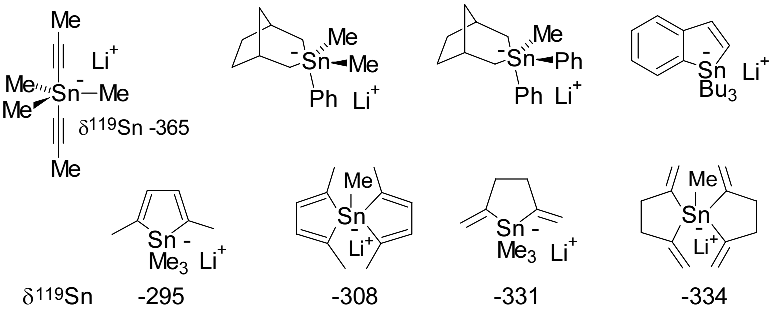
$$Me_4Sn + MeLi \rightleftharpoons Me_5Sn^- \; Li^+ \qquad (19\text{-}15)$$

Similar behaviour is observed when MeLi or PhLi is added to Ph_nSnMe_{4-n}, when the complete series of 5-coordinate anions, $Ph_nSnMe_{5-n}^-$ ($n = 0{-}5$), shown in Table 19-2, can be observed; the presence of electronegative phenyl ligands favours the formation of the complex.[35] The NMR spectra can be rationalised on the assumption that the compounds have a trigonal bipyramidal structure, with the phenyl groups preferring the apical positions, but with rapid pseudorotation.

Table 19-2 ^{119}Sn Chemical shifts of stannates $Ph_nSnMe_{5-n}^-$ Li^+.

$Ph_nSnMe_{5-n}^-$	$SnMe_5^-$	$PhSnMe_4^-$	$Ph_2SnMe_3^-$	$Ph_3SnMe_2^-$	Ph_4SnMe^-	Ph_5Sn^-
$\delta^{119}Sn$	−277	−291	−311	−300	−292	−307

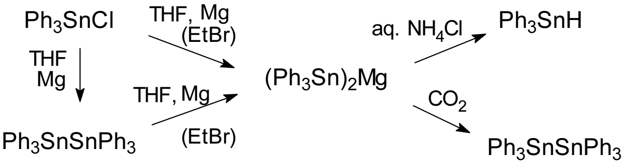
Some further examples of 10-Sn-5 ate complexes are shown in Scheme 19-2; [33, 36, 37] The stannacyclopentanes and stannacyclopentadienes are particularly prone to form these stannate ions, presumably because it relieves angle strain in the rings.



Scheme 19-2 Organotin 10-Sn-5 ate complexes, with values of δ^{119}Sn.

19.2 Magnesium[9]

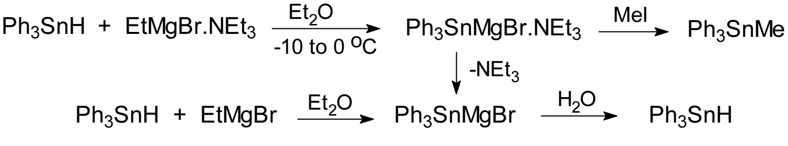
Relatively little attention has been paid to the tin-magnesium compounds, although $(Ph_3Sn)_2Mg$ was prepared from Ph_3SnCl and magnesium in THF in 1961.[38] Hexaphenylditin separates as an intermediate in the reaction, and then redissolves, and $(Ph_3Sn)_2Mg$ can alternatively be prepared from Ph_6Sn_2 and magnesium[38, 39] (Scheme 19-3). The reactions must be carried out below room temperature, or the product decomposes.



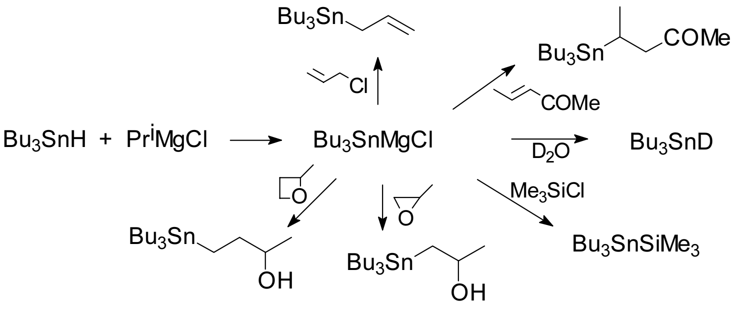
Scheme 19-3 Preparation and reactions of bis(triphenylstannyl)magnesium.

More conveniently, the reagents R_3SnMgX can be prepared by treating an organotin hydride with a Grignard reagent. EtMgBr Or its triethylamine complex can be used for the reaction with Ph_3SnH (Scheme 19-4),[40] but, for Bu_3SnH, a sterically hindered Grignard reagent such as Pr^iMgCl is necessary (Scheme 19-5).[41] $Bu_3SnMgMe$ Can be made from the reaction of Bu_3SnLi with MeMgI.[20]

The analogy with the Grignard reagents suggests that the structures of the stannylmagnesium halides may be more complex than are represented here: molecular weight measurements showed that $Ph_3SnMgBr$ is dimeric in freezing benzene, and it was inferred from the nature of some of the products of the reaction of $Ph_3SnMgBr$ that (by analogy with Ph_3SnLi) a phenyl group could be transferred from tin to magnesium to give a stannylene-magnesium complex.[40]



Scheme 19-4 Preparation and reactions of triphenylstannylmagnesium bromide.



Scheme 19-5 Preparation and reactions of tributylstannylmagnesium chloride.

19.3 Calcium, Strontium, and Barium

Bis(trimethylstannyl)calcium can be obtained as colourless crystals by stirring hexamethyldistannane with metallic calcium in THF. The molecule $(Me_3Sn)_2Ca \cdot 4\,THF$ has an octahedral structure with some distortion. The CSnC angles are approximately 96.5°, implying the use almost exclusively of p-orbitals on the tin, and, in line with this, $^1J(SnC)$ is very small at 106 Hz.[42] With more hexamethyldistannane, further reaction occurs to give the bis[tris(trimethylstannyl)stannyl]calcium.

$$Me_3SnSnMe_3 + Ca \xrightarrow{i} (Me_3Sn)_2Ca.4THF \xrightarrow{ii} [(Me_3Sn)_3Sn]_2Ca \qquad (19\text{-}16)$$

$$\text{i. THF, RT, 3 d, 62\%} \qquad \text{ii. } Me_6Sn_2$$

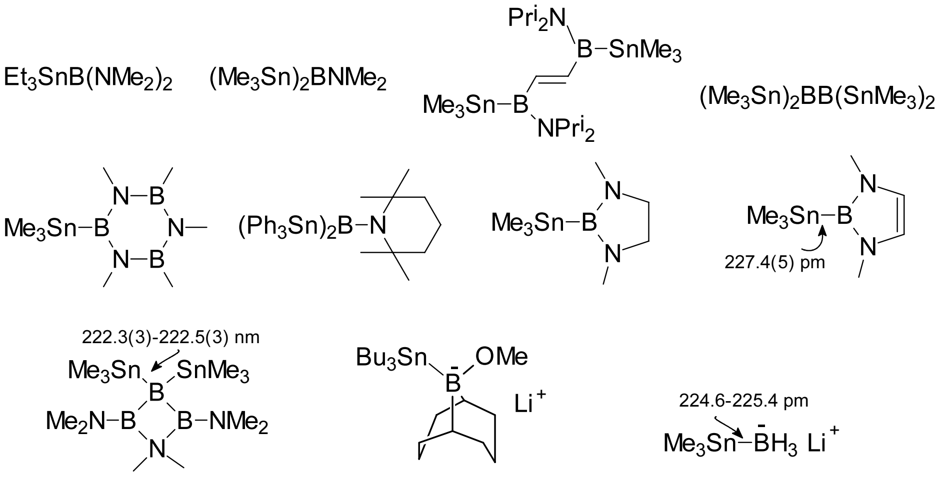
The distannanes react much more rapidly if the metal is dissolved in liquid ammonia, and the main products from Ph_6Sn_2 and calcium, strontium, or barium are the stannides $(Ph_3Sn)_2M$. Addition of HMPA and 18-crown-6 to the barium stannide gives crystals of the ionic complex $[Ph_3Sn]_2[Ba(18\text{-}c\text{-}6)(HMPA)_2]$, but, under the same conditions, the calcium and strontium stannides give the more complex compounds $[(Ph_3Sn)_3Sn]_2[M^{II}(18\text{-}c\text{-}6)(HMPA)_2]$.[43]

Bis[bis(trimethylsilyl)methyl]tin(II), $\{[(Me_3Si)_2CH]_2Sn{:} = R_2Sn\}$, reacts in dimethoxyethane with calcium metal by metal-metal exchange to give the compound R_2Ca, together with R_3SnH and, when toluene is present, R_3SnCH_2Ph.[44]

$$[(Me_3Si)_2CH]_2Sn{:} \xrightarrow[\text{DME}\\ \text{2 d}]{\text{Ca}} \underset{48\%}{[(Me_3Si)_2CH]_2Ca.2DME} + Sn + \underset{11\%}{[(Me_3Si)_2CH]_3SnH} \qquad (19\text{-}17)$$

19.4 Boron and Aluminium

A number of stannylboron compounds have been prepared by the reaction between R_3SnLi and the appropriate chloroborane; many of the boranes carry an amino group to increase the ease of handling.[45–49] Some examples are shown in Scheme 19-6.



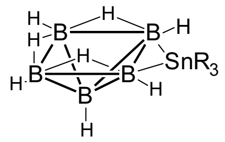
(**19-6**) (**19-7**)

Scheme 19.6 Sn–B Bonded compounds.

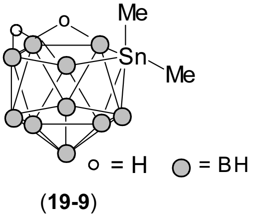
The ate complex **19-6** is obtained from the reaction of Bu_3SnLi with the methoxyborane. The trihydroborate **19-7** is formed from Me_3SnLi and BH_3, and acts as a hydrogen-transfer rather than a tin-transfer agent.[46]

Stannyl derivatives have also been prepared from higher boranes.[50] For example, $Li^+B_5H_8^-$ reacts with trimethyltin chloride to give μ-$Me_3SnB_5H_8$ (**19-8**), in which the bridging nature of the stannyl groups is inferred from the ^1H and ^{11}B NMR spectra.[51]

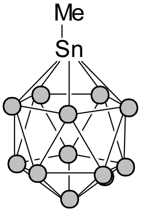
$NaB_{10}H_{13}$ Reacts with dimethyltin dichloride to give the *nido*-$Me_2SnB_{10}H_{12}$ (**19-9**); the bridging hydrogens are assumed to occupy the 8-9 and 9-10 positions.[52] [*Closo*-$B_{11}H_{11}SnMe]^-$ (**19-10**), with *r*SnC 210.5 pm, and *r*SnB 229.6 pm, is formed by treating [*closo*-$B_{11}H_{11}Sn]^{2-}$ with methyl iodide.[53]



(**19-8**)

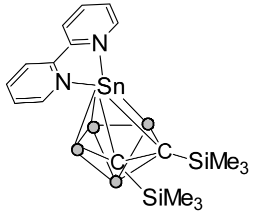


(**19-9**)

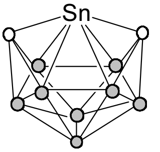


(**19-10**)

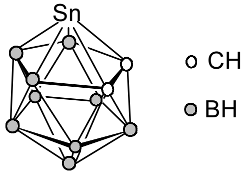
Stannacarbaboranes[54] can similarly be made by reaction of the mono- or di-anion of a *nido*-carbaborane with a tin halide,[55] and some examples are shown in formulae **19-11**,[56] **19-12**,[57] and **19-13**.[58] 1-Stanna-2,3-dicarba-*closo*-dodecaborane(11) (**19-13**) can be prepared from $B_9C_2H_{11}{}^{2-}$ and $SnCl_2$ (and the corresponding germanium and lead compounds can be prepared in the same way) and the tin can be removed with HCl or methoxide ion to regenerate the anion $B_9C_2H_{12}{}^-$.[58]



(**19-11**)



(**19-12**)



(**19-13**)

Stannylaluminium compounds have been prepared from the stannyllithium compounds (equation 19-18) and their cuprates have been used in the stannylmetallation of terminal alkynes and enynes.[21, 59]

$$\mathrm{Bu_3SnLi + Et_2AlCl \longrightarrow Bu_3SnAlEt_2} \qquad (19\text{-}18)$$

19.5 Silicon, Germanium, and Lead

The bond between tin and another Group 14 metal is usually made by elimination of an alkali metal halide between the two metals (e.g. equations 19-19,[60] 19-20,[61] and 19-21[62]) or by reducing an amino derivative of a metal with a tin hydride (equations 19-22 and 19-23). The first reaction is often accompanied by some metal-halogen exchange, so that the reaction between R_3MLi and $R'_3M'X$ leads to the formation of some R_3MMR_3 and $R'_3M'M'R'_3$ as well as the required $R_3MM'R'_3$, and the products may be difficult to separate. This complication can be minimised by adding the metallometallic reagent to the metal halide. The second method cannot be used for making an SiSn bond.

$$\mathrm{Ph_3GeLi + Me_3SnCl \longrightarrow Ph_3GeSnMe_3 + 2LiCl} \qquad (19\text{-}19)$$

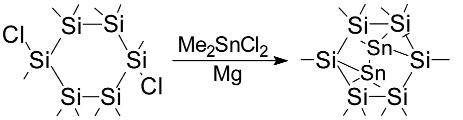
$$\mathrm{2Ph_3SnLi + Ph_2GeCl_2 \xrightarrow[-78\ ^{o}C]{THF} Ph_3SnGePh_2SnPh_3 + 2LiCl} \qquad (19\text{-}20)$$

$$\left.\begin{array}{l}\mathrm{Me_3SnLi + Me_3CSiMe_2GeMe_2Cl \xrightarrow[-78\ ^{o}C\ 45\%]{THF}} \\ \mathrm{Me_3SnNMe_2 + Me_3CSiMe_2GeMe_2H \xrightarrow[reflux.\ 34\%]{C_6H_6}}\end{array}\right] \longrightarrow \mathrm{Me_3SnGeMe_2SiMe_2CMe_3} \qquad (19\text{-}21)$$

$$\mathrm{Bu^tMe_2SiMe_2GeH + Me_3SnNEt_2 \longrightarrow Bu^tMe_2SiMe_2GeSnMe_3 + HNEt_2} \qquad (19\text{-}22)$$

$$\mathrm{Me_3SnH + Me_3PbNEt_2 \longrightarrow Me_3SnPbMe_3 + HNEt_2} \qquad (19\text{-}23)$$

Cyclic stannasilanes have been prepared by these methods, and by the Wurtz modification (e.g. equation 19-24)[63]

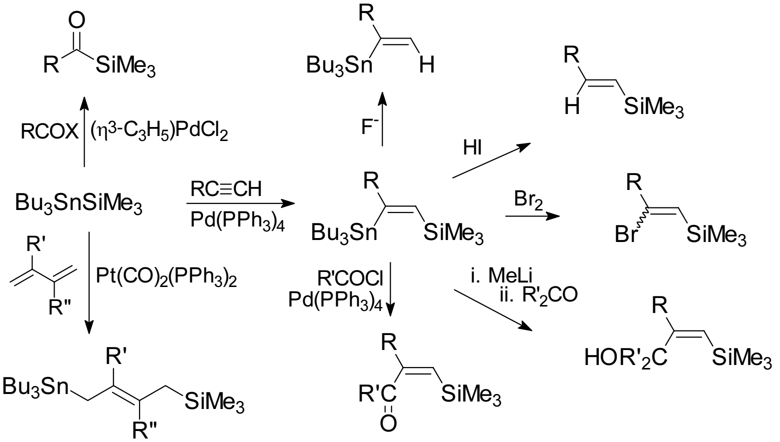


(19-24)

Electrochemical reduction of Bu_2SnCl_2 in a one-compartment cell with a platinum cathode and a silver anode gave a polymer $(Bu_2Sn)_n$ with M_W 6.7 × 10^4, and co-reduction with Bu_2SiCl_2 or Bu_2GeCl_2 gave copolymers $(Bu_2Si)_m(Bu_2Sn)_n$ or $(Bu_2Ge)_m(Bu_2Sn)_n$ in which m/n varied between zero and unity. The copolymers with a higher stannane content were the more sensitive to moisture.[64]

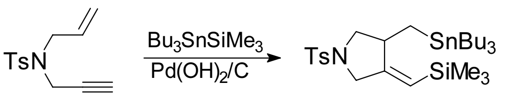
The stannylsilanes, particularly $Bu_3SnSiMe_3$, are finding increasing use in organic synthesis in the palladium- or platinum-catalysed stannylsilylation of alkynes and dienes, and in the reactions involving the halide-induced formation of stannyl anions.[65]

The metal-catalysed reactions are shown in Scheme 19-7.



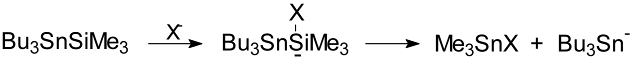
Scheme 19-7 Stannylsilylation of acetylenes and 1,3-dienes.

The stannylsilylation of terminal acetylenes occurs by *cis* addition, with silicon adding to the terminal carbon,[66] and the differentially bifunctional alkenes so obtained are valuable reagents for further transformations, as shown in Scheme 19-7.[67, 68] 1,6-Diynes[69] and 1-ene-6-ynes undergo bismetallative cyclisation.[65]



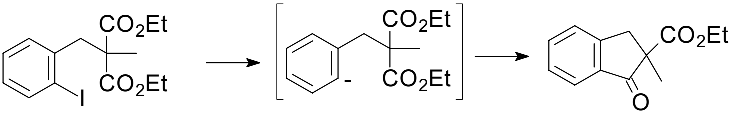
(19-25)

In the presence of a halide ion [from CsF, R_4NX, or $(Et_3N)_3S^+$ $Me_3SiF_2^-$], $Bu_3SnSiMe_3$ reacts to give the stannyl ion (equation 19.26),[65] though the degree of freedom of the ion is open to question. The ion (or incipient ion) can then react further by addition or substitution with suitable organic substrates (Scheme 19-8).

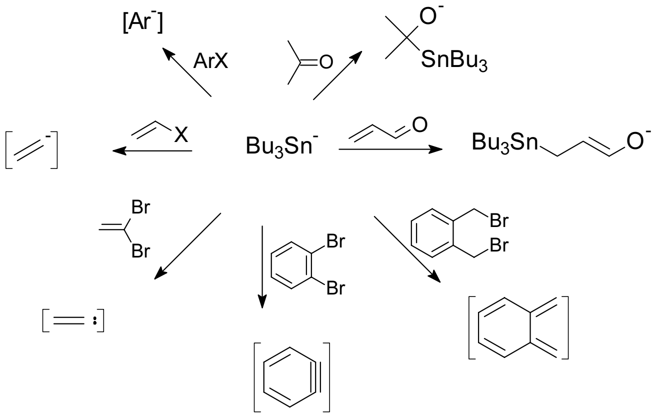


$$Bu_3SnSiMe_3 \xrightarrow{X^-} Bu_3Sn\overset{X}{\underset{-}{S}}iMe_3 \longrightarrow Me_3SnX + Bu_3Sn^- \qquad (19\text{-}26)$$

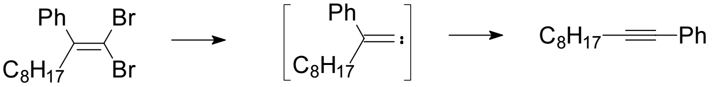
Some examples of the use of these reactions in organic synthesis are shown in equations 19-27, 19-28,[70] 19-29,[70, 71] and 19-30.[70, 72]



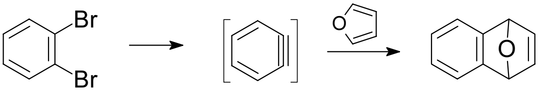
(19-27)



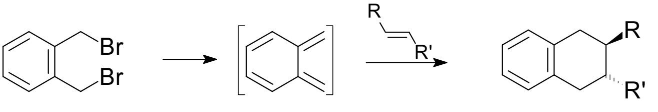
Scheme 19-8 Reactions of $Bu_3SnSiMe_3$ in the presence of halide ion.



(19-28)



(19-29)



(19-30)

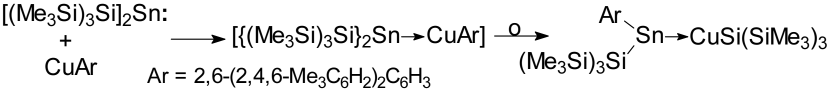
19.6 Copper[73]

Interest in stannylcuprates stems largely from their potential in organic synthesis, where they act as sources of nucleophilic tin that are less basic than stannyllithium compounds (Scheme 19-1), and which show some of the special reactivity that is normally associated with alkylcopper compounds. A variety of types of Sn^{IV}–Cu bonded compounds are available as illustrated in Table 19-3; all these are based on Cu(I), none has yet been isolated and subjected to X-ray crystallography, or studied in solution by NMR spectroscopy, and the detailed structures are uncertain. The last three reagents in the table have the advantage that they can be prepared and used in a one-pot operation. The stannylmetallation of alkynes by SnMg-, SnZn-, SnB-, and SnAl-bonded reagents can be brought about by Cu^I catalysis,[74] and it is reasonable to assume that these reactions also proceed through the intermediate formation of the SnCu-bonded species. Examples of the use of these cuprates in synthesis are shown in Table 8.1.

Table 19-3 Preparation of stannylcuprates.

Reagents		Stannylcuprate	Ref.
Ph_3SnLi	CuBr, LiBr	Ph_3SnCu	75
Me_3SnLi	CuBr, Me_2S	$(Me_3Sn)_2CuLi$	76
Me_3SnLi	PhSCu	$Me_3SnCu(SPh)Li$	77
Me_3SnLi	$CuBr_2 \cdot SMe_2$	$Me_3SnCu.SMe_2$	77
$Me_3SnSnMe_3$	C_4H_4S, Me_3SnLi	$Me_3SnCuCN(C_4H_4S)_2Li$	78
Bu_3SnH	$Bu_2Cu(CN)Li_2$	$Bu_3SnCuBu(CN)Li_2$	79
$Me_3SnSiMe_3$	$Bu_2Cu(CN)Li_2$	$Me_3SnCuBu(CN)Li_2$	80

Bis(hypersilyl)stannylene reacts with 2,6-dimesitylphenylcopper(I) to give the bright green compound **19-14**, presumably via a double rearrangement of an initial complex. The molecule contains an Sn^{II}–Cu^{I} bond, and is planar at the tin centre, with *r*SnCu 249.92(5) pm.[81]

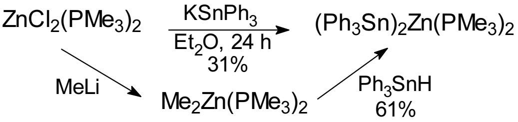


(19-31)

(**19-14**)

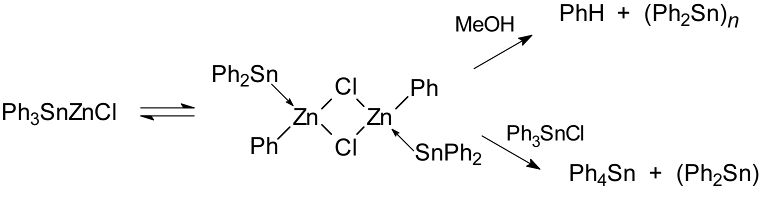
19.7 Zinc, Cadmium, and Mercury

A number of stannyl-zinc and -cadmium compounds have been prepared by reaction of a tin-alkali metal compound with a zinc or cadmium halide, or a tin hydride with an alkyl-zinc or -cadmium compound. The coordination of a ligand such as a triphenylphosphine, TMEDA, or bipyridyl, or a solvating solvent such as DME, both enhances the nucleophilicity of the alkyl group in the alkylmetallic compounds and stabilises the stannylmetallic product. Thus triphenyltin hydride reacts with diethylzinc or diethylcadmium in pentane or benzene with separation of metallic zinc or cadmium, but with a preformed complex, or in a coordinating solvent, the distannylmetallic compound is formed (e.g. equation 19-32).



(19-32)

The 4-coordinate complexes are stable, but the uncoordinated compounds appear to undergo migration of an organic ligand from tin to the bonded metal (equation 19-33). For example, $Ph_3SnZnCl.TMED$ reacts with Ph_3SnCl to give hexaphenyldistannane, but under the same conditions, $Ph_3SnZnCl$ gives Ph_4Sn and Ph_6Sn_2.[82]



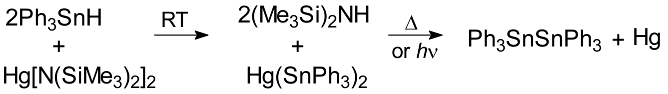
(19-33)

Examples of these compounds are given in Table 19-4. The stannylzinc compounds have been used in the presence of a copper or platinum catalyst for preparing vinylstannanes from terminal alkynes or from vinyl triflates,[20, 83, 84] but these reagents seem to have little advantage over the more readily available stannyllithium or stannylmagnesium compounds.

Table 19-4 Stannylzinc and stannylcadmium compounds.

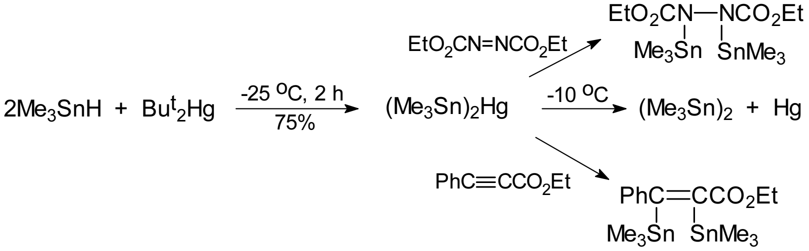
Compound	Method	Ref.	Compound	Method	Ref.
$(Ph_3Sn)_2Zn \cdot DME$	SnH + MR_2	82	$(Ph_3Sn)_2Zn(PMe_3)_2$	SnK + MCl_2	85
$Ph_3SnZnCl \cdot TMED$	SnH + MR_2	82	$(Ph_3Sn)_2Zn(PMe_3)_2$	SnH + MR_2	85
$(Ph_3Sn)_2Cd \cdot bipy$	SnH + MR_2	82	$(Bu_3Sn)_2Zn$	SnLi + MBr_2	83
$Ph_3SnCdCl \cdot TMED$	SnH + MRX	82	$Et_2SnZnEt_2Li$	SnLi + MR_2	86
$[(Me_3SiCH_2)_3Sn]_2Cd$	SnH + MR_2	87			

Bis(triphenylstannyl)mercury can be obtained as bright yellow crystals by the reaction of an diaminomercury compound with triphenyltin hydride. It is stable in the dark, but decomposes rapidly in the light or in solution to give hexaphenylditin and mercury.[88]



$$\begin{matrix}2Ph_3SnH\\+\\Hg[N(SiMe_3)_2]_2\end{matrix} \xrightarrow{RT} \begin{matrix}2(Me_3Si)_2NH\\+\\Hg(SnPh_3)_2\end{matrix} \xrightarrow[\text{or } h\nu]{\Delta} Ph_3SnSnPh_3 + Hg \qquad (19\text{-}34)$$

Distannylmercury compounds $(R_3Sn)_2Hg$, R = Me, Et, Pr, Bu^t, Ph, and Me_3SiCH_2, can also be prepared by reducing dialkylmercury compounds with tin hydrides (Scheme **19-9**).[87, 89]



Scheme 19-9 Formation and reactions of bis(trimethylstannyl)mercury.

The compounds $[(Me_3SiCH_2)_3Sn]_2Hg$ (m.p. 101–103 °C) and $(Bu^t_3Sn)_2Hg$ (red crystals, m.p. 196–198 °C) are stable in the absence of air and light, but the others decompose above −10 °C to give metallic mercury and the corresponding distannanes, and if the stannylmercurials are prepared in the presence of electron-deficient alkynes or azo compounds, the two R_3Sn groups add across the multiple bonds.[89]

19.8 Platinum and Palladium[4, 5, 90]

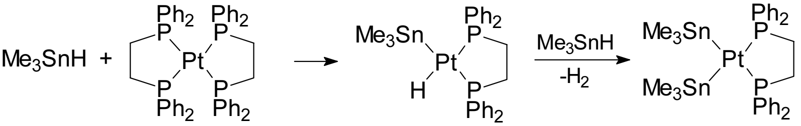
Many organotin reactions are catalysed by platinum or palladium compounds, and this has stimulated interest in compounds containing an Sn–Pt or Sn–Pd bond. The chemistry of the SnPt compounds is much the more thoroughly developed, and, if complexes of inorganic tin are included, derivatives are known with platinum in the Pt(0), Pt(II) and Pt(IV), and tin in the Sn(II) and Sn(IV) oxidation states.

At the platinum centre, the Pt(0) compounds are 3-coordinate and planar, or 4-coordinate and tetrahedral, the Pt(II) compounds are 4-coordinate and planar, or 5-coordinate and trigonal bipyramidal, and the Pt(IV) compounds are 6-coordinate and octahedral. Often, one of the ligands on the platinum is a phosphine, and ^{31}P NMR spectroscopy has played an important part in structural determinations, though many structures have now been established by X-ray diffraction.

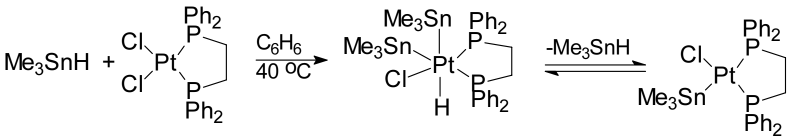
The Sn–Pt bond can be formed in a wide variety of reactions; they are classified here in terms of the reactive fragment of the organotin reagent: SnH, SnCl/Br/I, SnC, SnS/Se/Te, SnSn, and SnLi.

From SnH

Pt(0) And Pt(II) compounds "insert" into the SnH bond to give Pt(II) or Pt(IV) complexes, e.g. equation 19-35 and 19-36.[91]

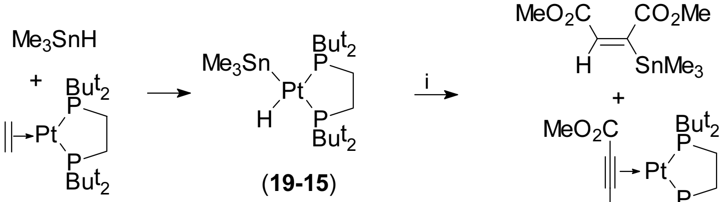


(19-35)



(19-36)

SnH Adducts are probably intermediates in the platinum-catalysed hydrostannation of alkenes and alkynes,[92] and this reaction has been demonstrated for the hydride **19-15**.[93]

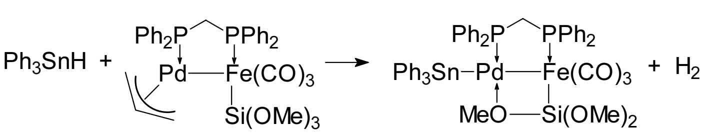


(19-37)

(**19-15**)

i. $MeO_2C{\equiv}CO_2Me$

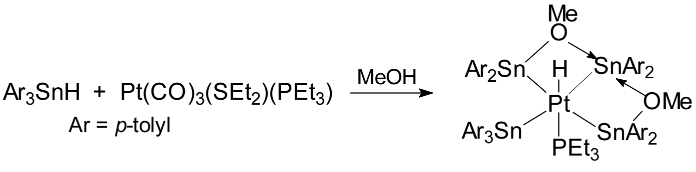
The trimetallic Fe-Pd-Sn complex **19-16** has been isolated as an intermediate in the catalytic dehydrogenative coupling of tin hydrides.[94]



(19-38)

(**19-16**)

A more complex reaction occurs between tri-*p*-tolyltin hydride and $Pt(CO)_3(SEt_2)(PEt_3)$ in methanol to give the complex **19-17** containing both tin(II) and tin(IV).[95]

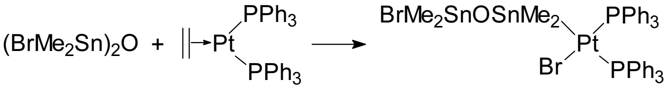


(19-39)

(**19-17**)

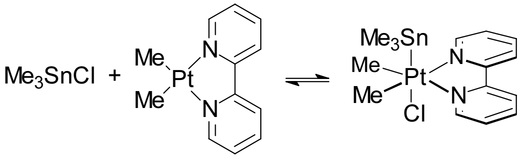
From SnCl/Br/I

The order of reactivity of organotin chlorides towards $(C_2H_4)Pt(PPh_3)_2$ is Me_3SnCl < Ph_3SnCl, Me_2SnCl_2 < Ph_2SnCl_2 < $MeSnCl_3$ < $PhSnCl_3$; the early members of this series (Me_3SnCl, Ph_3SnCl, and Ph_2SnCl_2) react by insertion of Pt into the SnC bond, but the later members (Ph_2SnCl_2, $MeSnCl_3$, $PhSnCl_3$) by insertion into the Sn-halogen bond (e.g. equation 19-40), and this change in chemoselectivity led in the early days to some confusion.[96]



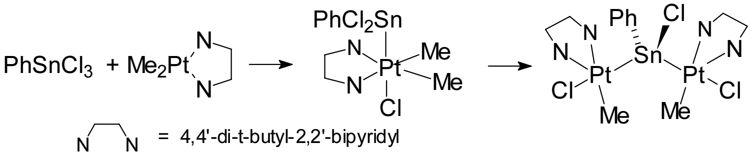
(19-40)

Trimethyltin chloride, bromide, and iodide react with $Me_2Pt(bipy)$ by insertion into the Sn–halogen bond, and the equilibrium constant favours the product in the sequence Cl < Br < I.[97, 98]



(19-41)

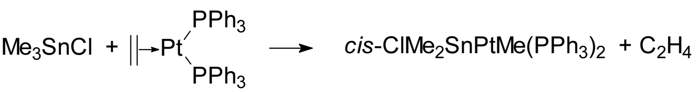
A compound containing the Pt–Sn–Pt unit has been obtained by the reaction shown in equation 19-42.[99]



(19-42)

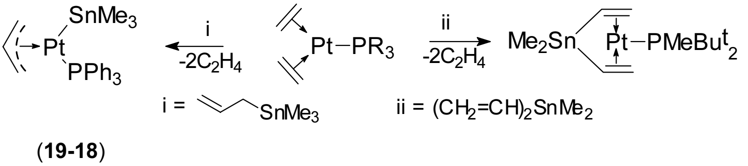
From SnC

Insertion of platinum into the Sn–C bond was first established with trimethyltin chloride:[100]



(19-43)

Tetramethyltin, tetraphenyltin, and tetraethynyltin react in a similar way. For a wide variety of aryl groups, the mixed stannanes Me_3SnAr react to give the products *cis*-$PtAr(SnMe_3)(PPh_3)_2$, but the system catalyses the conversion of Me_3SnAr to Me_4Sn and Me_2SnAr_2, and prolonged reaction can give $PtAr(SnMe_2Ar)(PPh_3)_2$.[101] Allyltrimethyltin reacts with $Pt(C_2H_4)_2PPh_3$ to give the π-allyl complex **19-18**, but dimethyldivinyltin stays intact and chelates through its vinyl groups to form the platinum di-π-complex.[102]

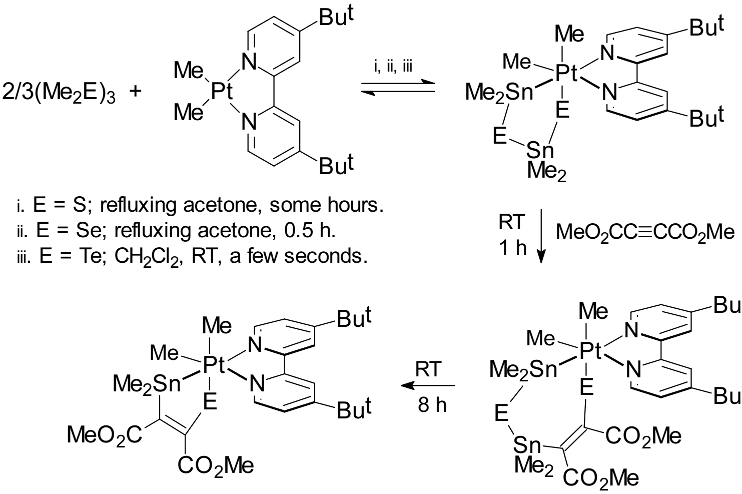


(19-44)

(**19-18**)

From SnS/Se/Te

Platinum readily inserts into the SnE bonds of the trimers $(Me_2SnE)_3$ (E = S, Se, or Te), the reactivity falling in the sequence S < Se < Te.[103] The Me_2SnE units can then be exchanged with other Me_2SnE' units, and dimethyl acetylenedicarboxylate can be inserted into the ring; this type of reaction is well known for SnO bonds, but not for SnS, SnSe, or SnTe bonds, and it is suggested that the nucleophilicity of E is enhanced by electron donation from the *trans*-MePd group.[104]



i. E = S; refluxing acetone, some hours.
ii. E = Se; refluxing acetone, 0.5 h.
iii. E = Te; CH_2Cl_2, RT, a few seconds.

(19-45)

From SnSn

Platinum is also readily inserted into the SnSn bond of hexamethyldistannane (equation 19-46),[105] and a similar reaction occurs with palladium(0) compounds.[106]

$$Me_3SnSnMe_3 + \| \!\rightarrow Pt(PPh_3)_2 \xrightarrow[Et_2O]{C_6H_6/} (Me_3Sn)_2Pt(PPh_3)_2 \qquad (19\text{-}46)$$

In daylight or under a tungsten filament lamp, the dialkyltin oligomers $(Me_2Sn)_6$, $(Ph_2Sn)_6$, and $(Et_2Sn)_9$ introduce stannylene units into the Pt–Cl bond of chloroplatinum(II) compounds, for example:

$$(Me_2Sn)_6 + PtCl_2(PEt_3)_2 \xrightarrow[\text{RT, 24 h}]{h\nu,\ C_6H_6} \textit{trans}\text{-}PtCl(SnMe_2Cl)(PEt_3)_2 \qquad (19\text{-}47)$$

When the stable stannylene $[(Me_3Si)_2CH]_2Sn\mathbf{:}$ reacts with $PtCl_2(PEt_3)_2$, one unit inserts into a Pt–Cl bond, while the other acts as a Lewis base, to form the complex $(R_2Sn)(ClR_2Sn)Pt(PEt_3)Cl$.[107]

From SnLi

Rather little use has been made of the reaction of stannyllithium reagents for forming the Pt-Sn bond, perhaps because other reagents such as the stannanes, distannanes, or stannyl chlorides are more readily available. The reaction of Ph_3SnLi with $PtCl_2(PPh_3)_2$, which was originally thought to give $Ph_3SnPtCl(PPh_3)_2$, was later shown to be more complicated, and this has perhaps further discouraged use of this route in the face of so many alternatives – though these too may involve complications; exchange between phenyl and chloro ligands on the tin and platinum occurs, and the product is actually $ClPh_2SnPtPh(PPh_3)_2$.[100, 108]

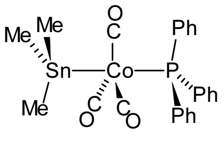
19.9 Other Transition Metals[1–4, 90, 109, 110]

Too many different types of reaction have been used for generating a bond between tin and a transition metal to permit a simple classification in terms of mechanism or of composition of reactants, but the principal methods involve one of the following processes. Examples of these have already been met in the above sections.

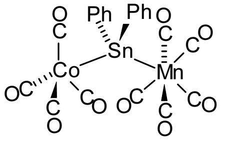
1. Elimination of an alkali-metal halide.
2. Elimination of a small molecule (eg. H_2, R_2NH, or C_2H_4).
3. Oxidative addition of tin halide, tin hydride, or distannane.
4. Addition or insertion of a stannylene, $R_2Sn\mathbf{:}$.

Some typical examples of products and reactants are shown in Table 19-5.

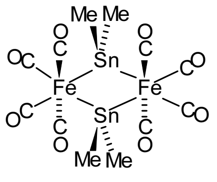
The structures of some typical compounds are shown in formulae **19-19**,[122] **19-20**,[123] **19-21**,[124] **19-22**,[125] **19-23**,[121] and **19-24**.[126]



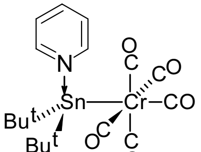
(19-19)



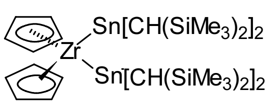
(19-20)



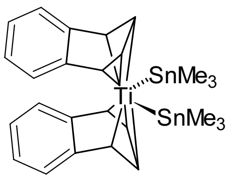
(19-21)



(19-22)



(19-23)



(19-24)

Table 19-5 Compounds with a tin–transition metal bond.

Product	Reactants	Ref.
$Ph_3Sn-TiCp_2Cl$	$Ph_3SnLi + Cp_2TiCl_2$	111
$(Ph_3Sn)_2TiCp_2$	ditto	
$Ph_3Sn-Ni(\eta\text{-}C_5Me_5)(CO)$	$(\eta\text{-}C_5Me_5)(OC)Ni^- Na^+ + Ph_3SnCl$	112
$Me_3Sn-Co(CO)_4$	$Co_2(CO)_8 + Me_3SnCl$	113
$(Ph_3Sn)_4Ti$	$Ph_3SnH + Zr(NEt_2)_4$	114
$Me_3Sn-TaH_2Cp_2$	$Me_3SnNMe_2 + Cp_2TaH_3$	115
$[Bu_2Sn-Fe(CO)_4]_2$	$Bu_2SnO + Fe(CO)_5$	116
$(Ph_3Sn)_2Os(CO)_4$	$(Ph_3Sn)_2O + H_2Os(CO)_4$	117
$Me_3Sn-RuCl(CO)(PPh_3)$	$Me_3SnCH{=}CH_2 + RuHCl(CO)(PPh_3)_2;\ h\nu$	118
$Bu_3Sn-Rh^{III}(H)(Cl)(PPh_3)_3$	$Bu_3SnH + Rh^{I}(Cl)(PPh_3)_3$	119
$Me_3Sn-Mn(CO)_5$	$Me_6Sn_2 + Mn_2(CO)_{10}$	120
$(Me_3Sn)_2\text{-}Fe(CO)_4$	$Me_6Sn_2 + Fe(CO)_5$	120
$R_2Sn{\to}Cr(CO)_5\,^a$	$R_2Sn{:} + Cr(CO)_6;\ h\nu$	107
$(R_2Sn{\to})_2Mo(CO)_4\,^a$	$R_2Sn{:} + Mo(CO)_4,^b\ \Delta$	107
$MeR_2Sn-Fe(\eta\text{-}Cp)(CO)_2\,^a$	$R_2Sn{:} + FeMe(\eta\text{-}Cp)(CO)_2$	107
$(R_2Sn{\to})_2Zr(\eta\text{-}MeC_5H_4)_2\,^a$	$R_2Sn{:} + ZrBu_2(\eta\text{-}MeC_5H_4)_2$	121

[a] $R = (Me_3Si)_2CH$ [b] L_2 = norbornadiene

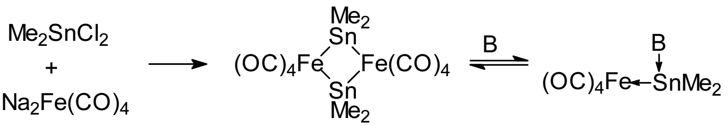
The Sn–M bond appears to be predominantly σ in character, with a little additional $d\pi$–$d\pi$ contribution.

The stannylene adducts $L_nM \leftarrow SnR_2$ appear to be stable only when the corresponding stannylenes $R_2Sn{:}$ are themselves stable [e.g. when $R = Cp$ or $(Me_3Si)_2CH$]. The η^5-bonded ring in Cp_2Sn: can give either an η^1 or η^5-bonded product.[127]

$$\eta^5\text{-}Cp_2Sn{\to}Mo(CO)_5 \xleftarrow{\text{i}} \eta^5\text{-}Cp_2Sn \xrightarrow{\text{ii}} [(CO)_4Fe{\leftarrow}Sn(\eta^1\text{-}Cp)_2]_2 \qquad (19\text{-}48)$$

$$\text{i. } Mo(CO)_5THF \qquad \text{ii. } Fe_2(CO)_9$$

With other stannylene units the R_2Sn group acts as a bridging ligand between two metals M, and the bridge can be opened by a base such as THF, pyridine, acetone, or acetonitrile, the stannylene moiety then acting as both a Lewis acid and a Lewis base.[128]



(19-49)

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20 Organotin Radicals and Radical Ions[1-3]

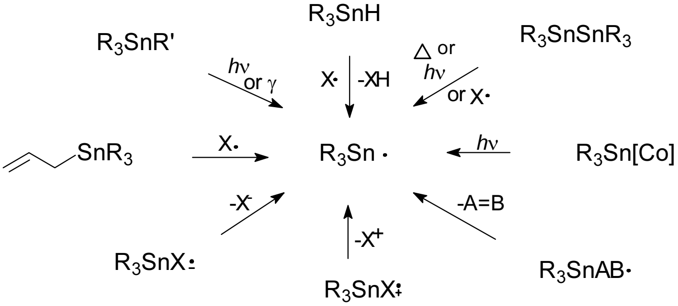
Reactions involving organotin hydrides, or allyltin compounds, or hexaalkyldistannanes as reactants, and stannyl radicals as intermediates, now hold an important place in organic synthesis, to the degree that this dominance of organotin reagents in mediating free radical reactions has been referred to as the tyranny of tin.[4]

A number of the stannyl radicals, $R_3Sn^{\bullet}$, have been characterised by ESR spectroscopy,[5] and their reaction kinetics have been determined, and used in interpreting and designing the radical chain syntheses. Radical ions $R_nSnX_{4\text{-}n}^{\bullet+}$, $R_nSnX_{4\text{-}n}^{\bullet-}$ and $R_2Sn^{\bullet-}$ have also been identified, again principally by ESR spectroscopy, and there is some spectroscopic evidence for the species $R_nSnX_{4\text{-}n}Y^{\bullet}$ which are postulated to be formed in the course of some S_H2 reactions at tin centres.

20.1 Organotin Radicals $R_3Sn\cdot$

20.1.1 Generation

The principal routes by which organotin radicals $R_3Sn^{\bullet}$ can be generated are shown in Scheme 20-1.



Scheme 20-1 Generation of stannyl radicals.

From SnH[6]

For studies of $R_3Sn^{\bullet}$ radicals in fluid solution by ESR spectroscopy, the radicals are usually generated by abstraction of hydrogen from an organotin hydride, and this can conveniently be carried out by photolysing a mixture of di-t-butyl peroxide and the hydride within the cavity. The spectral resolution is often better at low temperatures, and this was ascribed to the slowing of the symmetrical exchange reaction between stannyl radicals and the stannane (Section 15.3.5.1).[7, 8]

$$Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO^{\cdot} \tag{20-1}$$

$$Bu^tO\cdot + R_3SnH \longrightarrow Bu^tOH + R_3Sn\cdot \tag{20-2}$$

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Radiation has to be continuous to maintain an adequate standing concentration of the stannyl radicals. If the t-butoxyl radicals are generated by laser flash photolysis and the formation and decay of the $R_3Sn^{\bullet}$ radicals is monitored by optical spectroscopy (e.g. $Bu_3Sn^{\bullet}$, ν_{max} 400 nm), the rate constant at 295 K for the self-reaction of the $Bu_3Sn^{\bullet}$ radicals is found to be ca. 1.4×10^9 M^{-1} s^{-1}, and that for the reaction of $Bu^tO^{\bullet}$ radicals with the stannane is 1.9×10^8 M^{-1} s^{-1}.[9]

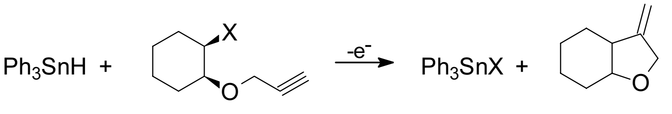
In organic synthesis, the t-butoxyl radicals are commonly generated thermally from di-t-butyl peroxide which has a half-life of 218 h at 100 °C and 6.4 h at 30 °C. If the reaction is to be carried out at a lower temperature, the peroxide may be photolysed, or initiation may be brought about by triethylborane[10, 11] or diethylzinc[12] in the presence of a trace of air or oxygen. The detailed mechanism of this type of initiation is not known, but the organo-boron and -zinc compounds react with oxygen by a radical chain mechanism involving the radicals $Et^{\bullet}$ and $EtOO^{\bullet}$, and giving the peroxymetallic compounds EtOOM which can generate the radicals $EtO^{\bullet}$ and $^{\bullet}OM$, and any or all of these radicals might be involved in the initiation.[13]

Azoisobutyronitrile, [$Me_2(NC)CN{=}NC(CN)Me_2$; AIBN], is an alternative initiator which can be used under either thermal or photolytic conditions.[14] It has a half-life of 10 h in toluene at 65 °C, and is often used in reactions which are carried out in refluxing benzene.

Ketone triplets react with tin hydrides in the same way as t-butoxyl radicals (equation 20-3), with a rate constant of 2×10^8 M^{-1} s^{-1} (presumably at room temperature); the hydroxyalkyl radical abstracts hydrogen from a second molecule of stannane to give isopropyl alcohol in unit quantum yield.[15]

$$Me_2CO^T + Bu_3SnH \longrightarrow Me_2\dot{C}OH + Bu_3Sn\cdot \qquad (20\text{-}3)$$

The stannyl radical can also be generated electrochemically. Cyclic voltammetry of triphenyltin hydride in THF containing tetrabutylammonium perchlorate shows that oxidation occurs at +0.80 V versus SCE to give $Ph_3SnH^{\bullet +}$ which dissociates into H^+ and $Ph_3Sn^{\bullet}$, and electrooxidation of Ph_3SnH in the presence of a suitable substrate can be used as a technique for bringing about reactions involving stannyl radical intermediates (e.g. equation 20-4).[16]



(20-4)

From SnSn

Triarylstannyl radicals with bulky *ortho*-substituted phenyl groups are in thermal equilibrium with the corresponding hexaaryldistannanes, and the lowest temperatures at which the radical can be detected by ESR spectroscopy in solutions of the distannanes, and the bond dissociation enthalpies, are shown in Table 18-2; the *g*-values of these radicals lie between 2.0057 and 2.0079.[17]

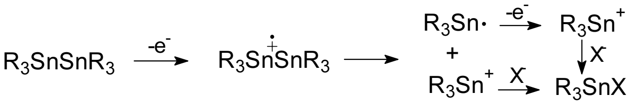
$$Ar_3SnH \xrightarrow{Me_2\dot{C}CN} Ar_3Sn\cdot \underset{\Delta}{\rightleftharpoons} Ar_3SnSnAr_3 \qquad (20\text{-}5)$$

Cleavage of the Sn-Sn bond can also be brought about by photolysis or by electrolytic or chemical oxidation. Hexabutyldistannane has an absorption maximum at 236 nm, but this tails off to 250–260 nm. The excitation energy is ≤300 kJ mol^{-1}, and irradiation with UV light leads to $\sigma \rightarrow \sigma^*$ excitation and homolysis of the Sn-Sn bond. A ^{119}Sn CIDNP effect which is observed when R_6Sn_2 (R = Me, Et, or Bu) is irradiated alone or in the presence of an alkyl halide, shows that the $R_3Sn^•$ radicals are formed through a long-lived triplet state.[18] The rate of formation of stannyl radicals is increased by the addition of di-t-butyl peroxide, when the S_H2 process of equation 20-7 supplements the unimolecular cleavage of the distannane.[19] Acetone, *p*-methoxyacetophenone, and diphenyl ether can act as photosensitisers (though the ketone triplets may also bring about S_H2 reactions equivalent to that of reaction 20-7);[20] by this technique, distannanes may be used instead of tin hydrides to initiate radical chain cascade reactions involving steps such as intermolecular additions or intramolecular cyclisations that may be too slow to compete with hydrogen abstraction from a tin hydride.

$$R_3SnSnR_3 \xrightarrow{h\nu} {}^1(R_3SnSnR_3)^* \longrightarrow {}^3(R_3SnSnR_3)^* \longrightarrow 2R_3Sn\cdot \qquad (20\text{-}6)$$

$$Me_3CO\cdot + R_3SnSnR_3 \longrightarrow Me_3COSnR_3 + \cdot SnR_3 \qquad (20\text{-}7)$$

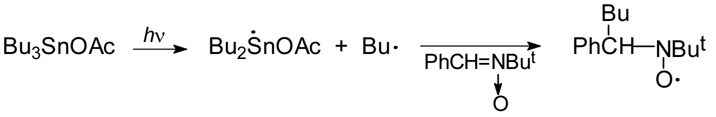
Electrochemical oxidation occurs at +0.141(4) V (versus SCE).[21, 22] The rates of the oxidation of $Me_3SnSnMe_3$, $Me_3SnSnBu_3$, $Bu_3SnSnBu_3$, and $Ph_3SnSnPh_3$ by $(phen)_3Fe(III)(ClO_4)_3$ correlate linearly with the oxidation potentials of the distannanes.[23] Quantitative oxidation of R_3SnSnR_3 to R_3SnX can be brought about by $AgNO_3$, $AgClO_4$, $Hg_2(NO_3)_2$, or $HgCl_2$ (equation 20-8).[22]



$$R_3SnSnR_3 \xrightarrow{-e^-} R_3Sn\overset{\overset{\bullet}{+}}{}SnR_3 \longrightarrow \begin{array}{ccc} R_3Sn\cdot & \xrightarrow{-e^-} & R_3Sn^+ \\ + & & \downarrow X^- \\ R_3Sn^+ & \xrightarrow{X^-} & R_3SnX \end{array} \qquad (20\text{-}8)$$

From SnR

Irradiation of organotin compounds R_nSnX_{4-n} with UV light[24] or with ultrasound[25] in the presence of a spin trap such as phenyl-t-butylnitrone or nitrosodurene gives rise to the spectrum of the spin adduct of the radical $R^•$ (e.g. equation 20-9).



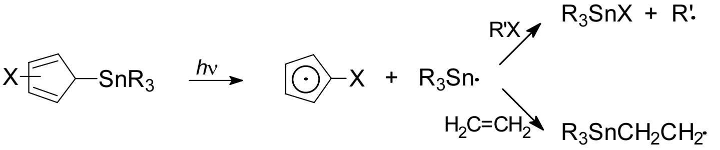
$$Bu_3SnOAc \xrightarrow{h\nu} Bu_2\dot{S}nOAc + Bu\cdot \xrightarrow[\substack{PhCH=NBu^t\\ \downarrow\\ O}]{} \begin{array}{c} Bu \\ | \\ PhCH{-}NBu^t \\ \quad\ \ | \\ \quad\ \ O\cdot \end{array} \qquad (20\text{-}9)$$

The ESR spectra of organotin radicals themselves have been observed in the solid state in γ-irradiated organotin compounds, neat or in a host matrix such as adamantane (e.g. $Me_nCl_{3-n}Sn^•$, $n = 0-3$).[26, 27] Apart from the $Me_3Sn^•$ radical, Me_4Sn gave another species with a(4 or 6H) ca. 1.8 mT, which was tentatively identified with the trigonal bipyramidal radical $Me_5Sn^•$.[27]

Allyl-, benzyl-, 1-naphthylmethyl- and 9,10-dihydro-9-anthracenyl-tin compounds undergo photocleavage more readily and then show the typical reactions of stannyl radicals[28] and a CIDNP effect can be observed in the ^1H NMR signal of the methylene group of benzyltin compounds.[29] Acylstannanes, R_3SnCOR', have an absorption band at ca. 380 nm, and CIDNP studies show that irradiation with light in the range 300-450 nm leads to cleavage of the Sn-CO bond by a Norrish 1 mechanism, through the triplet excited state; pairing of the stannyl radicals then gives the distannane, R_3SnSnR_3.[30]

$$Pr_3SnCOPr^i \xrightarrow{h\nu} {}^1(Pr_3SnCOPr^i)^* \longrightarrow {}^3(Pr_3SnCOPr^i)^* \longrightarrow Pr_3Sn\cdot + \cdot COPr^i \qquad (20\text{-}10)$$

The cyclopentadienyltin compounds $CpSnR_3$ are much more sensitive to photolysis, and on irradiation with UV light they show a strong ESR spectrum of the corresponding cyclopentadienyl radicals. It is difficult to observe the spectrum of the $R_3Sn^\bullet$ fragment under these conditions because the cyclopentadienyl radical is not readily saturated with microwave power (see below), but the system shows the characteristic reactions of the stannyl radical towards alkyl halides, alkenes and 1,2-diones.[31–33] These systems have been used for investigating the substituent effect of the group X on the cyclopentadienyl π-system, including the case where X = R_3Sn (Section 20.2).[34]



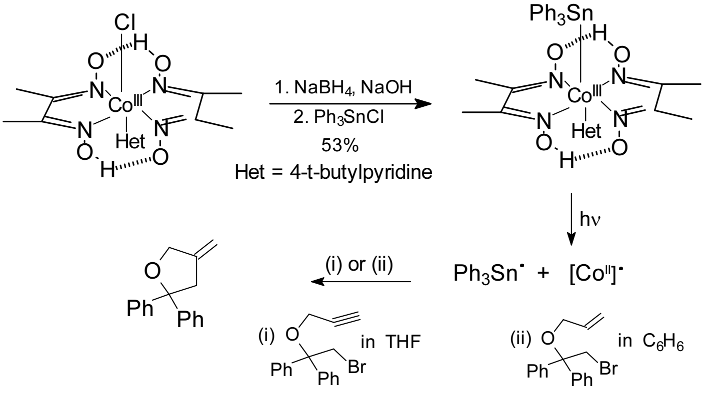
(20-11)

If a solution of the stable stannylene $[(Me_3Si)_2CH]_2Sn$:, (R_2Sn:)] is irradiated with UV light at room temperature, the ESR spectrum of the persistent radical $R_3Sn^\bullet$ can be observed; it may be speculated that the reaction involves the intermediates $R^\bullet$ and $RSn^\bullet$, followed by addition of $R^\bullet$ to R_2Sn:, but no evidence could be found for the addition of other radicals to R_2Sn:.[35, 36] Similarly, photolysis of $[(2\text{-}Bu^t\text{-}4,5,6\text{-}Me_3C_6H)_2Sn]_2$ gives the radical $(2\text{-}Bu^t\text{-}4,5,6\text{-}Me_3C_6H)_3Sn^\bullet$ in which both ^{13}C and $^{117/119}Sn$ hyperfine coupling could be observed; again, the fate of the presumed $RSn^\bullet$ fragment is not known.[37]

An exception to this rule of cleavage of the SnC bond is provided by trimethyl(diethylamino)tin, Me_3SnNEt_2, which on irradiation gives $Me_3SnSnMe_3$, Et_2NH and MeCH=NEt via the $Me_3Sn^\bullet$ and $^\bullet NEt_2$ radicals. The CIDNP effect which is observed in the ^1H NMR spectra of the products is consistent with homolytic Sn-N cleavage in the singlet excited state.[38] Similarly, irradiation of trimethyltin iodide in hexane at 254 nm gives $Me_3SnSnMe_3$ and I_2 via the $Me_3Sn^\bullet$ and $I^\bullet$ radicals.[39]

From SnCo

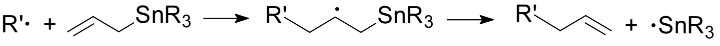
A promising source of stannyl radicals for use in organic synthesis is provided by the stannylcobaloximes. The Sn-Co bond is cleaved on photolysis, and the $R_3Sn^\bullet$ radical which is formed then reacts in the conventional manner; alkyl bromides carrying suitably placed double or triple bonds can undergo intramolecular cycloaddition of the resulting alkyl radicals, termination being by abstraction of a hydrogen atom from the solvent or by loss of a hydrogen atom to the $[Co^{II}]$.[40, 41]



Scheme 20-2 Generation of stannyl radicals from stannylcobaloximes.

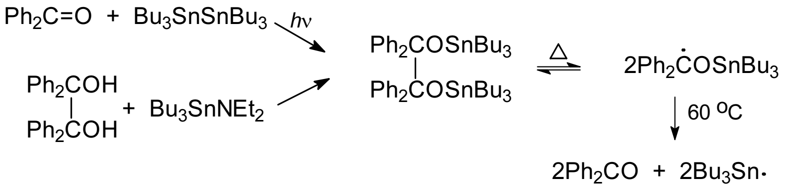
By β-Scission

Both allyl- and cyclopentadienyl-stannanes will undergo S_H2' (S_H2-γ) reactions to generate a stannyl radical.[42, 43] The intermediate adduct radical is stabilised by the presence of the β-stannyl substituent (see below). These reactions find application in organic synthesis and are discussed in Section 9.1.3.3.


(20-12)

A number of other β-stannylalkyl radicals have been used as sources of stannyl radicals. Thus isobutyltrimethyltin can be used as a photolytic source of trimethylstannyl radicals (equation 20-13),[44] and bis(*O*-trialkylstannyl) derivatives of benzpinacol can be used as a thermal source (equation 20-14).[42, 45–47]

$$\mathrm{Me_2CHCH_2SnMe_3} \xrightarrow{\mathrm{Bu^tO\cdot}} \mathrm{Me_2\dot{C}CH_2SnMe_3} \longrightarrow \mathrm{Me_2C{=}CH_2} + \cdot\mathrm{SnMe_3} \tag{20-13}$$

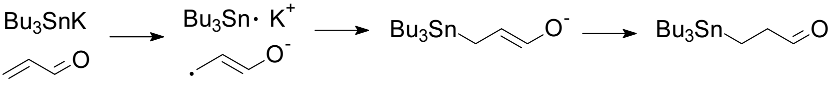

(20-14)

From R_3Sn^-

The UV spectra of the radicals $R_3Sn^\bullet$ have been observed in the non-chain reaction of Bu_3SnK with s- and t-butyl bromides.[48] A CIDNP effect in the ^{119}Sn NMR spectra of the $Bu_3SnSnBu_3$ and Bu_4Sn which are formed from the reaction of Bu_3SnK with n-butyl bromide and iodide, similarly confirms the formation of intermediate $R_3Sn^\bullet$ radicals.[49]

$$\begin{matrix}\mathrm{Bu_3SnK}\\ \mathrm{R'X}\end{matrix} \longrightarrow \begin{bmatrix}\mathrm{Bu_3Sn\cdot}\ \mathrm{K^+}\\ \mathrm{R'X^{\cdot-}}\end{bmatrix} \longrightarrow \begin{bmatrix}\mathrm{Bu_3Sn\cdot}\ \mathrm{K^+}\\ \mathrm{R'\cdot}\ \mathrm{X^-}\end{bmatrix} \longrightarrow \begin{matrix}\mathrm{Bu_3SnSnBu_3}\\ \mathrm{Bu_3SnR'}\end{matrix}\ \mathrm{KX} \tag{20-15}$$

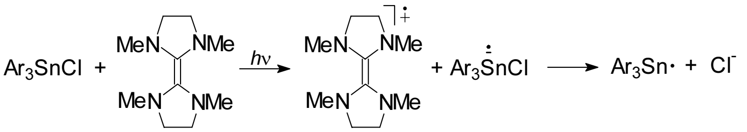
Similarly, galvinoxyl and *p*-dinitrobenzene partially or totally inhibit the addition of Bu_3SnK or Ph_3SnK to enones, again indicating an electron transfer reaction involving radicals.[50]


(20-16)

By Electron Transfer

Many of the reactions described above include a step of electron transfer. The formation of R_3SnM or R_3SnSnR_3 from the reaction between R_3SnX and an alkali metal probably also involves electron transfer to give $R_3SnX^{\bullet-}$, which then dissociates, and the ESR spectrum of the $Me_3Sn^\bullet$ radical in a sodium matrix has been observed at 77 K from the reaction between sodium atoms and Me_3SnCl in a rotating cryostat.[51]

Photoassisted electron transfer can be induced between a triaryltin chloride and an electron-rich olefin to give the organotin radical anion and then the neutral stannyl radical (equation 20-17).[46]



(20-17)

20.1.2 ESR Spectra[5]

The signals in the ESR spectra of stannyl radicals are usually rather broad compared with those of alkyl radicals, and are best observed at high microwave power, when the spectra of any interfering carbon-centred radicals can be saturated. Hyperfine coupling to neighbouring protons on alkyl groups can usually be resolved, but not that in attached aryl groups (though this should be possible by ENDOR spectroscopy); thus the radicals $Ph_nMe_{3-n}Sn^\bullet$ show coupling to only the methyl protons.[8] The resolution is often better at low temperature, and the dependence of the coupling constants on temperature is usually small. In strong spectra, hyperfine coupling to ^{117}Sn and ^{119}Sn can be detected. From the ^{119}Sn CIDNP spectra of the $Me_3SnSnMe_3$ which is formed when hydrogen is abstracted from Me_3SnH, it is concluded that in $Me_3Sn^\bullet$ the sign of $a(^{117}Sn)$ and $a(^{119}Sn)$ is negative and that of $a(^1H)$ is positive.[52]

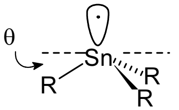
A comprehensive list (21) of spectra which had been observed up to 1985 is given in Landolt-Börnstein and these should be updated in the forthcoming new edition. A selection is given in Table 20-1.

Table 20-1 ESR Spectra of stannyl radicals.

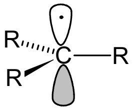
Radical	T(K)	a(H)/mT	a(Sn)/mT	g	Ref.
$Me_3Sn^\bullet$	193	0.31 (9H)	161.1	2.0163	19
$Et_3Sn^\bullet$	198	ΔH ca. 1[a]	155	2.015	8
$Pr_3Sn^\bullet$	193	0.30 (6H)		2.0160	8
$Bu_3Sn^\bullet$	193	0.30 (6H)	155	2.0158	8
$[(Me_3Si)_2CH]_3Sn^\bullet$	298	0.21 (3H)	177.6	2.0094	35
$Ph_3Sn^\bullet$	223	ΔH 0.23[a]	186.6	2.0023	8
$PhMe_2Sn^\bullet$	198	0.30 (6H)		2.0124	8
$Ph_2MeSn^\bullet$	203	0.20 (3H)		2.0082	8
$(PhMe_2CCH_2)_3Sn^\bullet$	373	0.125 (6H)	138.0	2.0150	53
$(2,4,6\text{-}Me_3C_6H_2)_3Sn^\bullet$	453			2.0073	17
$(2\text{-}Bu^t\text{-}4,5,6\text{-}Me_3C_6H)_3Sn^\bullet$	298	1.8 (^{13}C)	175.6/182.7	2.0012	37
$Me_3SnMe_2Sn^\bullet$	77	0.45 (6H)	117.1 and 25.0		27

[a] δH = peak to peak linewidth.

The high value of the hyperfine coupling to tin implies a large direct interaction of the electron at the nucleus, hence the electron must occupy an orbital with a large s-character. Thus stannyl radicals, (like silyl and germyl radicals), are accepted to involve approximate sp^3 hybridisation of the tin with the unpaired electron in an sp^3 orbital (**20-1**); in contrast, alkyl radicals, unless they carry electronegative substituents, have sp^2 hybridised carbon (**20-2**) with the unpaired electron in a p-orbital. For the $Me_3Sn^\bullet$ radical, the angle θ is calculated to be about 12°.[54]



(20-1)



(20-2)

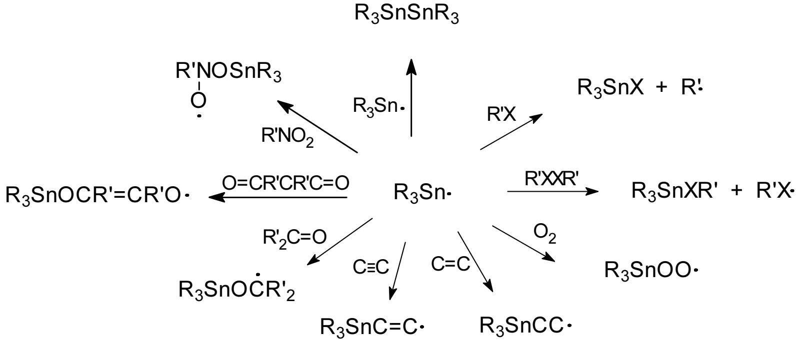
This pyramidal structure of stannyl radicals is supported by the negative temperature dependence of $a(^{119}Sn)$ and by the fact that optically active organotin compounds with the asymmetry centred on the tin can react through the intermediate stannyl radical and show retention of optical activity. Again, the fact that the trineophyltin radical $(PhMe_2CCH_2)_3Sn^\bullet$ shows non-equivalent methylene protons in the ESR spectrum below –20 °C is most readily explained by the fact that the radicals are non-planar at tin.[53]

It is generally accepted that there is a direct relationship between $a(^{119}Sn)$ and the angle θ at the tin centre (though this has been questioned in the context of the corresponding silyl radicals[55]). The introduction of electronegative phenyl groups at the tin centre causes the angle θ to increase, with a corresponding increase in $a(^{119}Sn)$.

Hyperfine coupling to β-CH in radicals $R_3M^\bullet$ (R = alkyl) and to aryl protons in $Ar_3M^\bullet$ is about an order of magnitude less in stannyl radicals than in alkyl radicals [e.g. $a(\beta H)$ $Me_3C^\bullet$ 2.27, $Me_3Si^\bullet$ 0.63, $Me_3Ge^\bullet$ 0.55, $Me_3Sn^\bullet$ 0.31 mT; $a(p\text{-H})$ $Ph_3C^\bullet$ 0.56, $Ph_3Si^\bullet$ 0.12, $Ph_3Ge^\bullet$ 0.09, $Ph_3Sn^\bullet \leq 0.05$ mT]. Further, the value of a(Me) in the radicals $Me_3Sn^\bullet$, $PhMe_2Sn^\bullet$, and $Ph_2MeSn^\bullet$, stays constant, whereas in the carbon-centred radicals $Me_3C^\bullet$, $PhMe_2C^\bullet$, and $Ph_2MeC^\bullet$ the values of a(Me) are 2.27, 1.62, and 1.56 mT, respectively. It follows that the unpaired electron is centred largely on the tin atom, and there is no substantial delocalisation into the alkyl or aryl ligands.[8]

20.1.3 Reactions

The triorganotin radicals are very reactive species, and their principal elementary reactions are summarised in Scheme 20-3. In organic syntheses these elementary reactions often occur as one component in competition or in sequence with a number of other steps, and the absolute or relative rate constants of many of these reactions have been determined to aid in the design of these syntheses.



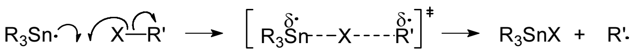
Scheme 20-3 Reactions of stannyl radicals.

As mentioned in Section 15.3.5, the sequence of reactivity of the various functional groups X towards the $Bu_3Sn^\bullet$ radical is Br > PhSe > Cl > $p\text{-NCC}_6H_4S$ > PhS > $p\text{-MeC}_6H_4S$ > MeS.[56]

Simple organotin radicals self-react at rates close to diffusion control to give the corresponding distannanes; representative rate constants at 298 K are $Me_3Sn^\bullet$ 2.8×10^9, $Bu_3Sn^\bullet$ 1.4×10^9, and $Ph_3Sn^\bullet$ 2.8×10^9 M^{-1} s^{-1}.[19, 57] The presence of bulky ligands can slow the reaction [e.g. $(PhMe_2CCH_2)_3Sn^\bullet$, 2.98×10^7 M^{-1} s^{-1}];[53] triphenylstannyl radicals carrying *ortho* substituents can be long-lived, and the decay to the distannanes is thermally reversible (Sections 18.2.3 and 20.1.1).

Substitution Reactions

The accidental observation in 1957 that allyl halides reacted with tin hydrides not by addition across the double bond, but by replacement of the halogen by hydrogen, provided the basis for the extensive use which the tin hydrides (Section 15.3.5), distannanes (Section 18.2.3), allylstannanes (Section 9.1.3.3), and related compounds now find in organic synthesis. The reaction involves bimolecular homolytic substitution (S_H2) at the halogen centre, and a*b initio* calculations indicate that, when R = H, R′ = Me, and X = Cl, Br, or I, the transition state is colinear, as illustrated in equation 20-18.[58]



(20-18)

Absolute rate constants were first measured by the rotating sector ESR technique[59, 60] and supplemented by competition experiments to give further relative values;[56, 61–63] for example, for the $Bu_3Sn^{\bullet}$ radical at 298 K, $k(CH_2{=}CHCH_2Br)/k(BuBr) = 30.5$. n-Octyl bromide and 4-t-butylbromobenzene are commonly used as standards.

The absolute rate constants have been refined by time-resolved laser flash photolysis in which the change in concentration of the stannyl radical, or a reaction product, or an added probe is monitored by UV/vis spectroscopy.[60] Rate constants for the reactions covering the literature up to 1981 are listed in Landoldt-Börnstein (1983, **II13c**, pp 323-336). A selection of current values is given in Table 20-2.

Table 20-2 Rate constants for the S_H2 reaction of stannyl radicals with substrates R′X in non-polar solvents at 298 K.

$R_3Sn^{\bullet}$	R′	X	$k/M^{-1}\ s^{-1}$
$Me_3Sn^{\bullet}$	Me_3C	Cl	5.9×10^3
$Bu_3Sn^{\bullet}$	Me_3C	Cl	2.7×10^4
$Bu_3Sn^{\bullet}$	Me_3C	Br	1.7×10^8
$Bu_2ClSn^{\bullet}$	Me_3C	Cl	3.9×10^3
$Bu_2HSn^{\bullet}$	Me_3C	Cl	4.7×10^3
$Ph_3Sn^{\bullet}$	Me_3C	Cl	2.0×10^4
$Bu_3Sn^{\bullet}$	Me	I	4.3×10^9
$Bu_3Sn^{\bullet}$	Pr	Br	2.6×10^7
$Bu_3Sn^{\bullet}$	C_6H_{11}	Cl	4.9×10^2
$Bu_3Sn^{\bullet}$	C_6H_{11}	Br	2.2×10^7
$Bu_3Sn^{\bullet}$	C_8H_{17}	Br	2.6×10^7
$Bu_3Sn^{\bullet}$	$PhCH_2$	Cl	1.1×10^6
$Bu_3Sn^{\bullet}$	$PhCH_2$	Br	1.5×10^9
$Bu_3Sn^{\bullet}$	PrCH=CPr	Br	1.3×10^{6a}
$Bu_3Sn^{\bullet}$	PhCH=CH	Br	2.7×10^{6a}
$Bu_3Sn^{\bullet}$	$4\text{-}Bu^tC_6H_4$	Br	2.4×10^{6a}
$Bu_3Sn^{\bullet}$	$2,4,6\text{-}Bu^tC_6H_2$	Br	9.5×10^{7a}
$Bu_3Sn^{\bullet}$	F_5C_6	Br	$> 1 \times 10^{8a}$
$Bu_3Sn^{\bullet}$	Me	SMe	$< 10^4$
$Bu_3Sn^{\bullet}$	$BuOCH_2$	SPh	1.0×10^3
$Bu_3Sn^{\bullet}$	Me	SeMe	3.7×10^5
$Bu_3Sn^{\bullet}$	$BuOCH_2$	SePh	6.0×10^6
$Bu_3Sn^{\bullet}$	Bu^tO	Bu^tO	10^2
$Bu_3Sn^{\bullet}$	Bu^tS	Bu^tS	7.9×10^4

[a] At 353 K.

Curran gives the approximate scale of reactivities towards tributylstannyl radicals that is shown in Table 20.3.[61].

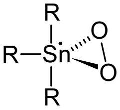
Table 20-3 Approximate range of rate constants for the reactions of tributystannyl radicals.

k/M^{-1} s^{-1}	Substrate
$\geq 10^9$	Alkyl iodides
$10^8 - 10^7$	Alkyl bromides, aryl iodides
$10^6 - 10^5$	Alkyl phenyl selenides, aryl bromides, vinyl bromides, α-chloro esters, α-thiophenyl esters
$10^4 - 10^2$	α-Chloro and α-thiophenyl ethers, alkyl chlorides, alkyl phenyl sulfides

For any given halide R′X, as R′ is varied, the activation energies of the reaction correlate with the R′-X bond dissociation energies.[63] Within the limited series of stannyl radicals $R_3Sn^•$ which have been studied, as R varies, the range of the rate constants in the reaction with a particular substrate is within a factor of 5. The reactivity increases in the sequence X = Cl < Br < I [and there appears to be no example (yet) of the reaction when X = F], and R′ = benzyl ≈ allyl ≈ t-alkyl > s-alkyl > p-alkyl > vinyl or aryl, reflecting the relative stabilities of the radicals $R'^•$, though polar effects on the transition state also appear to be important.[64, 65] The enhancement of the reactivity of bromobenzenes with large *ortho* substituents is ascribed to the relief of steric strain.[62, 63]

Sulfides, selenides, and tellurides, though not ethers, react similarly.[56, 66–68] Peroxides and disulfides, RYYR, similarly undergo S_H2 reaction at the heteroatom with cleavage of YY, and disulfides are more reactive than peroxides.

The triorganotin radicals react rapidly with oxygen [Bu_3Sn, k 7.5(1.4) × 10^9 M^{-1} s^{-1} at 295 K], and the autoxidation of tin hydrides and distannanes to distannoxanes will involve this step. ESR Studies of the radicals $R_3MOO^•$ (M = Si, Ge, or Sn) labelled with the ^{17}O isotope show that, when M = Si or Ge, the two oxygen atoms are non-equivalent, but when X = Sn they are apparently equivalent [$Bu_3SnOO^•$, $a(^{17}O)$ 2.5 mT, g 2.0265], implying a (perhaps time-averaged) structure such as **20-3**.[69, 70]



(20-3)

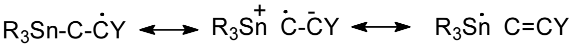
Addition Reactions

Some rate constants for addition reactions of $Bu_3Sn^•$ radicals are collected in Table 20-4.

Table 20-4 Rate constants for addition reactions of $Bu_3Sn^•$ radicals.[60]

Substrate	k/M^{-1} s^{-1}	Substrate	k/M^{-1} s^{-1}
CH_2=CHPh	9.9×10^7	benzene	$< 2 \times 10^4$
CH_2=CHCN	8.8×10^7	cyclohexanone	$< 5 \times 10^4$
CH_2=CMeCO_2Me	1.2×10^8	fluorenone	3.8×10^8
CH_2=CHCH=CHMe	6.8×10^7	PhCOCOPh	1.3×10^8
β-pinene	$< 2 \times 10^5$	duroquinone	1.4×10^9

Addition to alkenes is reversible, and is accelerated by substituents Y which can stabilise the β-stannylalkyl adduct radical **20-4** by resonance, or the negative charge which the radical carries in the canonical form **20-5** in the transition state. The β-stannylalkyl adduct radicals $R_3SnCC^{\bullet}Y$ can be observed by ESR spectroscopy (e.g. equation 20-20),[71] and are discussed below.



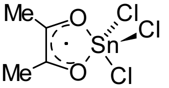
$$R_3Sn\text{-}C\text{-}\dot{C}Y \longleftrightarrow R_3\overset{+}{\dot{S}n}\ \dot{C}\text{-}\overset{-}{C}Y \longleftrightarrow R_3\dot{S}n\ C{=}CY \qquad (20\text{-}19)$$

(20-4) **(20-5)**

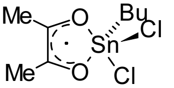
$$Bu_3Sn\cdot + CH_2{=}CH_2 \xrightarrow{183\ K} Bu_3SnCH_2CH_2\cdot \qquad (20\text{-}20)$$

$a(2H\alpha)$ 1.96 mT, $a(2H\beta)$ 1.60 mT

The adducts $R_3SnOCR_2^{\bullet}$ which are formed reversibly with ketones can similarly be observed by ESR spectroscopy,[72, 73] and the reactivity falls in the sequence $R_3Si^{\bullet} > R_3Ge^{\bullet} \approx R_3Sn^{\bullet} > R_3Pb^{\bullet}$. 1,2-Diones and *ortho*-quinones are particularly reactive,[74] and the ESR spectra show that the structures of the adducts depend on the electronegativity of the ligands on the tin. For example, in the reactions of the radicals $R_nCl_{3-n}Sn^{\bullet}$ with biacetyl, the adducts **20-6**–**20-10** have been identified. When n = 0 or 1, the adducts are believed to have the structures **20-6** and **20-7** respectively; these are static on the ESR timescale at low temperature, but at room temperature the ligands are in positional exchange. When n = 2, the adduct has the static structure **20-8**, but, when n = 3, two adducts can be observed, the *cis* adduct (**20-9**) being rapidly fluxional, and the *trans* adduct (**20-10**) being slowly fluxional.[71] The further possibility of an ion pair structure has been proposed for the radicals that are formed by the aerobic oxidation of the monotriphenyltin derivatives of catechols.[75]



(20-6)



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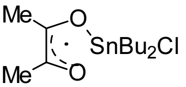

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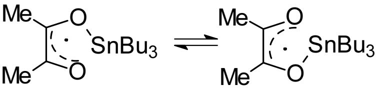

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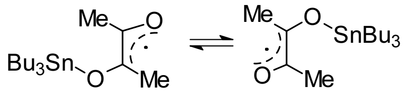
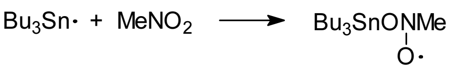


(20-10)

Hexaphenyldistannane reacts with 9,10-phenanthraquinone (OPQO) to give first the expected monoradical $Ph_3SnOPQO^{\bullet}$ which decomposes on standing to give the crystalline diradical $Ph_2Sn(OPQO^{\bullet})_2$, which has a distorted octahedral structure in which each semiquinone unit is unsymmetrically bonded to the tin, with rSnO ca. 213 and 221 pm.[76]

Stannyl radicals react with nitroalkanes or nitroarenes to give the persistent radicals $R'N(O^{\bullet})OSnR_3$ which show a high hyperfine coupling to nitrogen[77] (e.g. equation 20-21).[32] When R′ is prim- or sec-alkyl, or benzyl or allyl, the hydrocarbon R′H is formed, presumably by β-scission to give R_3SnONO and the $R'^{\bullet}$ radical, which extracts hydrogen from the tin hydride.[78, 79]



$$Bu_3Sn\cdot + MeNO_2 \longrightarrow Bu_3SnO\underset{\displaystyle O\cdot}{\underset{|}{N}}Me \qquad (20\text{-}21)$$

a(N) 2.85 mT
a(3H) 1.02 mT
a(Sn) 0.36 mT

20.2 Stannylalkyl Radicals $R_3SnC_n^{\bullet}$

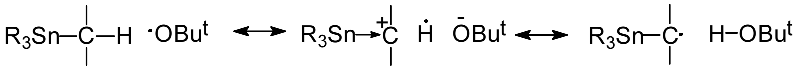
Stannylalkyl radicals $R_3SnC_n^{\bullet}$ are formed when a radical abstracts hydrogen from an alkyltin compound. The reactivity is enhanced at the α- and β-methylene groups (equation 20-22), and approximate rate constants are given in Table 20-5.

$$R_3Sn\overset{\alpha}{C}H_2\overset{\beta}{C}H_2R' \xrightarrow[-Bu^tOH]{Bu^tO\cdot} R_3Sn\dot{C}HCH_2R' + R_3SnCH_2\dot{C}HR' \qquad (20\text{-}22)$$

Table 20-5 Approximate rate constants ($M^{-1}\ s^{-1}$ at 313 K) for the reaction 20-22.

$R_3MCH_2CH_2R'$	α-Reactivity	β-Reactivity
$R_3CCH_2CH_2R'$	7×10^3	6.1×10^3
$R_3SnCH_2CH_2R'$	1.7×10^5	3×10^4

The high α-reactivity probably results principally from stabilisation of the canonical form **20-11** in the transition state by the electron release from the tin, and the β-reactivity from stabilisation of the resulting β-stannylalkyl radical by hyperconjugation (Section 3.1).



$$R_3Sn-\overset{|}{\underset{|}{C}}-H\ \ {}^{\bullet}OBu^t \longleftrightarrow R_3Sn\rightarrow\overset{+|}{\underset{|}{C}}\ \ \dot{H}\ \ \bar{O}Bu^t \longleftrightarrow R_3Sn-\overset{|}{\underset{|}{C}}\cdot\ \ H-OBu^t$$

(**20-11**)

β-Stannylalkyl radicals, $R_3SnCC^{\bullet}$, are also formed by the addition of a stannyl radical to an alkene, or of any radical to an allylstannane.

$$R_3Sn\cdot + C{=}C \longrightarrow R_3SnCC\cdot \qquad (20\text{-}23)$$

$$X\cdot + C{=}CCSnR_3 \longrightarrow XC\dot{C}CSnR_3 \qquad (20\text{-}24)$$

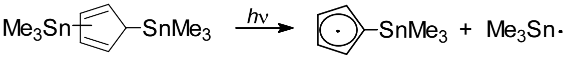
The ESR parameters for the radicals $Me_3MCH_2CH_2^{\bullet}$ are given in Table 20-6.[80]

Table 20-6 ESR parameters for the radicals $Me_3MCH_2CH_2^{\bullet}$ at ca. –100 °C.

Radical	T/°C	a(2Hα)/mT	a(2Hβ)/mT	g
$Me_3CCH_2CH_2^{\bullet}$	–105	2.206	2.471	2.00268
$Me_3SiCH_2CH_2^{\bullet}$	–112	2.105	1.768	2.00265
$Me_3GeCH_2CH_2^{\bullet}$	–100	2.070	1.657	2.00255
$Me_3SnCH_2CH_2^{\bullet}$	–101	1.969	1.584	2.00205

Hyperfine coupling to Hβ is related to the dihedral angle θ between the Cβ-H bond and the axis of the singly-occupied 2*p* orbital as described by the Heller-McConnell equation (equation 3-28). The radicals $R_3MCH_2CH_2^{\bullet}$ show a lower value of a(2Hβ) when M is silicon, germanium, or tin than when M = carbon. This implies that when M = Si, Ge, or Sn the radical is most stable in the conformation **3-8** in which the Cβ-M bond eclipses the axis of the 2*p* orbital.[80–82] This is believed to result from both C-Sn (*p*-σ) hyperconjugation and (*p*-*d*) homoconjugation, and from the positive temperature coefficient of a(2Hβ) this is estimated to result in a stabilisation of about 8 kJ mol^{-1}, accounting for the ease of formation of these β-stannylalkyl radicals (Section 3.1.2).

Stannylcyclopentadienyl radicals can be generated by photolysis of bis(stannyl)cyclopentadienes (equation 20-25), and are interesting because the ESR spectra provide information about the interaction of the stannyl substituent with the cyclopentadienyl π-electron system.[31, 33, 34, 71]



(20-25)

The degeneracy of the ψ_A and ψ_S molecular orbitals in the cyclopentadienyl radical can be broken by the electronic effect of the substituent. The ψ_A orbital has a node at C1, and is unaffected, but the ψ_S orbital, with a high coefficient at C1, has its energy raised by an electon-releasing substituent, and lowered by an electron-attracting substituent, placing the unpaired electron preferentially in the ψ_S or ψ_A orbital, respectively, as shown in Figure 20-1.

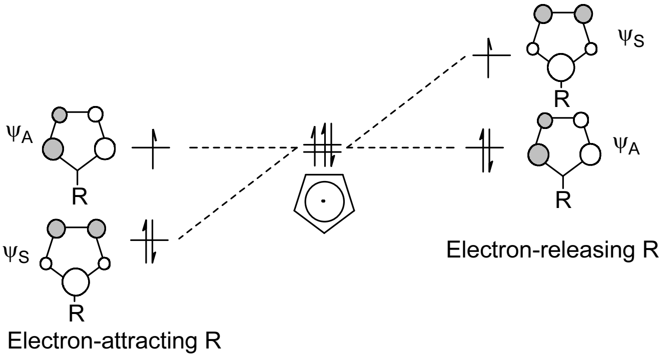


Figure 20-1 The effect of substituents on orbital energy levels.

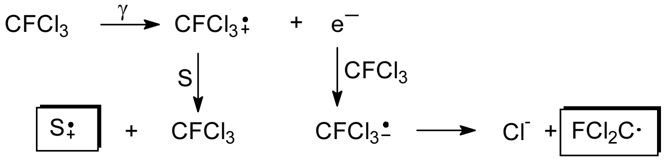
As the hyperfine coupling to hydrogen attached to a carbon atom of the ring is proportional to the unpaired electron density on that carbon atom, the spectra can be interpreted in terms of the relative contribution of ψ_S and ψ_A to the SOMO, and the energy separation between ψ_S and ψ_A. This leads to the conclusion that, in this context, the Me_3Sn substituent is electron-attracting. The Me_3Si group is more strongly electron-attracting, the Me_3C group is strongly electron-releasing, and the Me_3Ge group is very weakly electron-releasing.[34]

20.3 Radical Cations $R_nSnX_{4-n}^{\bullet+}$

Chemical reactions of alkyltin compounds which occur by way of radical cations are described in Section 5.3.7. The radical cations themselves have been examined in frozen matrices mainly by the technique of ESR spectroscopy, and in the gas phase by mass spectrometry.

A standard technique for generating radical cations $S^{\bullet+}$ is to irradiate with γ-rays a dilute frozen solution of the substrate S in a Freon such as $CFCl_3$. An electron is ejected from the solvent to give the radical cation $CFCl_3^{\bullet+}$ which reacts with the substrate S to give $S^{\bullet+}$; the ejected electron goes on to give the $FCl_2C^{\bullet}$ radical which has such a broad spectrum that only that of $S^{\bullet+}$ is observed.

The results with organotin compounds (Table 20-7) can be discussed using SnH_4 as a model.[83-85]



Scheme 20-4 Generation of radical cations by irradiation of Freon matrices.

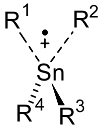
Table 20-7 ESR parameters for organotin radical cations in $CFCl_3$.

Radical cation	Structure	Nucleus	$A_\perp$/mT	$A_\parallel$/mT	Ref.
$SnH_4^{\bullet+}$	C_{2v}	^{119}Sn	–237	–310	83
		2H	8.5	8.5	
$SnH_4^{\bullet+}$	C_{3v}	^{119}Sn	–318	–365	83
		1H	17.5	17.5	
$MeSnH_3^{\bullet+}$	C_{2v}	^{119}Sn	–238	–315	83
		2H	8.5	8.5	
$Me_2SnH_2^{\bullet+}$	C_{2v}	^{119}Sn	–238	–322	83
		2H	8.5	8.5	
$Me_2SnH_2^{\bullet+}$	C_{3v}	^{119}Sn	–119	–270	83
		1H	6.8	6.8	
$Me_3SnH^{\bullet+}$	C_{2v} or C_{3v}	^{119}Sn	–167	–242	83
$Me_4Sn^{\bullet+}$	C_{3v}	^{119}Sn	–7.8	–21	83
		3H	–1.35	–1.35	
$Me_4Sn^{\bullet+}$ [a]	C_{2v}	^{119}Sn	–13.3	–15.0	85
		6H	–1.32	–1.32	
$Me_3SnCMe_3^{\bullet+}$	C_{3v}	^{119}Sn	8.8		84
		9H	0.76		
$Me_3SnSnMe_3^{\bullet+}$		^{119}Sn	11.5		83
$Me_3SnSnMe_3^{\bullet+}$		18H	0.34		84
		^{119}Sn	10.0		
$Me_3SnSnMe_3^{\bullet+}$ [a]		3H	–0.8		85

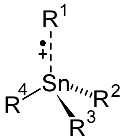
[a] In $SnCl_4$.

Irradiation of SnH_4 in $CFCl_3$ shows two spectra. In the first, the unpaired electron is strongly coupled to two hydrogen atoms, and in the second, to only one. The first species transforms into the second on storage at 77 K or on annealing. The first is ascribed the C_{2v} structure **20-12** in which the electron deficiency is shared between two SnH bonds (SnR^1 and SnR^2), and the second is ascribed the C_{3v} structure **20-13** where the electron deficiency is localised in one SnH bond (SnR^1).[83] In the methyltin hydrides, the unpaired electron occupies the SnH rather than the SnMe bonds with the C_{2v} or C_{3v} configurations as shown in the Table.

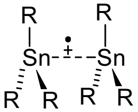
In Me_4Sn the C_{3v} structure **20-13** is adopted in a $CFCl_3$ matrix and the low hyperfine coupling to tin implies that the Me_3Sn base is near-planar;[83] calculations by the MNDO[86] and PM3[87] methods agree with this result. In an $SnCl_4$ matrix, however, the C_{2v} structure appears to be adopted, and in the compounds Me_4M the spin density moves towards two methyl groups in the series Si < Ge < Sn, and intramolecular exchange between the methyl groups becomes more difficult.[85] The radical cation $Me_3SnCMe_3^{\bullet+}$ in $CFCl_3$ adopts a similar C_{3v} structure with the unpaired electron localised in the Sn-CMe_3 bond, with hyperfine coupling to the 9 equivalent protons, and at higher temperatures, dissociation occurs to give Me_3Sn^+ and $Me_3C^\bullet$, reflecting the relative stabilities of the $Me^\bullet$ and $Me_3C^\bullet$ radicals.[83, 84] Me_3SnEt And Me_3SnPr^i showed only the spectrum of the $Et^\bullet$ and $Pr^{i\bullet}$ radicals, respectively, even at 77 K.



(20-12)



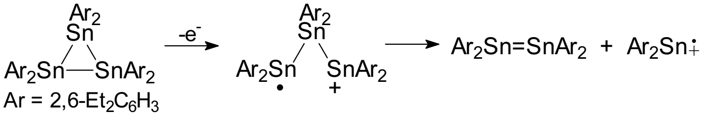
(20-13)



(20-14)

With $Me_3SnSnMe_3^{\bullet+}$ in $CFCl_3$, the coupling by 18 equivalent protons and the low coupling to tin implies that the electron vacancy is localised in the Sn-Sn bond between near-planar Me_3Sn groups as shown in **20-14**.[83]

Simultaneous electrolysis and ESR observation of the cyclotristannane **20-15** showed the presence of two spectra which were assigned to the distonic radical cation **20-16**, with *g* 2.020, $a(^{117/119}Sn)$ 11.2 and 39.4 mT and, more tentatively, to the stannylene radical cation **20-17** with *g* 2.022, $a(^{117/119}Sn)$ 25.0 mT.[88]



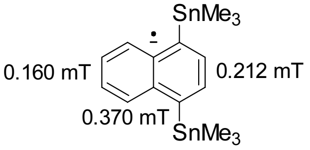
(20-15) **(20-16)** **(20-17)**

(20-26)

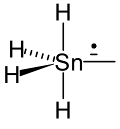
20.4 Radical Anions $R_nSnX_{4-n}^{\bullet-}$ and $R_2Sn^{\bullet-}$

In principle, the electronic effect of an SnR_3 substituent on the π-electron system of a benzene ring can be determined from the ESR spectrum of the radical ion $PhSnR_3^{\bullet+}$ or $PhSnR_3^{\bullet-}$, as outlined above for the radical $C_5H_4SnR_3^{\bullet}$, but there are experimental difficulties. The acidic conditions under which the radical cations are generated in solution lead to protodestannylation of the benzene ring and condensation to biphenyl, and the basic conditions under which the radical anions are prepared lead to exchange between the phenyl and alkyl groups about tin. The radical anion can be generated by γ-irradiation of a solution in a frozen matrix such as Me_4Si, but the resolution is then too poor.

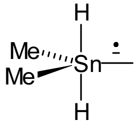
There has been an incomplete report of the ESR spectrum of $PhSnMe_3^{\bullet-}$ with a(2H-*ortho*) 0.40 mT and a(H-*para*) 0.82 mT, suggesting that the ψ_S MO is stabilised and that the Me_3Sn substituent is electron-attracting.[89] The spectrum of the radical anion of 1,4-bis(trimethylstannyl)naphthalene (**20-18**) has also been obtained by treating the substrate with potassium in DME,[90] but this is not so informative as naphthalene is not orbitally degenerate, and the spin distribution is not so sensitive to substituent effects.



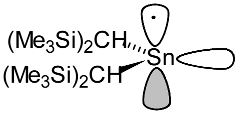
(20-18)



(20-19)



(20-20)



(20-21)

Organotin radical anions which have been observed in solid matrices are listed in Table 20-8.

Table 20-8 ESR spectra of organotin radical anions at 77 K.

Radical anion	Matrix	Nucleus	$A_{\perp}$/mT	$A_{\parallel}$/mT	Ref.
$SnH_4^{\bullet-}$	Me_4C	$2H_{ax}$	14.35	14.35	91
		$2H_{eq}$	0.80	0.80	
		^{119}Sn	–222.72	–222.72	
$SnH_4^{\bullet-}$	$SiMe_4$	$2H_{ax}$	13.8	13.7	92
		$2H_{eq}$	0.77	0.77	
$MeSnH_3^{\bullet-}$	$SiMe_4$	$2H_{ax}$	13.2	13.1	92
		$2H_{eq}$	8.0	8.0	
$Me_2SnH_2^{\bullet-}$		$2H_{ax}$	12.7	12.6	92
$Me_3SnH^{\bullet-}$		$1H_{ax}$	14.0	13.9	92
$Me_4Sn^{\bullet-}$	Self	^{119}Sn	167.2	210.1	93

Again, SnH_4 provides a model for discussing the organotin compounds. The spectrum of $SnH_4^{\bullet-}$ shows two strongly-coupled and two weakly-coupled hydrogen atoms, which are thought to be, respectively, the axial and equatorial atoms in a trigonal bipyramidal structure in which the electron acts as an equatorial “phantom ligand” (**20-19**). The methyltin compounds Me_nSnH_{4-n}, $n = 1-4$, then have a similar structure (e.g. **20-20**), with the hydrogen preferentially occupying the axial positions.

Only two tin(II) radical anions appear to have been reported. $[(Me_3Si)_2CH]_2Sn^{\bullet-}$ Has been obtained by treating the corresponding stannylene with sodium in THF at –80 °C for 5–10 seconds. Its ESR spectrum shows a single broad line (ΔH_{pp} 0.7 mT) with tin satellites, $a(^{117/119}Sn)$ 11.6 mT.[94] This low hyperfine coupling to tin suggests that this is a π-radical with the unpaired electron in a 5*p* orbital with a node at the nucleus, as shown in **20-21**. A similar radical anion, $Ar_2Sn^{\bullet-}$ (Ar = 2,6-diethylphenyl), with *g* 2.015 and $a(^{117/119}Sn)$ 15.1 mT, can be observed by reducing the tristannane $(Ar_2Sn)_3$ either with lithium, or electrochemically.[88]

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21 Stannylenes, Distannenes, and Stannenes

The organic stannylenes are derivatives of tin(II), R_2Sn**:** and RXSn**:**, and two different types exist. The first is the simple σ-bonded alkyl or aryl derivatives, equivalent to the familiar carbenes of organic chemistry; they are both Lewis acids and Lewis bases, and, in the absence of some factor to stabilise them against oligomerisation, they exist only as transient intermediates. If R is a very bulky group or carries an intramolecularly bonding substituent which raises the coordination of the tin from two to three or four, oligomerisation can be prevented and the stannylenes may be stable in solution and, in the solid state, they may exist as the monomers, or as the distannenes, $R_2Sn{=}SnR_2$, or the trimers $(R_2Sn)_3$. The second type of stannylenes comprises the compounds with a cyclopentadienyl ligand; these are not self-reactive, and they range from pentahapto Cp_2Sn**:**, to trihapto or dihapto compounds CpXSn**:** depending on the nature of X.

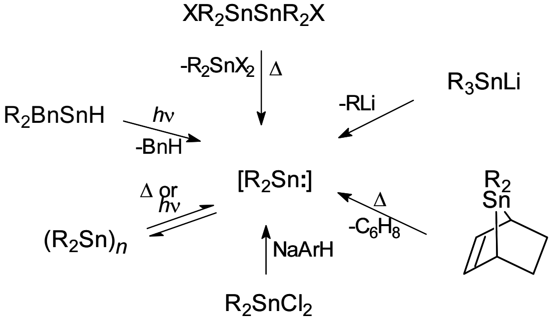
Studies of the organotin(II) compounds have frequently been preceded or accompanied by work on the corresponding silicon(II) and germanium (II) compounds, and a number of reviews (e.g. references[1–4]) illustrate the symbiotic development of these topics.

21.1 σ-Bonded Stannylenes[4–7]

21.1.1 Transient Stannylenes[8]

Stannyl radicals $R_3Sn^\bullet$ can be identified by ESR spectroscopy, but there is no equivalent sensitive and selective technique for observing the transient simple (singlet) stannylenes, R_2Sn**:**. Their formation usually has to be inferred from their reactions, and it is not always unambiguous as to whether monomeric R_2Sn**:** has existed as a kinetically free entity; the same problem of course occurs with the carbenes R_2C**:**.

In contrast to the stannyl radicals, the stannylenes have not yet found wide application in organic synthesis. The principal routes to the simple dialkyl- and diarylstannylenes are shown in Scheme 21-1.



Scheme 21-1 Generation of transient stannylenes.

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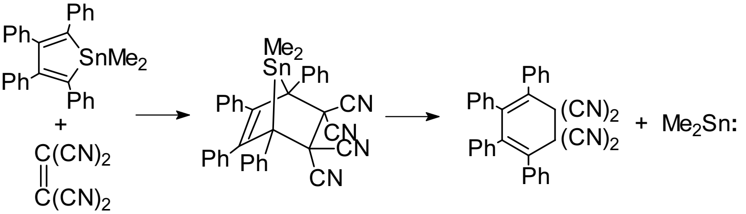
In the older literature, many reports of the isolation of stannylenes are in error, and the compounds which were obtained were actually cyclic or open-chain oligomers (e.g. reference[9]). The most convincing early evidence for the formation of authentic stannylenes comes from experiments in which they were matrix-isolated and identified by IR and Raman spectroscopy. Thermal decomposition of $(Me_2Sn)_6$ or $[(CD_3)_2Sn]_6$, or decomposition of Me_2SnH_2 in argon by a microwave discharge gives dimethylstannylene which can be trapped in an argon matrix at 5–10 K. The IR and Raman spectra show that the molecule has C_{2v} symmetry, with Me-Sn stretching frequencies ν_s 504 and ν_{as} 518 cm^{-1}.[9, 10]

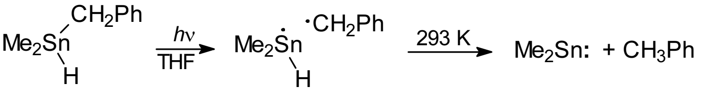
Supporting evidence came from the retrochelotropic decomposition of the 7-stannanorbornene (equation 21-1). The reaction is first order with k 6.8×10^4 s^{-1} at –10 °C, the hexadiene is formed quantitatively, and there was no evidence for free radical intermediates.[11]

These conclusions are reinforced by the subsequent isolation of kinetically stable stannylenes (see below).



(21-1)

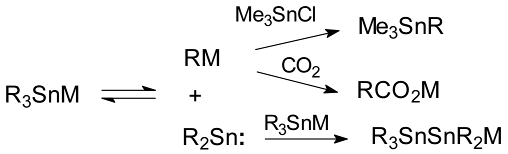
The photolytic decomposition of benzyltin hydrides is a promising source of stannylenes which has not yet been exploited. In THF at 293 K, the benzyl and stannyl radicals which are formed interact to give toluene quantitatively and $(Me_2Sn)_n$, presumably via monomeric Me_2Sn:, but in a THF matrix at 4 K, the radicals recombine to give back the hydride.[9]



$$Me_2Sn(CH_2Ph)H \xrightarrow[THF]{h\nu} Me_2\dot{Sn}H \;\; {}^\bullet CH_2Ph \xrightarrow{293\ K} Me_2Sn: + CH_3Ph \qquad (21\text{-}2)$$

For preparative purposes the cyclooligostannanes $(R_2Sn)_n$ can be used as thermal sources for stannylene transfer, but the free stannylenes are not necessarily involved.[12]

Compounds R_3SnM, where M is an alkali metal, magnesium, zinc, or cadmium, (Sections 19.1, 19.2 and 19.7) often behave as though they are in equilibrium with RM and R_2Sn:, as shown in Scheme 21-2.[13, 14]



Scheme 21-2 Reversible dissociation of R_3SnM.

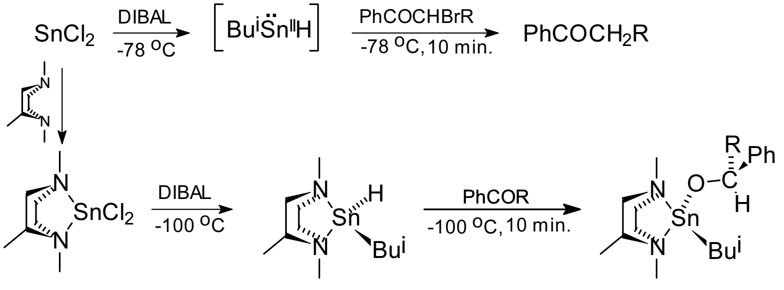
The simple stannylenes such as Me_2Sn:, Bu_2Sn:, and Ph_2Sn: rapidly self-react to give cyclooligostannanes [e.g. $(Ph_2Sn)_6$; see Section 18.4] with a rate constant of ca. 10^8 M^{-1} s^{-1} at room temperature. They insert into certain tin-halide or tin-tin bonds (e.g. equations 21-3 and 21-4) and into the C-halogen bond of more reactive alkyl halides (e.g. equation 21-5).[8] The corresponding elimination reactions, particularly of the thiolates $\mathrm{(PhS)R_2SnSnR_2(SPh)}$, provide a convenient thermal source of stannylenes.[12]

$$\mathrm{Et_2Sn{:} + Me_2SnCl_2 \longrightarrow ClMe_2SnSnEt_2Cl} \tag{21-3}$$

$$\mathrm{(CD_3)_2Sn{:} + BrMe_2SnSnMe_2Br \longrightarrow \begin{array}{c} BrMe_2SnSn(CD_3)_2SnMe_2Br \\ + \qquad\qquad (ca.\ 1{:}2) \\ Br(CD_3)_2SnSnMe_2SnMe_2Br \end{array}} \tag{21-4}$$

$$\mathrm{Me_2Sn{:} + MeI \longrightarrow Me_3SnI} \tag{21-5}$$

A reducing system involving what has been suggested to be a divalent alkyltin hydride is shown in Scheme 21-3. If $\mathrm{SnCl_2}$ is reduced with $\mathrm{Bu^i{}_2AlH}$ at –78 °C, the reagent which is formed will rapidly reduce an α-bromoketone to the corresponding ketone in up to 81% yield. The key intermediate is assumed to be a divalent tin hydride.[15, 16] If the reagent is prepared at –100 °C in the presence of a chiral diamine, it will reduce a prochiral ketone to the corresponding optically active alcohol in up to 78% ee, and the reagent has been suggested to be the chelated $\mathrm{Bu^iSn^{II}H}$. The nature of these reagents, and the mechanism by which they carry out reduction, deserve further attention.[17, 18]



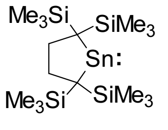
Scheme 21-3 Formation and reactions of $\mathrm{Bu^iSnH}$.

21.1.2 Persistent Stannylenes

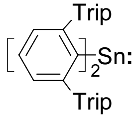
Examples of long-lived stannylenes $\mathrm{R_2Sn{:}}$ or $\mathrm{RXSn{:}}$ that are stabilised by a very bulky group R, and are 2-coordinate, are shown in Scheme 21-4 and those that are stabilised by intramolecular coordination by a Lewis-basic group R, or intermolecular coordination by a ligand X, and are thereby raised to 3- or 4-coordination, are shown in Scheme 21-5 (Mes = mesityl, Trip = 2,4,6-triisopropylphenyl). Most of these compounds have been prepared by the reaction between RLi and $\mathrm{SnX_2}$; exceptions are: **21-2** from $\mathrm{R_2SnCl_2}$ + Li or $\mathrm{KC_8}$, **21-6** from $\mathrm{R_3GeLi}$ + ArSnCl, **21-7** from $\mathrm{NaCrCp(CO)_3}$ + ArSnCl, and **21-15** from **21-14** + DIBAL.

$\mathrm{[(Me_3Si)_2CH]_2Sn{:}}$

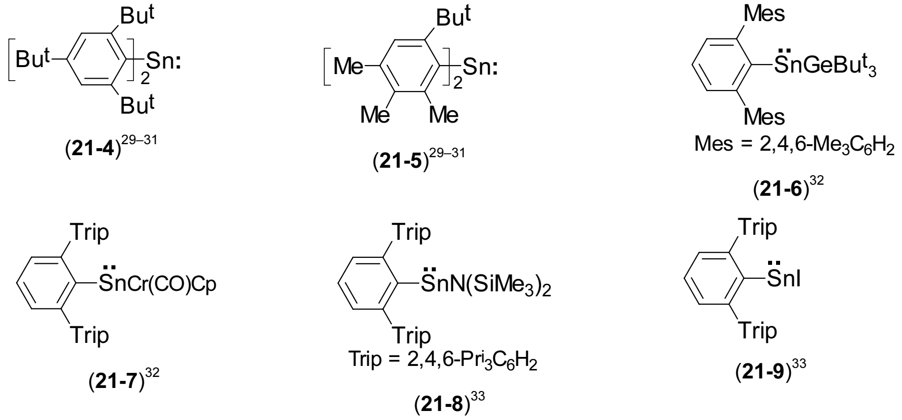
(21-1)[19–24]



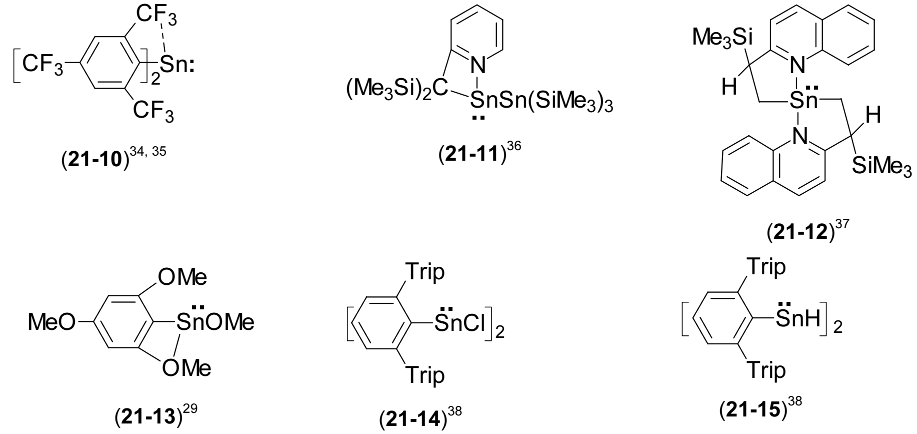
(21-2)[25, 26]



(21-3)[27, 28]

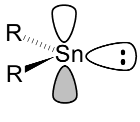


Scheme 21-4 2-Coordinate stannylenes.

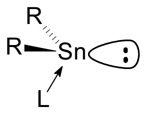


Scheme 21-5 3- And 4-coordinate stannylenes.

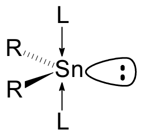
The 2-coordinate stannylenes (Scheme 21-4) can be regarded as being approximately *sp*^{2} hybridised, with a low-lying vacant 5*p* orbital and a stereochemically active lone pair (**21-16**).[23] They are coloured, often red, the absorption being due to an *n*(Sn) → 5*p*(Sn) transition. Compound **21-1** ("Lappert's stannylene") was the first to be characterised and has been studied most thoroughly; in the gas phase it is a V-shaped monomer with *r*CSn 222(2) pm and CSnC 97(2)°; in dilute solution it is a singlet monomer (δSn 2328), in equilibrium with its (distannene) dimer $R_2Sn{=}SnR_2$ (δSn 725 and 740), and it is the dimer that separates from solution.



(**21-16**)



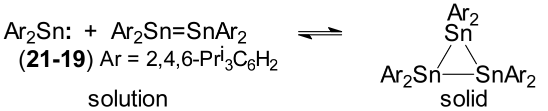
(**21-17**)



(**21-18**)

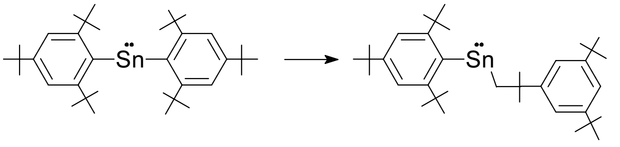
The 3-coordinate stannylenes are notionally sp^3 hybridised and tetrahedral (**21-17**), and the 4-coordinate stannylenes sp^3d hybridised and trigonal bipyramidal (**21-18**), though these ideal structures may be heavily distorted. The 2-coordinated compounds separate from solution as monomers only when the tin is heavily sterically protected (e.g. compounds **21-2**, **21-8**, and **21-9**); in its absence, they solidify as the distannenes (equation 21-6), but bis(2,4,6-triisopropylphenyl)stannylene (**21-19**) separates out, not as the dimer, but as the cyclic trimer which, in solution, is in equilibrium with the stannylene and the distannene.[27]

$$2R_2Sn \rightleftharpoons R_2Sn{=}SnR_2 \qquad (21\text{-}6)$$



(21-7)

Bis(2,4,6-tri-t-butylphenyl)stannylene (**21-4**) is stable in the crystal, but in solution it rearranges to the less-hindered stannylene **21-20**.[31]



(**21-4**) (**21-20**) (21-8)

The 3- and 4-coordinate stannylenes are protected against self reaction, and show the same structures in solution and the solid state. Bis[2,4,6-tris(trifluoromethyl)phenyl] stannylene (**21-10**) is classified here as 3-coordinate because it and related *ortho*-trifluoromethylphenylstannylenes, in the solid state, show a weak interaction between tin and a trifluoromethyl group, and in the crystal the Sn..Sn distance is 364 pm,[34] much longer than that in authentic stannylene dimers (ca. 277–291 pm).

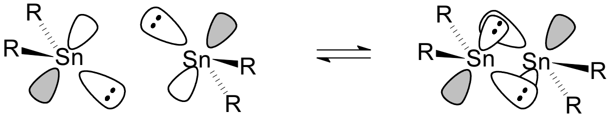
The 2-coordinate stannylenes (Scheme 21-4) are characterised by very large positive values of δ(Sn) ranging normally from 1140 (compound **21-9**) when one of the ligands is electronegative, to 2960 (compound **21-6**) when it is electropositive; there are, however, a few surprising exceptions that are outside this range.

In the 3- or 4-coordinate stannylenes, the increase in the coordination number moves the chemical shift of the tin upfield, and the range in Scheme 21-5 is from 142 (compound **21-12**) to 897 (the Sn^{II}–Sn^{IV} compound **21-11**).

Only a few Mössbauer data have been reported, relating of course to the solid phase,[29] and, ignoring the fact that some of the stannylenes may dimerise on solidification, the isomer shifts lie between 2.76 and 3.37 mm s^{-1}, and are typical for those of tin(II) rather than of tin(IV) compounds which, for the latter, lie in the region of 0.5 to 1.8 mm s^{-1} (Section 2.1.2).

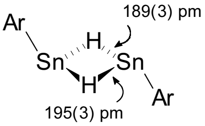
If a solution of $[(Me_3Si)_2CH]_2Sn$**:** (**21-1**) or of $(2\text{-}Bu^t\text{-}4,5,6\text{-}Me_3C_6H)_2Sn$**:** (**21-5**) is irradiated with UV light at room temperature, it shows the ESR spectrum of the long-lived corresponding radical $R_3Sn^{\bullet}$ (Section 20.1.1).[39, 40] Reduction of the stannylene (**21-1**) with sodium in THF gives the radical anion $[(Me_3Si)_2CH]_2Sn^{\bullet-}$ which has been observed by ESR spectroscopy.[41] The radical ions $Ar_2Sn^{\bullet-}$ and $Ar_2Sn^{\bullet+}$ (Ar = 2,6-diethylphenyl) have been prepared by the electrochemical reduction or oxidation of the cyclic trimer $(Ar_2Sn)_3$, and show *g* 2.015, *a*($^{117/119}Sn$) 15.1 mT, and *g* 2.022, *a*($^{117/119}Sn$) 11.2 mT, respectively.[42]

The two most characteristic properties of the stannylenes are their behaviour as Lewis acids and Lewis bases, and their ready oxidative addition to give Sn(IV) compounds. The amphoteric nature provides the model for the structure of the dimers, the distannenes, and for the oligomerisation that occurs with the less hindered examples: two dative bonds are assumed to be formed between the doubly-occupied *sp*^{2} orbital and the vacant *p* orbital, affording a *trans* non-planar distannene (equation 21-9). These structures are discussed in more detail below.



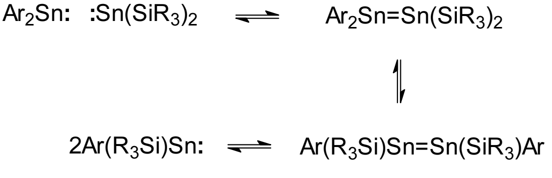
(21-9)

The behaviour as a Lewis acid is illustrated by the structures, and the stability as monomers, of the stannylenes which carry an intramolecular Lewis-basic group (**21-10**–**21-15**) and by the solvent dependence of the NMR spectra of the stannylenes that are not intramolecularly associated. For example, compound **21-10** in C_6D_{12} shows δ(^{119}Sn) 723, but, in ether, it shows δ(^{119}Sn) 661 at room temperature and 530 at −80 °C, due to the formation of a complex.[34] The heavily-hindered hydride **21-15** is blue in solution but dimerises in the solid state, not by Sn−Sn bonding, but by hydrogen bridging, to give the structure **21-21**, and similar dimerisation occurs with the chloride **21-14**.



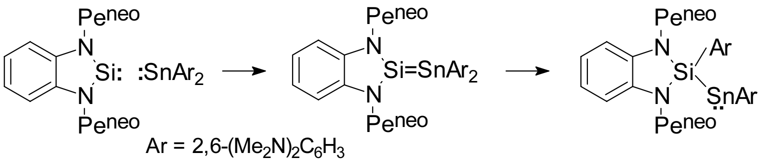
(**21-21**)

When two different stannylenes dimerise, the ligands may exchange to give heteroleptic stannylenes as shown in equation 21-10, where R = $SiMe_3$ and Ar = 2,4,6-$(CF_3)_3C_6H_2$[43] or 2-Bu^t-4,5,6-Me_3C_6H[44]; a similar reaction occurs between stannylenes and plumbylenes.



(21-10)

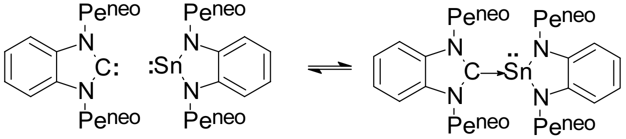
A related migration, now of only one ligand (from tin to silicon), can occur between silylenes and stannylenes, to give a new stannylene, for example:[45]



Ar = 2,6-$(Me_2N)_2C_6H_3$

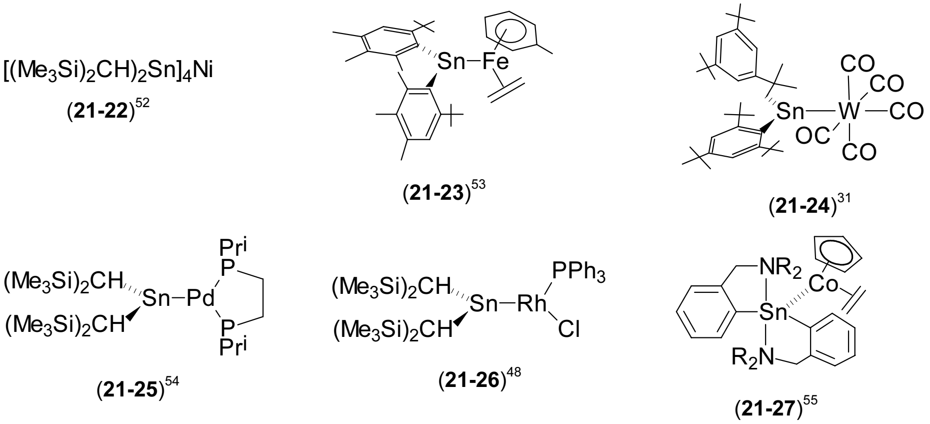
(21-11)

When carbenes react with stannylenes, a long, weak C–Sn bond is formed that appears to have the character of a coordinate bond, and the two components are in equilibrium in solution.[46, 47]



(21-12)

The most characteristic reaction of stannylenes as Lewis bases is their coordination to a variety of transition metals.[48–51] Some examples are given in Scheme 21-6.



$[((Me_3Si)_2CH)_2Sn]_4Ni$

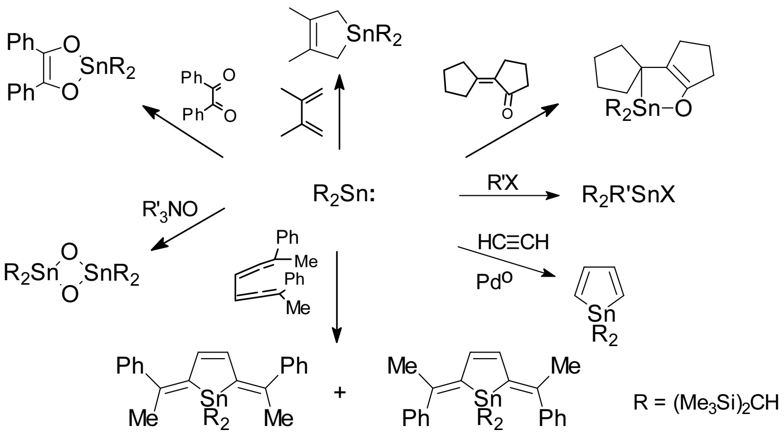
(**21-22**)[52] (**21-23**)[53] (**21-24**)[31] (**21-25**)[54] (**21-26**)[48] (**21-27**)[55]

Scheme 21-6 Stannylenes bonded to a transition metal.

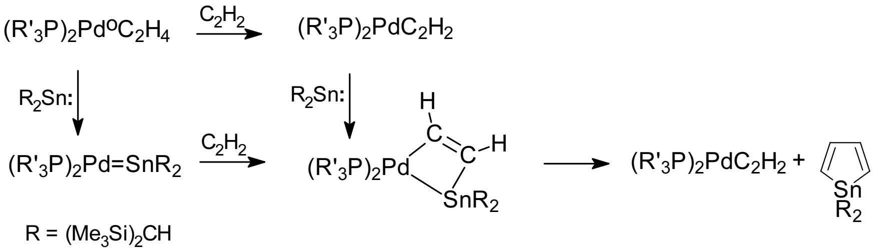
The organostannylenes are yellow to red solids which are sensitive to air and to moisture, and bis[2,4,6-tris(trifluoromethyl)phenyl]stannylene (**21-10**) has been shown to react with triplet oxygen to give the cyclic tristannoxane.[56]

The reactions of di[bis(trimethylsilyl)methyl]stannylene (**21-1**) have been investigated most thoroughly (Scheme 21-7), and appear to be typical of the group. It shows insertion reactions (oxidative addition) with reagents such as HCl, MeI, CCl_4 and halogens, and the reaction with alkyl halides appears to follow a radical chain mechanism. It reacts with O_2 or NO to give the stannoxane $(R_2SnO)_2$, and acts as a ligand to transition metals in complexes such as (**21-22**), (**21-25**), (**21-26**), or $[Cr(CO)_5(SnR_2)]$ (Sections 19.8 and 19.9).[48] It reacts with metallic calcium to give $(R_2Sn)_2Ca$ which, in solution, decomposes to give the radicals $R_3Sn^•$ and $R_3SnCa^•$ which can be observed by ESR spectroscopy.[57] Chelotropic cycloaddition occurs with 1,2-diones, enones, 1,3-dienes, and 1,2,4,5-tetraenes, as shown in Scheme 21-7, and the reactivity decreases in that sequence.[58, 59]

The stannylene and ethyne react in the presence of a diphosphosphinopalladium(0) catalyst to give the stannole $(CHCH)_2SnR_2$; with $(Pr^i_3P)_2Pd$ as the catalyst, the yield is 87% at −30 °C, with a turnover number of 87. The reaction can be carried out with stoichiometric amounts of reactants as shown in Scheme 21-8, and the structures of the intermediate $(R'_3P)_2Pd{=}SnR_2$, and of the stannete $(R'_3P)_2PdC_2H_2SnR_2$, where $(R'_3P)_2 = Pr^i_2PCH_2CH_2PPr^i_2$, have been determined by X-ray crystallography.[54]

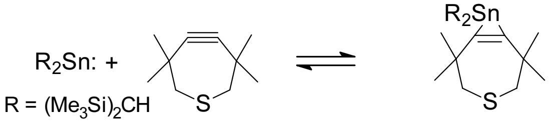


Scheme 21-7 Reactions of $[(Me_3Si)_2CH]_2Sn$:.



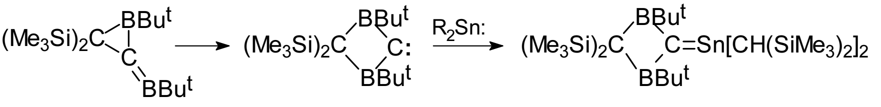
Scheme 21-8 Palladium-catalysed stannole synthesis.

Two remarkable reactions are shown in equations 21-13 and 21-14. The stannylene **21-1** reacts with the cycloalkyne **21-28** to give the adduct **21-29** [δ(^{119}Sn) −536.8] which in solution is in equilibrium with its factors, but can be isolated as a pale yellow solid. It has *r*SnC 213.6(5) and 213.4(5) pm, and *r*C=C 134.0 pm, and its structure is probably best described as a π-complex on the Dewar-Chatt-Duncanson model.[60] The same stannylene reacts with the boranediylborirane **21-30**, which behaves as a pseudo-carbene, to give the stannene **21-31** (see Section 21-2).[46]



(21-13)

(**21-28**) (**21-29**)

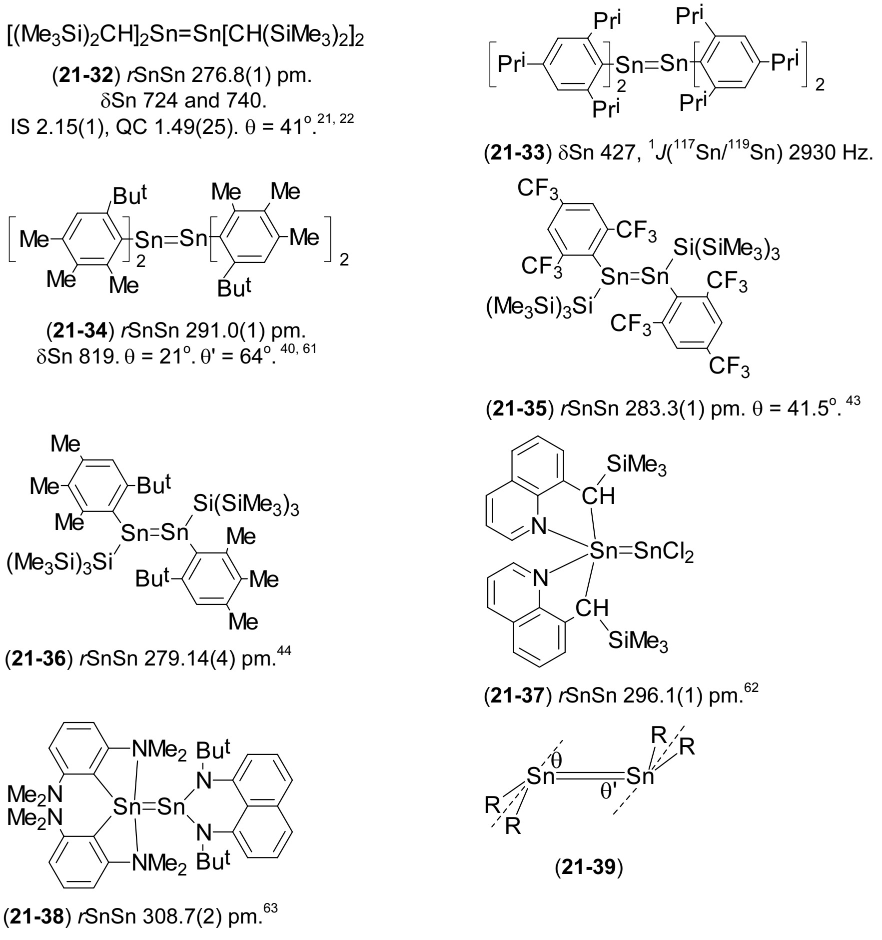


(21-14)

(**21-30**) (**21-31**)

21.2 Distannenes $R_2Sn{=}SnR_2$

With few exceptions, the stannylenes separate from solution as the distannenes $R_2Sn{=}SnR_2$. A selection of the distannenes that have (except **21-33**) been subjected to X-ray crystallography are shown in Scheme 21-9.



$[(Me_3Si)_2CH]_2Sn{=}Sn[CH(SiMe_3)_2]_2$

(**21-32**) rSnSn 276.8(1) pm. δSn 724 and 740. IS 2.15(1), QC 1.49(25). θ = 41°.[21, 22]

(**21-33**) δSn 427, $^1J(^{117}Sn/^{119}Sn)$ 2930 Hz.

(**21-34**) rSnSn 291.0(1) pm. δSn 819. θ = 21°. θ' = 64°.[40, 61]

(**21-35**) rSnSn 283.3(1) pm. θ = 41.5°.[43]

(**21-36**) rSnSn 279.14(4) pm.[44]

(**21-37**) rSnSn 296.1(1) pm.[62]

(**21-38**) rSnSn 308.7(2) pm.[63]

(**21-39**)

Scheme 21-9 Distannenes.

The nature of the bonding in the symmetrical distannenes, with the mutual donation of one pair of electrons of one notionally sp^2 hybridised SnR_2 fragment into the vacant p orbital of the other fragment, is illustrated in equation 21-9.[22, 64–66] On the basis of an Electron Localization Function (ELF) and Atoms in Molecules (AIM) study, it has been suggested that the difference between the $R_2C{=}CR_2$ and $R_2Sn{=}SnR_2$ molecules is that, in the latter, the electrons are less localised and less attracted into the bonding region because of the larger size and lower electronegativity of the tin atoms.[67] The bonding is weak, and the structures are easily distorted.

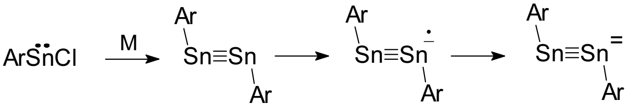
In an unsymmetrical distannene, $R_2Sn{=}SnR'_2$, when the electronegativity of the two stannylene fragments is different, the mutual interactions may be very different in degree, and the Sn-Sn bonding is then more in the nature of a coordinate bond, $R_2Sn \rightarrow SnR'_2$, and the geometry at the two tin sites may be different (e.g. **21-37**).

The dimer, **21-32**, of Lappert's stannylene **21-1**, is centrosymmetric with fold angles θ and θ' of 41° (see formula **21-39**), *r*SnSn 276.8 pm, and CSnC 109.2°. It shows $\delta(^{119}Sn)$ 692 in the solid state, but 740 and 725 in solution, perhaps signifying two conformational isomers.[24]. The SnSn bond dissociation energy is 90 kJ mol^{-1}, about half that it is in hexamethylditin.[22] The reactions of the distannene **21-32** are those of the stannylene **21-1** which are described above. In the distannene **21-34**, the two fold angles θ and θ' are different at 21.4° and 64.4°. This might be taken to imply that only one of the two dative bonds is fully developed, but it might also result from the effects of crystal forces.[40, 61]

Tetrakis(triisopropylphenyl)distannene (**21-33**) is obtained as an intense red solid by the photolysis or thermolysis of hexakis(triisopropylphenyl)tristannane, by way of the intermediate stannylene which can be trapped with 1,3-dienes or 1,2-diones (see Section 21.1.2); the photolytic conversion is quantitative at –78 °C. In solution at 0 °C, the stannylene slowly reverts back to the the cyclotristannane. The X-ray crystal structure has not yet been determined, but the molecule is believed to be twisted with little pyramidalisation.[68] The distannene reacts with phenylacetylene to give the distannacyclobutene, with *r*SnSn 284.0(1) pm. The distannenes **21-35** and **21-36** are formed in the disproportionation reaction shown in equation 21-10.

21.3 Distannynes RSn≡SnR

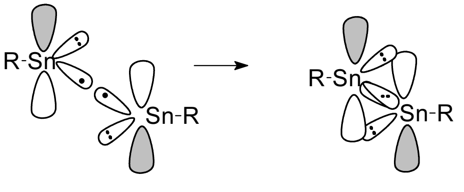
The first distannyne, Ar′Sn≡SnAr′, where Ar′ is $2,5\text{-}Dip_2C_6H_3$ (Dip = $2,6\text{-}Pr^i_2C_6H_3$), has recently been isolated from the reaction of Ar′SnCl with potassium;[69] it has a *trans* bent structure with *r*SnSn 266.75(4) pm, and CSnSn 125.24(3)°.



(21-15)

A similar reduction of Ar*SnCl, where Ar* is $2,6\text{-}Trip_2C_6H_3$ (Trip = $2,4,6\text{-}Pr^i_3C_6H_2$), proceeds directly through to the distannyne radial anion; the salts $Ar^*Sn{\equiv}SnAr^{*\bullet-}\ M^+$ have been isolated, where M^+ is $K(THF)_6{}^+$,[70] $K(THF)_2(18\text{-crown-}6)^+$,[70] and $Na(THF)_3{}^+$,[71] and show *r*SnSn between 278.2 and 282.4 pm, CSnSn between 93.6 and 98.0°, and *g* 2.0069, $a^{117}Sn$ 0.83, $a^{119}Sn$ 0.85 mT. Further reduction has given the dianion $Ar^*Sn{\equiv}SnAr^{*=}\ 2K^+$, with *r*SnSn 277.63(9) pm and CSnSn 107.50(14) pm.[72]

The nature of the bonding in a distannyne can be represented in a similar way to that which is given above (equation 21-9) for the distannenes; in equation 21-16, the component stannylyne units are represented as being formally sp^2 hybridised. The Lewis description of the bonding is that it is a single bond with a small amount of triple bond character.[67, 69]



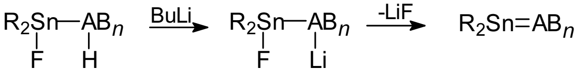
(21-16)

21.4 Stannenes and Heterostannenes $R_2Sn^{IV}=CR'_2$ and $R_2Sn^{IV}=X$ [64, 73]

Stannenes contain the unit $R_2Sn^{IV}=CR'_2$ and heterostannenes the unit $R_2Sn^{IV}=X$, where $X=SiR'_2$ (stannasilenes), GeR'_2 (stannagermenes), S (stannathiones), Se (stannaselenones), NR′ (stannaimines), PR′ (stannaphosphenes), etc. As with the distannenes, when the groups R and R′ are small the stannenes and heterostannenes exist only as transient intermediates which, in the absence of other reagents, undergo self reaction to give oligomers, and their formation is usually demonstrated by their characteristic reactions. Kinetic stability can be built into the structures by making the groups R and R′ large, and long-lived stannenes, stannaimines (Section 16-5), and stannaphosphenes (Section 16-6) have been characterised. Less steric protection can be built into the stannathiones and stannaselenones as there is no group R′, and, as yet, these compounds are known only as transient intermediates.

The Sn=X double bond can be formed either by the coupling of a stannylene R_2Sn**:** with an equivalent species **:**AB_n with 6 valence electrons (equation 21-17), or by the elimination of MX from the structure MSn-AX (M = alkali metal, X = halide) (equation 21-18). Examples of the stannenes and heterostannenes are shown in Scheme 21-10.

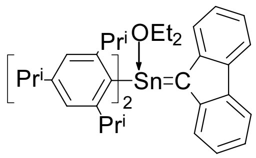
$$\mathrm{R_2Sn{:}} + \mathrm{{:}AB}_n \longrightarrow \mathrm{R_2Sn{=}AB}_n \qquad (21\text{-}17)$$



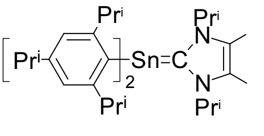
$$\mathrm{R_2}\underset{\mathrm{F}}{\mathrm{Sn}}-\underset{\mathrm{H}}{\mathrm{AB}_n} \xrightarrow{\mathrm{BuLi}} \mathrm{R_2}\underset{\mathrm{F}}{\mathrm{Sn}}-\underset{\mathrm{Li}}{\mathrm{AB}_n} \xrightarrow{\mathrm{-LiF}} \mathrm{R_2Sn{=}AB}_n \qquad (21\text{-}18)$$

$Me_2Sn=C(SiMe_3)_2$

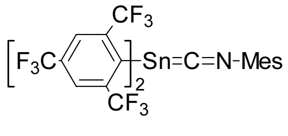
(**21-40**) [74]



(**21-41**) δSn 288 [75, 76]



(**21-42**) *r*SnC 237.9(5) pm [30, 77]



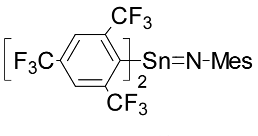
(**21-43**) *r*SnC 238.7 pm [78]

$(2,4,6\text{-}Pr^i_3C_6H_2)_2Sn=SiMe_2Bu^t$

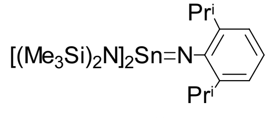
(**21-44**) *r*SnSi 241.9 pm, δSn +516.7[79]

$(2,4,6\text{-}Pr^i_3C_6H_2)_2Sn=Ge(Mes)_2$

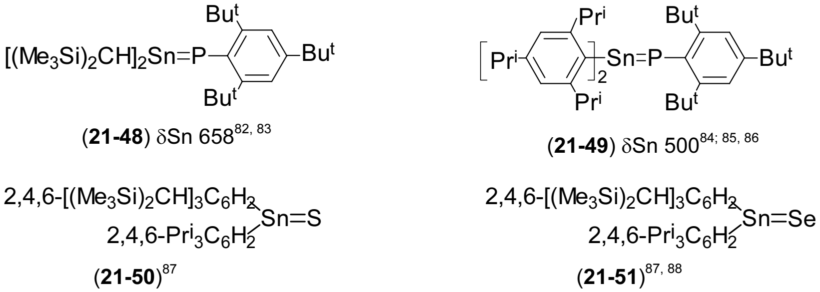
(**21-45**) δSn +360[80]



(**21-46**)[81]

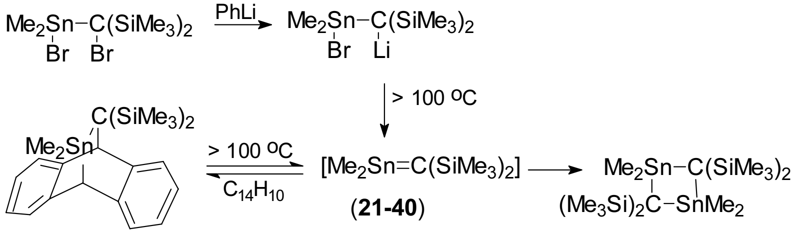


(**21-47**)[82]



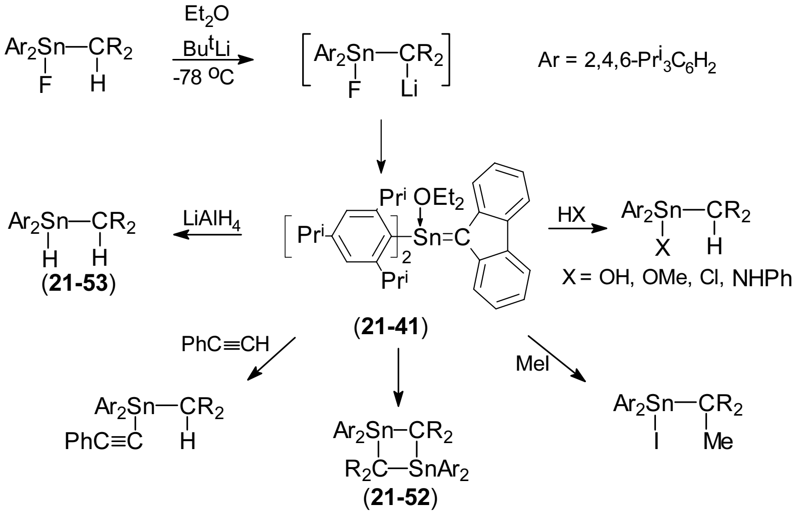
Scheme 21-10 Stannenes and heterostannenes.

The formation and reactions of the transient stannene (**21-40**) are shown in Scheme 21-11.



Scheme 21-11 Formation and reactions of the stannene **21-40**.

The deep violet stannene (**21-41**) is formed by elimination of LiF as shown in Scheme 21-12.[75] The upfield ^{119}Sn chemical shift reflects the fact that it forms a complex with ether. It dimerises at room temperature to form the planar distannacyclobutane (**21-52**), and is reduced by lithium aluminium hydride to the triorganotin hydride (**21-53**). Protic acids add to place the anionic group on tin, and methyl iodide reacts to give a near-quantitative yield of the triorganotin iodide.[76]



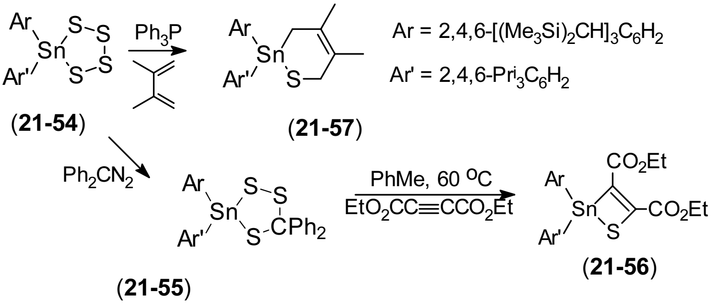
Scheme 21-12 Formation and reactions of the stannene **21-41**.

The stannaketenimine **21-43** separates as yellow crystals when a solution of the stannylene and mesityl isocyanide is cooled to –78 °C. In solution at room temperature it is in equilibrium with its progenitors and shows the reactions of the stannylene, reacting with t-butyl alcohol to give $Sn(OBu^t)_2$ and MesNC, and with 2,3-dimethylbutadiene to give the stannacyclopentene cycloadduct.[78]

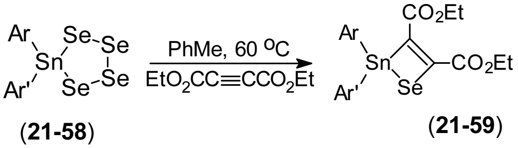
The stannaimines are described in Section 16.5.

The stannaphosphenes **21-48** and **21-49** are formed by lithiation of the FSn-PH unit to give FSn-PLi, followed by the elimination of LiF. Methanol adds across the Sn=P double bond in the same way as with the Sn=N structure, and **21-49** shows cycloaddition reactions with enones and orthoquinones.[83-86] No X-ray diffraction study of a stannaphosphene has yet been reported

In solution and the solid state the sulfides R_2SnS are cyclic trimers when R = Me or Ph, and a cyclic dimer when R = Bu^t, and the situation with the selenides R_2SnSe is similar (Section 17.2). When the groups R are very bulky, however, there is evidence that the monomers $R_2Sn{=}S$ (**21-50**) and $R_2Sn{=}Se$ (**21-51**) may exist as transient species (equations 21-19 and 21-20).



(21-19)

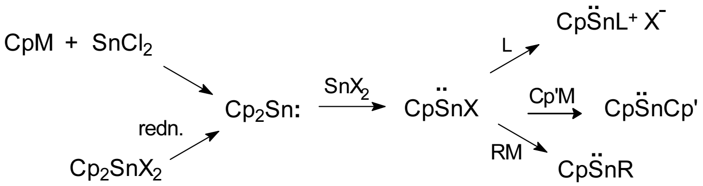


(21-20)

If the trithiastannolane **21-55** is heated in the presence of diethyl acetylenedicarboxylate, the thiastannete **21-56** is formed; similarly, the tetrathiastannolane **21-54** reacts with dimethylbutadiene in the presence of triphenylphosphine to give the stannathiacyclohexene (**21-57**),[87, 89] and the tetraselenastannolane (**21-58**) with diethyl acetylenedicarboxylate gives the selenastannete **21-59**.[87] These reactions are best accounted for in terms of [2 + 2] cycloaddition reactions of the stannathione ArAr′Sn=S **21-50** and the stannaselenone ArAr′Sn=Se **21-51**, respectively.

21.5 π-Bonded Stannylenes[3, 6, 90–95]

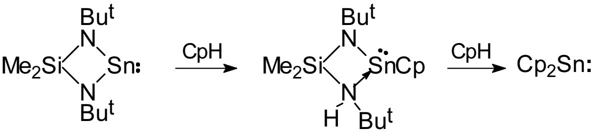
General routes for preparing cyclopentadienyltin(II) compounds are shown in Scheme 21-13. The rings may carry a variety of alkyl or aryl substituents [e.g. $(MeC_5H_4)_2Sn$, $(Me_5C_5)_2Sn$, $(Bn_5C_5)_2Sn$, $(Ph_5C_5)Sn(C_5H_5)$, or $(Ph_5C_5)_2Sn$], and a lot of attention has been given to the effect that substituents have on the structure and reactivity. Much of the recent work in this field has been carried out by Jutzi's group, and the subject is placed in the context of the cyclopentadienyl complexes of other Main Group metals in reference 3, which tabulates data on 26 CpSnX, 29 Cp_2Sn, and three Cp_3Sn_2 compounds.



Scheme 21-13 Preparation of cyclopentadienyltin(II) compounds.

Di(cyclopentadienyl)tin(II) (stannocene, Cp_2Sn**:**) can readily be prepared as a white air-sensitive solid, m.p. 105 °C, from the reaction of cyclopentadienyllithium or cyclopentadienylsodium with stannous chloride.[96] Cp_2Sn Readily exchanges its cyclopentadienyl groups with other electronegative ligands on tin, and reaction with $SnCl_2$ gives CpSnCl through which other cyclopentadienyltin(II) derivatives CpSnX can be prepared.[97]

Stannocene can also be prepared, via the cyclopentadienyltin(II) amine (**21-61**), by acidolysis of the diaminotin(II) compound **21-60** with cyclopentadiene.[98, 99]

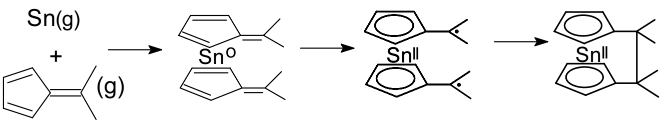


(21-21)

(**21-60**) (**21-61**)

Di(pentamethylcyclopentadienyl)tin(II) (decamethylstannocene, Cp^*_2Sn**:**) can be obtained from Cp*Br and Sn, or Cp*M and $SnCl_2$, or by reducing $Cp^*_2SnCl_2$ with lithium naphthalenide or dilithium cyclooctatetraendiide.[100]

The stannocenophane (**21-62**) with δ(Sn) –2122, is formed in 2% yield by the mechanism shown in equation 21.22, when gaseous tin and dimethylfulvene are co-condensed at 77 K.[101]



(21-22)

(**21-62**)

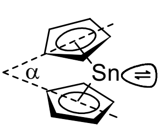
Electron diffraction[102] and X-ray crystallography[103] show that in both the gas phase and the solid the two rings in $(C_5H_5)_2Sn$**:** are non-parallel, and the angle α between the planes of the two rings is 46° (formula **21-63**). The structure can be described in terms of sp^2 hybridised tin, with two of the orbitals involved in bonding to the two cyclopentadienyl rings, and the third orbital containing the unshared electron pair. The MO picture of the bonding is outlined in reference 3. The ^{119}Sn NMR chemical shift is at very high field (Cp_2Sn –2199) in contrast to that of the σ-bonded stannylenes which may often be greater than +2000.

If the rings are alkylated, steric repulsions open up the bending angle and reduce the reactivity.[104] Values of α for a selection of ring-substituted stannocenes are given in Table 21-1. In the extreme, decaphenylstannocene (**21-64**) has coparallel cyclopentadienyl rings, with the phenyl groups twisted to give the molecule S_{10} symmetry,[105] and this structure has become something of an icon in organometallic chemistry.

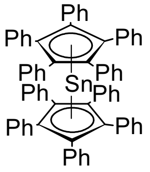
Table 21-1 Ring dihedral angles in stannocenes.

Stannocene	$(C_5H_5)_2Sn$	$(Me_5C_5)_2Sn$	$(Bn_5C_5)_2Sn$	$(Pr^i{}_2C_5H_3)_2Sn$	$(Ph_5C_5)Sn$
α	46°	36°	33°	28°	0°

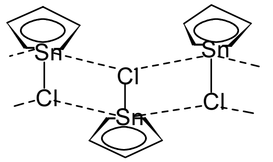
In the crystal of CpSnCl, the tin is unsymmetrically associated by one intramolecular short bond and two intermolecular long bonds to three chlorine atoms as shown in **21-65**.[106] Similarly, the cyclopentadienyl ring in the tin amine **21-66** is asymmetrically η^3-bonded.[107]



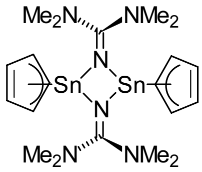
(21-63)



(21-64)



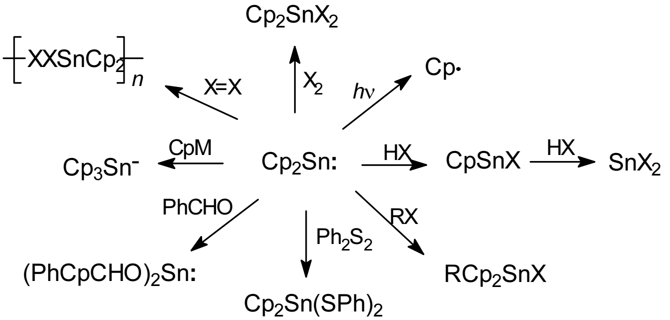
(21-65)



(21-66)

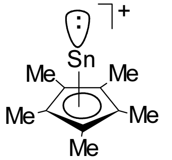
$(Me_2Bu^tSi)C_5Me_4SnCl$ Adds to $SnCl_2$ to give a complex $[Sn_9(\eta Cp')_6Cl_{12}]$ which can be regarded as a combination, through Sn..Cl..Sn bridging, of the components $SnCl_2.3Cp'SnCl.SnCl_2.3Cp'SnCl.SnCl_2$.[108]

The principal reactions of Cp_2Sn are shown in Scheme 21-14; these include reactions with obvious electrophiles (e.g. strong protic acids) and nucleophiles (e.g. organolithium reagents), and processes which involve radicals (e.g. photolysis), but the mechanisms of some of the other reactions are uncertain.

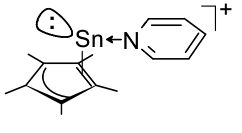


Scheme 21-14 Reactions of di(cyclopentadienyl)tin.

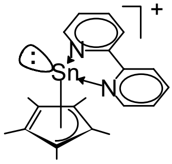
Protic acids HX readily cleave the CpSn bond, providing a useful route to compounds CpSnX and SnX_2 (e.g. X = MeO, AcO, NC, $R_2C{=}NO$, R_2NO etc.).[109] The structures of the products depend on the nucleophilic power of X. Thus the carboxylates Cp*SnOCOR (R = CF_3 or CCl_3) are covalently bonded, but the tetrafluoroborate and trifluoromethanesulfonate are ionic compounds of the pentagonal pyramidal Cp*Sn$^+$ cation **21-67**.[100, 110, 111] The tetrakis(pentafluorophenyl)borate Cp*Sn$^+$ $B(C_6F_5)_4^-$ is an effective cocatalyst with zirconocenes for the polymerisation of ethylene and propylene.[111] The triflate forms complexes with nitrogen bases with a reduction in hapticity: the pyridine complex is dihapto-bonded, as in **21-68**, and the bipyridyl complex is trihapto-bonded, as shown in **21-69**.



(**21-67**)



(**21-68**)



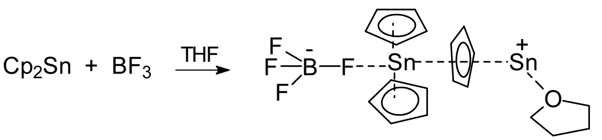
(**21-69**)

Stannocene reacts with CyNHLi (Cy = cyclohexyl) to give CpSnNHCy, which then eliminates CpH to give the Sn^{II} cubane $[Sn(NCy)]_4$.[112]

Tin(IV) halides show exchange reactions similar to those with tin(II) halides, for example in equation 21-23.[113]

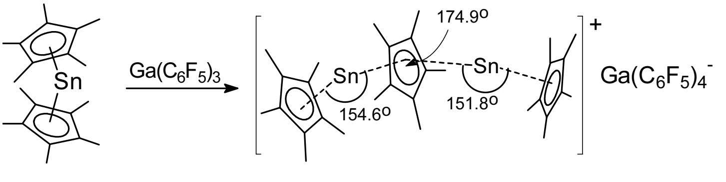
$$Cp_2Sn + Me_2SnCl_2 \longrightarrow Me_2CpSnCl + CpSnCl \qquad (21\text{-}23)$$

The Lewis acids BBr_3, $AlCl_3$ and $AlBr_3$ react with Cp_2Sn to give 1 : 1 complexes $Cp_2Sn \rightarrow MX_3$,[114] but reaction with BF_3 gives a complex containing the four units BF_4, Cp_2Sn, $CpSn^+$ and THF (equation 21-24), and, under the same conditions, $Cp^*{}_2Sn$ gives Cp^*Sn^+ BF_4^-.[115]



(21-24)

$(Me_5C_5)_2Sn$**:** reacts with $Ga(C_6F_5)_3$ to give, via $(Me_5C_5)Sn^+$ $(Me_5C_5)Ga(C_6F_5)_3^-$, the complex $[(\eta^5\text{-}C_5Me_5)Sn(\mu\text{-}\eta^5\text{-}C_5Me_5)Sn(\eta^5\text{-}C_5Me_5)]^+$ $Ga(C_6F_5)_4^-$ with the structure shown in equation 21-25.[116]



(21-25)

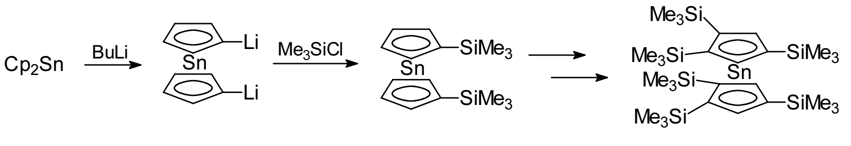
The reaction with transition metal derivatives ML_n may give products containing the Sn-M bond, in which the cyclopentadienyl groups may be either σ- or π-bonded (see Sections 19.8 and 19.9), for example:

$$\eta^5\text{-}Cp_2Sn + Fe_2(CO)_9 \longrightarrow [\eta^1\text{-}Cp_2Sn\text{-}Fe(CO)_4]_2 \qquad (21\text{-}26)$$

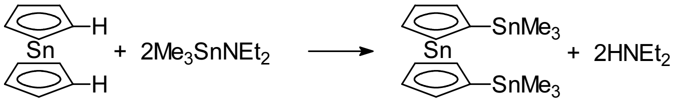
$$\eta^5\text{-}Cp_2Sn + Mo(CO)_5.THF \longrightarrow \eta^5\text{-}Cp_2Sn\text{-}Mo(CO)_5 \qquad (21\text{-}27)$$

The course of the reaction of nucleophiles $A^{\delta+}-B^{\delta-}$ depends on the basicity and the nucleophilic power of B for tin and can involve deprotonation [giving $(C_5H_4A)_2Sn)$], or addition [giving $(C_5H_5)_2SnB^-$], or substitution (giving SnB_2).

Butyllithium removes a proton from each Cp group, and the dilithio derivative then reacts with trimethylchlorosilane to give the disilylstannocene, and this process can be repeated to put three silyl groups in each ring.[117] Trimethyl(diethylamino)tin similarly acts as a strong base, and gives the distannylated stannocene.[118]

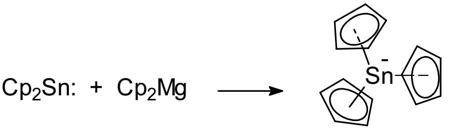


(21-28)



(21-29)

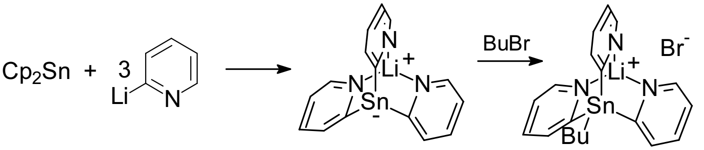
Cyclopentadienylsodium and dicyclopentadienylmagnesium are weaker bases and add to the tin to give "paddle-wheel" tri(cyclopentadienyl)tin(II) anions, for example the $Mg(THF)_4^{2+}$ salt of Cp_3Sn^-, which is slightly pyramidal at tin, with CpSnCp 118.8°, and a *r*SnCp 265 pm.[119, 120]



(21-30)

With methyllithium, η^5-Cp^*_2Sn forms η^1-$Cp^*_2SnMeLi$ which rapidly decomposes into Cp*Li, η^5-Cp^*_2Sn and polymeric $(Me_2Sn)_n$, but the intermediate can be trapped with MeI or CD_3I giving $Cp^*_2SnMe_2$ or $Cp^*_2SnMe(CD_3)$, respectively.[121]

More powerful nucleophiles bring about nucleophilic displacement of a cyclopentadienyl group. Stannocene reacts with 2-lithiopyridine to give the triptych product shown in equation 21-31,[122] and Cp^*_2Sn reacts with bis(trimethylsilyl)methyllithium to give $[(Me_3Si)_2CH]_2Sn$:.[121]

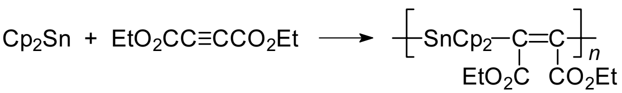


(21-31)

Electron transfer reactions usually lead to cleavage of the CpSn bond, and there are no reports yet of radical anions of the type $Cp_2Sn^{\bullet-}$, comparable with the known $[(Me_3Si)_2CH]_2Sn^{\bullet-}$.[92]

If Cp_2Sn**:** is irradiated with UV light, it shows the ESR spectrum of the $Cp^\bullet$ radical (Section 21.1.1 and 20.2), but the fate of the $CpSn^\bullet$ radical, which is presumably also formed, is not known.[123] This is parallel to the photolysis of $[(Me_3Si)_2CH]_2Sn$**:**, but the radical $(Me_3Si)_2CH^\bullet$ which is formed, is then trapped by the parent stannylene to give the stannyl radical $[(Me_3Si)_2CH]_3Sn^\bullet$.[39] Chlorine or bromine act by oxidative addition to give Cp_2SnX_2, reactive organic halides, RX (methyl iodide, ethyl iodide, allyl bromide, or benzyl bromide), give RCp_2SnX,[124] Disulfides, RSSR, give $Cp_2Sn(SR)_2$, but there is some evidence that radical chain reactions may be involved.[113]

Reactive carbonyl compounds such as benzaldehyde undergo addition to give tin(II) alkoxides, but diethyl azodicarboxylate and diethyl acetylenedicarboxylate react to give tin(IV) co-oligomers[113] (e.g. equation 21-32).



$$\mathrm{Cp_2Sn + EtO_2CC{\equiv}CCO_2Et \longrightarrow \left[SnCp_2{-}\underset{EtO_2C}{C}{=}\underset{CO_2Et}{C} \right]_{\mathit{n}}} \qquad (21\text{-}32)$$

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22 Organic Synthesis: Tin/lithium Transmetallation, the Stille Reaction, and the Removal of Tin Residues[1]

Many of the applications of organotin compounds are specific to one class of compounds (e.g. tin hydrides or allylstannanes) and these topics are covered in the corresponding chapters. On the other hand, reactions involving tin/lithium transmetallation, or palladium-catalysed coupling, can be carried out with a variety of types of organostannanes, and these reactions are collected together in this chapter. These topics have an extensive literature that is beyond the scope of this book, and the treatment here is limited to an outline of the fields, and a guide to the literature.

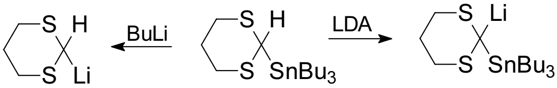
22.1 Tin/lithium Transmetallation[2–6]

In Section 19.1 we have seen that tetraorganostannanes react reversibly with organolithium compounds by tin/lithium transmetallation via anionic 5-coordinate trigonal bipyramidal intermediates.

$$\mathrm{RSnR'_3 + R''Li \rightleftharpoons [SnRR'_3R'']^- Li^+ \rightleftharpoons R''SnR'_3 + RLi \rightleftharpoons} \text{ etc.} \qquad (22\text{-}1)$$

These reactions are preparatively useful when R is more electronegative than R′ or R″, so that RLi is relatively stable and the equilibrium is displaced towards the right, and it provides a clean route to RLi when R is vinyl, allyl, aryl, cyclopropyl, or α-alkoxy-, α-dialkylamino-, α-alkylthioalkoxy-, or α-halogeno-alkyl. The accompanying $R''SnR'_3$ is fairly inert and volatile, and is easily removed; alternative routes to RLi often give a mixture of compounds (e.g. RHal reacts with lithium to give RLi and RR, together with LiHal), and most of the organolithium compounds that have been subjected to studies by spectroscopy or X-ray crystallography have been prepared by Sn/Li transmetallation.

The reaction is usually fast and is tolerant of most types of functional substituent, such as epoxy groups or unprotected carbonyl groups; a variety of solvents can be used, most commonly THF at low temperature. Generally, when tin and hydrogen are present as competing electrophilic centres, alkyllithium compounds give transmetallation, whereas lithium diisopropylamide gives deprotonation (equation 22-2).[7]



(22-2)

Usually the compound RLi is not isolated, but is caused to react *in situ* with the appropriate electrophile. A variety of simple examples is given in Table 22-1, and a more extensive list is available in Schlosser's recent review (which also describes typical working procedures)[6] and in the articles by Pereyre and his colleagues.[4, 5]

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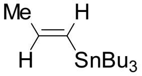
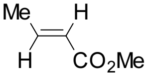
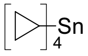
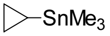
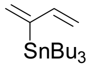
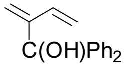
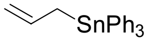
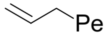
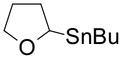
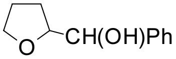
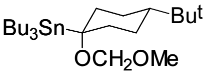
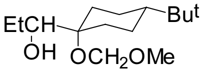
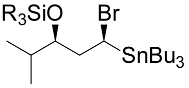
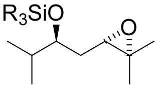
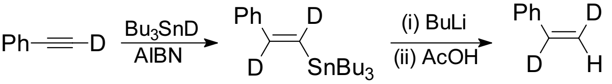
Table 22-1 Transmetallation of organotin compounds with butyllithium, followed by trapping with an electrophile.

	$RSnR'_3$	Solvent T/°C	Electrophile	Product	Yield (%)	Ref.
1	$(CH_2{=}CH)_4Sn$	Et_2O RT	$Me_2C{=}O$	$(CH_2{=}CH)Me_2COH$	74	8
2		Et_2O 25	CO_2/CH_2N_2		28	9
3		RH 25	Me_3SnBr		79	10
4		THF –78	$Ph_2C{=}O$		61	11
5		THF	PeI		52	12
6	$PhCH_2SnMe_3$	Et_2O –35	MeI	$PhCH_2Me$	93	13
7	$PhOCH_2SnBu_3$	THF –75	$PhCH{=}O$	$PhOCH_2CH(OH)Ph$	78	14, 15
8		THF –75	$PhCH{=}O$		71	16
9	$Me_2NCH_2SnBu_3$	RH 0	$PhCH{=}O$	$Me_2NCH_2CH(OH)Ph$	73	17
10		DME –60	$EtCH{=}O$		82	18
11	$(Bu_3SnCH_2)_2S$	THF –30	$Me_2PhSiCl$	$(Me_2PhSiCH_2)_2S$	84	19
12		Et_2O/RH –110	Me_2CO		80	20

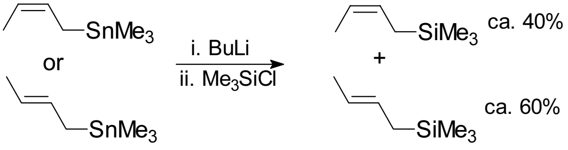
The synthetic application of Sn/Li transmetallations dates from Seyferth and Weiner's report of the transmetallation of tetravinyltin in 1959 (Table 22.1, entry 1).[8] The vinylstannane can conveniently be prepared by the hydrostannation of an alkyne (e.g. equation 22-3)[9]. The transmetallation takes place with retention of configuration in the vinyl group (entry 2), and provides an easy route to vinyl derivatives of known configuration.



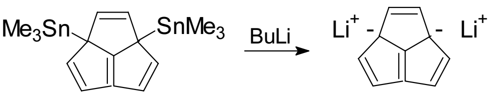
(22-3)

The cyclopropyl group shows its customary pseudo-vinyl behaviour (entry 3), and, as with the vinyl compounds, the transmetallations take place with retention of configuration.[15] Allyl compounds (entry 5), on the other hand, lose their structural identity (e.g. equation 22-4) because of the symmetrical structure of the allyllithium compounds.[12, 21]

The bis(trimethylstannyl) derivative of triquinacene, which can be regarded as a bis(triallylstannane), was used for preparing the triquinacene dianion (equation 22-5).[22] A secondary benzyl system provides an exception to the rule that the transmetallations involve configurational retention.[23]



(22-4)



(22-5)

α-Alkoxyalkylstannanes (e.g. entry 10) can often be prepared by addition of Bu_3SnLi to a carbonyl compound followed by alkylation of the OLi group with an alkyl halide (see Section 6.2). The Sn/Li transmetallation of these and other α-substituted alkyltin compounds usually proceeds with complete retention of configuration at the carbon centre (e.g. entry 12), and, by working at low temperature with a suitable solvent, stereospecific syntheses can be achieved.

22.2 Stille Coupling Reactions[24–31]

The Stille reaction (equation 22-6), in which an organotin compound $RSnR'_3$ and an organic electrophile, R″X, are treated with a palladium(0) or palladium(II) catalyst to form a new C–C bond in R–R″ is an important reaction in organic synthesis.

$$\mathrm{RSnR'_3 + R''X \xrightarrow{Pd^0L_2} RR'' + R'_3SnX} \qquad (22\text{-}6)$$

The literature on these reactions is very extensive. The 50th volume of *Organic Synthesis*, which was devoted to the topic, and covered material published up to 1995, comprised 560 pages and included some 4,500 examples of the reaction,[29] and subsequent work has not slackened. Fortunately there a number of good reviews available, as listed at the head of this Section.

Negishi has pointed out that in Pd-catalysed coupling, as in most important scientific discoveries, there are people who discover something new, and those that recognise its potential and develop it – and usually receive the major credit.[32] A number of people, from about 1976 onwards, come into the first category,[33, 34] but it was Stille's thorough studies and his review in 1986[35] that highlighted the synthetic potential of the system and catalysed its rapid development.

The group R in the organotin compound may vary widely, the reactivity following the sequence ethynyl > vinyl > aryl > benzyl ≅ allyl > acetonyl > alkyl. Usually only one of the four groups on tin is transferred, and a mixed stannane, $RSnR'_3$, is used where less reactive alkyl groups, particularly methyl or butyl, act as spectator ligands R′. The reaction can be also carried out with the organotin group bound to a polymer through an alkyl chain.[36]

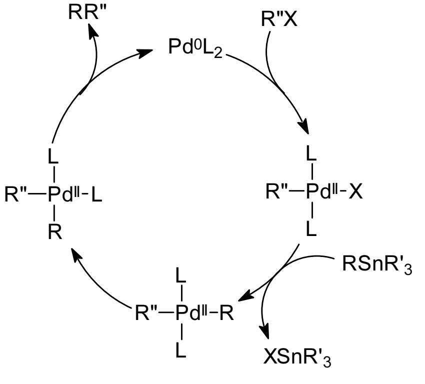
The reagent R″X is usually a vinyl, allyl, aryl, acyl, benzyl, or propargyl halide or triflate; simple alkyl halides do not normally couple unless they carry an α-activating group such as Cl, OR, or SR, and the presence of β-hydrogen in the alkyl group may lead to elimination to give the alkene R(−H). The reaction can be carried out under mild conditions, particularly with the more reactive groups R, and is tolerant of functional groups in R and R", such as carboxylic acid, ester, ether, nitrile, hydroxyl, nitro, amine, and carbonyl. Typical experimental procedures are given in the reviews by Farina[29] and by Marshall,[31] and some reaction conditions are noted in Table 22-2.

A wide variety of solvents can be used such as THF, MeCN, $CHCl_3$, DMF, DME, *N*-methylpyrrolidone, benzene, toluene, or water. The most common catalysts are $Pd(PPh_3)_4$ or $Pd(dba)_2$ (dba = dibenzylideneacetone) but Pd(II) compounds such as $PdCl_2(PPh_3)_2$ or $PdCl_2(MeCN)_2$, which are more stable to oxygen, can also be used. A triarylphosphine or triarylarsine, or copper(I) can act as a cocatalyst. Oxygen has an accelerating effect, and then $PhCH_2PdCl(PPh_3)_2$, which is oxygen-resistant, is used as catalyst.[29]

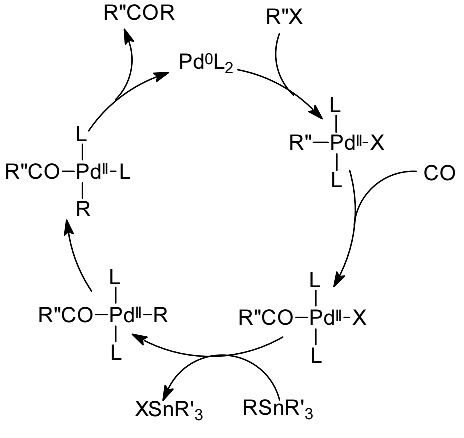
If the reaction is carried out under an atmosphere of CO, this can be incorporated into the couple to give RCOR″.

$$RSnR'_3 + R''X + CO \xrightarrow{Pd^0L_2} RCOR'' + R'_3SnX \qquad (22\text{-}7)$$

The mechanisms of the reactions are not understood in detail, but the models which are normally accepted are shown in Schemes 22-1 and 22-2. Oxidative addition of the organic halide to the palladium(0) catalyst gives an organopalladium(II) halide which then undergoes transmetallation with the tetraorganotin compound to give the diorganopalladium(II) compound and triorganotin halide. The two organic groups then couple in a reductive elimination of RR″, regenerating the Pd(0) catalyst. When a Pd(II) catalyst is used, it is rapidly reduced to Pd(0) before the coupling. The reactivity is higher when the ligands on the Pd have a lower donicity. The transmetallation step is often rate-determining. Transfer of the group R from tin can be nucleophilically-assisted, and the stannatranes $RSn(CH_2CH_2CH_2)_3N$ are particularly reactive.



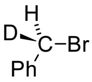
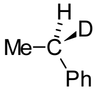
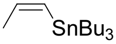
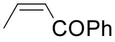
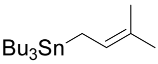
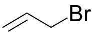
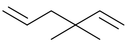
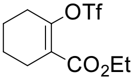
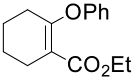
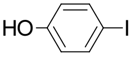
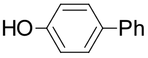
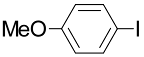
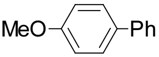
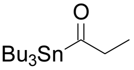
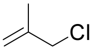
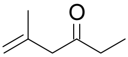
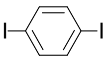
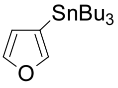
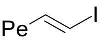
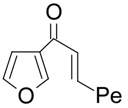
Scheme 22-1 Proposed mechanism for R−R″ coupling.



Scheme 22-2 Proposed mechanism for RCO−R″ coupling.

Some simple examples of Stille coupling reactions are shown in Table 22-2.

Table 22-2 Stille coupling reactions.

	$RSnR'_3$	Catalyst, Solvent, T/°C	$R''X$	Product	Ref.
1	Me_4Sn	$Pd(PPh_3)_4$ HMPT 64–66			37
2		$Pd_2(dba)_3$/ TFP[a] THF, RT	PhCOCl		38
3	$Bu_3Sn{-}{\equiv}{-}SnBu_3$	$Pd(PPh_3)_4$ Dioxane, 100	ArI	$Ar{-}{\equiv}{-}Ar$	39
4		$BnPdCl(PPh_3)_2$ $HCCl_3$, 65			40
5	Bu_3SnPh	$Pd(OAc)_2$ PPh_3 THF, 65			41
6	Cl_3SnPh	$PdCl_2$, KOH H_2O, 100			42
7	$(C_6F_{13}C_2H_4)_3SnPh$	$Pd(OAc)_2$, LiCl $P(p\text{-}Tol)_3$, DMF Microwave			43
8		$Pd(PPh_3)_4$ C_6H_6 60			44
9	Me_3SnPh	CO (15 psi) $C_3H_7PdCl_2$ HMPA, 20		1,4-$(PhCO)_2C_6H_4$	45
10		CO (30 psi) $Pd(PPh_3)_2Cl_2$ THF, 55–60			46

[a] TFP = tri(2-furylphosphine)

Tetramethyltin reacts with optically active α-deuteriobenzyl bromide to give α-deuterioethylbenzene with inversion (Table 22-2, entry 1), which occurs during the step of oxidative addition.

Conditions can usually be found (e.g. entry 2) that are mild enough for vinylic compounds to react with retention of configuration. Intramolecular Stille reactions involving a vinylstannane and, often, a vinyl iodide or vinyl triflate, have been widely used for closing rings in natural product synthesis.[30] 1,2-Distannylethene has been used for "stitching" together the ends of a bifunctional precursor to produce a cyclic structure,[47] and distannylacetylene (entry 3) has the potential for similar applications. Allyl compounds usually react with allylic inversion (entry 4).

Aryltin trichlorides (entry 6) can be used as alternatives to aryltributylstannanes (entry 5) for aryl transfer. The reactions of fluorous tin compounds are relatively slow, but they can be greatly accelerated by microwave irradiation. For example, arylations such as that in entry 7 require about a day for completion under normal conditions, but can be completed in 90–120 s under irradiation.[43]

Acylstannanes will couple with acyl halides to give mixtures of mono- and diketones, but decarbonylation can be prevented by an atmosphere of CO, when the diketone is the predominant product.[48]

Carbonylative coupling (entries 9 and 10) appears to proceed with the same substrates and under similar conditions to direct coupling, and any intrusion of the former reaction can usually be avoided by working at a higher pressure of CO.

The stannylene $:Sn[N(TMS)_2]_2$ undergoes oxidative addition with halides RX, where R = alkyl, allyl, allenyl, hexynyl, phenyl, or styryl, to give the Sn(IV) compounds, $RSnX[N(TMS)_2]_2$, then these can be used in Stille coupling reactions where the organotin(IV) compound is activated by fluoride ion.[49–51]

22.3 Removal of Tin Residues

Organotin compounds are used in many synthetic procedures as stoichiometric reagents (hydrostannolysis, hydrostannation, allylation, Stille coupling, Sn/Li transmetallation, transesterification, etc), and this presents the problem of removing the organotin residues from the required product. This is particularly important in the preparation of pharmaceuticals as these organotin compounds are to some degree toxic.

Sometimes the problem can be reduced by using the organotin compound as a catalyst rather than as a stoichiometric reagent. A familiar example is a hydrostannolysis reaction which can be carried out with a catalytic amount of tin hydride in the presence of a borohydride.

The methods for removing the organotin residues depend on the nature of the organic product and of the tin compound and involve (1) using conventional reagents and modifying the working-up technique, (2) using special reagents, or (3) using polymer-supported reagents. Most of these methods have been aimed at removing trialkyltin halides, triflates, oxides, or hydroxides; any residual tin hydride can be first converted into the iodide with iodine. Little work has been reported on the removal of dialkyl- or monoalkyl-tin residues, though many of the techniques that are described below could be adapted for this purpose.

Normal Reagents

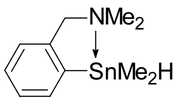
Trimethyltin halides are fairly soluble in water, and can often be washed out of a solution of the reaction mixture in an immiscible solvent. If the desired product is polar, it can be separated from tributyltin halides by partition between acetonitrile and hexanes, which are immiscible.[52, 53]

Tributyltin halides are relatively insoluble in water. If the required product is soluble in a non-polar solvent, the solution can be shaken with aqueous KF; the insoluble organotin fluoride is filtered off, and the solution washed and the product separated by chromatography.[54, 55] Alternatively, the solution can be stirred with a suspension of KF on Celite,[56] or of CsF and CsOH on silica,[57] then treated similarly. If the required product has a more polar character, the byproduct Bu_3SnX can be reduced with $NaBH_3(CN)$,[58] or methylated with Me_3Al,[59] then chromatographed on silica gel with a hydrocarbon eluant, when the Bu_3SnH or Bu_3SnMe are rapidly washed through the column. Alternatively, if the required product is non-polar, the organotin compounds can be hydrolysed with NaOH to $Bu_3SnOH/(Bu_3Sn)_2O$ which is strongly adsorbed on a silica column, and the organic product can be washed through.[59] Again, an amount of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) that is equivalent to the organotin reagent can be added in moist ether, then any remaining distannane or tin hydride is converted to the organotin iodide by titration with iodine and hydrolysed to the oxide or hydroxide with the precipitation of DBU.HX, and the required product can be separated by filtration through silica gel.[60]

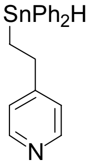
Modified Reagents

When Bu_2SnClH is used in hydrostannolysis, the problem of separation is reduced as the compounds Bu_2SnX_2 can be hydrolysed to insoluble Bu_2SnO, and a number of other organotin hydrides have been developed with the aim of simplifying the work-up procedure and recovering the organotin compound. Residues from the amine-functional stannanes **22-1**,[61] **22-2**,[62] **22-3** and **22-4,**[63] and **22-5**[64] can be separated into aqueous acid, those from reactions of **22-6** can be hydrolysed to the corresponding acid which is soluble in aqueous $NaHCO_3$,[65] and those from reactions with the 3-pyrenylpropylstannane **22-7** can readily be separated by absorption on activated carbon.[66]

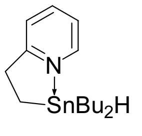
Curran has developed the chemistry of tris[2-(perfluorohexyl)ethyl]tin hydride (see Section 5.4), again with the aim of making it easy to separate the organotin byproduct.[67] The polar polyethylene oxide groups of the hydrides **22-8** and **22-9** make it possible to carry out radical reactions in aqueous solution.[68, 69]



(**22-1**)



(**22-2**)



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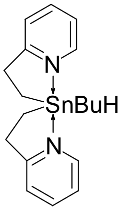

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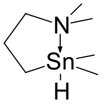

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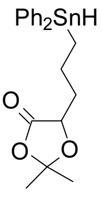

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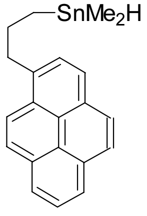
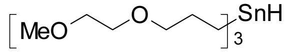


(**22-7**)



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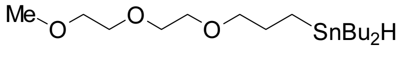
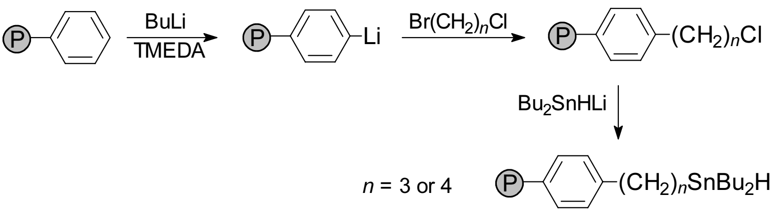


(**22-9**)

Polymer-supported Reagents[70, 71]

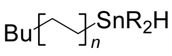
An alternative solution is to use organotin reagents supported on an insoluble, but porous, polymer; at the end of the reaction, the polymer can be filtered off, and the catalyst can be regenerated.[72] Most of the work in this field has involved polymer-bound tin hydrides (for hydrogenolysis of halides, thiocarbonyl compounds, or hydrostannation of ketones),[73–76] but also tin chlorides (for use as Lewis acids),[77] allylstannanes (for allylation),[78] distannanes (for photolytic generation of stannyl radicals),[79] oxides and hydroxides (for lactonisation of hydroxyacids),[80] and vinylstannanes (for Stille coupling)[36]. The polymer-bound $SeSnBu_3$ group has been used as a nucleophilic source of selenium.[81]

The organotin group is usually attached to the polymer (usually polystyrene) by using conventional organotin methodology, for example:[82]



(22-8)

In a rather different approach, the oligomeric stannanes **22-10** and **22-11** have been prepared by treating the “living” polyethylene or polystyrene anions with the appropriate tin halide. These stannanes are soluble in boiling toluene, where they can be used for reducing alkyl or aryl halides, but on cooling the organotin compounds separate and can be recovered.[83]



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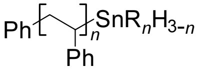

(**22-11**)

References to Chapter 22

22.1 In the database, the keyword for the use of organotin reagents in organic synthesis is *orgsyn*; the keyword *synthesis* is used for the synthesis of organotin compounds.
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23 Applications, Environmental Issues, and Analysis

23.1 Applications[1–3]

Triorganotin compounds generally have a high biological activity, and are used as agricultural biocides, as marine antifoulants, and as wood preservatives. Diorganotin compounds are used as stabilisers for poly(vinyl chloride) (PVC) and as homogeneous catalysts, and monoorganotin compounds find applications as synergists for PVC stabilisation, and in glass coating. A more detailed list is given in Table 23-1. These applications, together with a number of relatively minor ones, account for the consumption of about 25,000 tonnes of tin a year,[3] some 10% of the total production of tin being used to make organotin chemicals.

Table 23-1 Applications of organotin compounds.

Application	Compound
	R_3SnX
Agriculture	
fungicides	Ph_3SnX (X = OH, OAc)
acaricides	$[(PhCMe_2CH_2)_2Sn]_2O$
Antifoulants	$(Bu_3Sn)_2O$ Ph_3SnX (X = OH, OAc, F, Cl etc.) $(CH_2CHMeCO_2SnBu_3)_n$
Wood preservatives	$(Bu_3Sn)_2O$ Bu_3Sn(naphthenate)
Disinfectants	$(Bu_3Sn)_2O$ $Bu_3SnOCOPh$
	R_2SnX_2
PVC stabilisers	$R_2Sn(SCH_2CO_2CH_2CHEtBu)_2$ (R = Me, Bu, Oct) $(R_2SnOCOCH{=}CHCO_2)_n$ $R_2Sn(OCOCH{=}CHCO_2R)_2$ (R = Bu, Oct) $R_2Sn(OCOC_{11}H_{23})_2$ (R = Bu, Oct)
Homogeneous catalysts	
polyurethane formation	$Bu_2Sn(OCOC_{11}H_{23})_2$
transesterification	Bu_2SnO $(ClBu_2SnOSnBu_2Cl)_2$
silicone vulcanisation	$Bu_2Sn(OCOC_{11}H_{23})_2$
Film-forming on glass	Me_2SnCl_2
	$RSnX_3$
PVC stabilisers	$RSn(SCH_2CO_2Oct^i)_3$ (R = Me, Bu, Oct) $(BuSnS_{1.5})_4$
Homogeneous catalysts	$(BuSnO_2H)_n$
Film-forming on glass	$BuSnCl_3$

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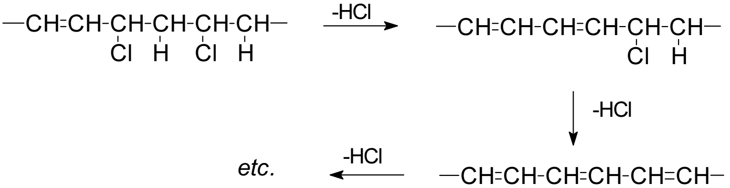
Many of the chemical applications of organotin compounds, apart from their use in the synthesis of fine chemicals, depend on the enhanced reactivity that results from replacing the proton in a compound HX by an organotin group to give the more polar $\equiv Sn^{\delta+}X^{\delta-}$, when the behaviour of the compound both as a nucleophile and an electrophile (or Lewis acid or base) is increased (Section 3.1.1).

PVC Stabilisation

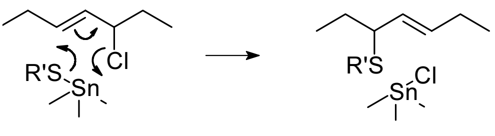
The principal industrial application of organotin compounds is as stabilisers for poly(vinyl chloride).[1, 2, 4] This accounts for the consumption of about 20,000 tonnes of tin a year, and the market is growing by about 4% annually.[3] A variety of derivatives have been used such as dibutyltin dilaurate and dibutyltin maleate, but it is the dialkyltin dithiolates, $R_2Sn(SR')_2$, that dominate the field, the most important examples being the dialkyltin "diisooctylthioglycolates", $R_2Sn(SCH_2CO_2CH_2CHEtBu)_2$ (Table 23-1). These are often used in synergistic mixture with the corresponding monoorganotin trithiolates, $RSn(SR')_3$.

In the course of its fabrication, poly(vinyl chloride) is heated to about 200 °C, which may lead to the progressive elimination of HCl with the formation of a conjugated polyene (equation 23-1), during which the colour changes to yellow, then red, and then black, and the polymer becomes hard and brittle. The elimination is initiated at allylic defect sites in the polymer, and the HCl which is eliminated catalyses further elimination. Organotin compounds, at the level of 5–20 g per kg of polymer, are very effective in preventing this colouration and embrittlement. This makes it possible, for example, to manufacture clear PVC bottles by blow moulding, which have gained approval for food packaging because of the low leach rate and low toxicity of the stabilisers.



(23-1)

The organotin thiolate stabilisers appear to perform at least a dual function.[5–7] First they exchange the chloride at the allylic sites to give an allyl mercaptan which is thermally more stable and does not act as a site for initiating the elimination.



(23-2)

Second, they scavenge the HCl which is eliminated, to give the dialkyltin dichloride and thiol, which do not catalyse further elimination.

$$R_2Sn(SR')_2 \xrightarrow{HCl} R_2Sn(SR')Cl + HSR' \xrightarrow{HCl} R_2SnCl_2 + 2HSR' \qquad (23\text{-}3)$$

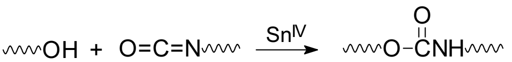
The synergism between the compounds $R_2Sn(SR')_2$ and $RSn(SR')_3$ results from the ready exchange between the ligands Cl and SR′. The monoalkyltin compound $RSn(SR')_3$ is the more effective in deactivating the allylic sites and scavenging the HCl, but this results in the formation of the trichloride $RSnCl_3$ which, by virtue of its Lewis acidity, catalyses further HCl elimination. The function of the dialkyltin dithiolate is to exchange its SR′ ligands for Cl in the trichloride, to give $RSn(SR')_2Cl$, $RSn(SR')Cl_2$, and R_2SnCl_2, which are weaker Lewis acids and are not catalytic.[8, 9]

$$RSnCl_3 + R_2Sn(SR')_2 \longrightarrow R_2Sn(SR')Cl + RSnCl_2(SR') \qquad (23\text{-}4)$$

$$RSnCl_3 + 2R_2Sn(SR')_2 \longrightarrow 2R_2Sn(SR')Cl + RSnCl(SR')_2 \qquad (23\text{-}5)$$

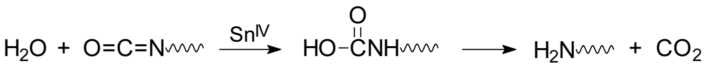
Polyurethane Formation

The role of organotin compounds in catalysing the reaction of polyfunctional alcohols and isocyanates (equation 23-6) to give polyurethanes is discussed in Section 14.1.2; at 1 mol% concentration, the reactivity can be increased 30,000–80,000 fold.[10] Amines can be used as co-catalysts when they enhance the nucleophilicity of the oxygen of the SnOR group by coordinating to the tin. The products may be used as surface coatings, or as flexible or rigid foams.



$$\sim\sim OH + O{=}C{=}N\sim\sim \xrightarrow{Sn^{IV}} \sim\sim O\text{-}\overset{\displaystyle O}{\overset{\|}{C}}NH\sim\sim \qquad (23\text{-}6)$$

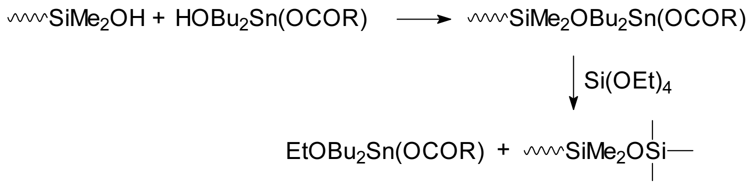
The most common catalysts are dibutyltin dioctanoate, dibutyltin dilaurate, or stannous octanoate at 0.1–1.0% concentration, and the distannoxanes $(XR_2Sn)_2O$ are particularly effective.[11] When foams are being formed, the "blowing" can be carried out by CO_2 which is released by the hydrolysis reaction (equation 23-7).



$$H_2O + O{=}C{=}N\sim\sim \xrightarrow{Sn^{IV}} HO\text{-}\overset{\displaystyle O}{\overset{\|}{C}}NH\sim\sim \longrightarrow H_2N\sim\sim + CO_2 \qquad (23\text{-}7)$$

Silicone Vulcanisation

Silicone elastomers are used as moulding agents in, for example, taking dental impressions, and organotin compounds are used as catalysts for room temperature vulcanisation (RTV). A liquid linear polydimethylsiloxane, with terminal OH groups, is mixed with $Si(OEt)_4$ as a cross-linking agent, together with a catalyst such as dibutyltin dilaurate, dibutyltin dioctanoate, or stannous octanoate in 0.1–1% concentration. In the presence of moisture, the organotin dicarboxylate is hydrolysed to the hydroxycarboxylate, which transforms the terminal OH groups into the more reactive SiOSn groups, which react with the tetraethoxysilane to initiate the cross-linking and regenerate the catalyst as the tin ethoxide.[12]



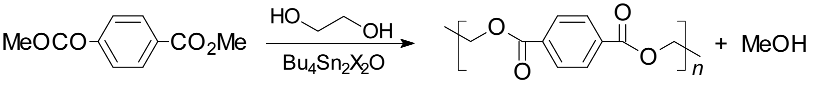
$$\begin{aligned}&\sim\sim SiMe_2OH + HOBu_2Sn(OCOR) \longrightarrow \sim\sim SiMe_2OBu_2Sn(OCOR)\\ &\xrightarrow{Si(OEt)_4} EtOBu_2Sn(OCOR) + \sim\sim SiMe_2O\overset{|}{\underset{|}{Si}}\text{—}\end{aligned} \qquad (23\text{-}8)$$

The distannanes $(RCO_2)R_2SnSnR_2(O_2CR)$ (Section 18.2.2) can be used as latent catalysts; in the absence of air they are not catalytic, but in air they are oxidised to the distannoxanes $(RCO_2)R_2SnOSnR_2(O_2CR)$ which catalyse the condensation.[13–15] β-Acyloxystannanes, which eliminate tin carboxylates at elevated temperatures, can also be used as latent catalysts.

Transesterification[16, 17]

Transesterification of an ester is commonly carried out by heating it with an excess of an alcohol in the presence of a strong acid catalyst such as toluene p-sulfonic acid. On the industrial scale, this presents problems of corrosion and of decomposition and colouration of the excess alcohol. Organotin compounds are alternative catalysts: they can be used in small amounts (0.1–0.25%), they present no corrosion problem, and the excess of alcohol is not dehydrated or decolourised, and can be recirculated.

Many different types of organotin compounds have been patented as catalysts, e.g. Bu_2SnO, $BuSnO_2H$, $Bu_2Sn(OAc)_2$, but the most effective appear to be the tetraalkyldistannoxanes, $XR_2SnOSnR_2X$[16, 18] which may act as bidentate Lewis acids. An example is provided by the transesterification of methyl terephthalate with ethylene glycol to give poly(ethylene terephthalate) (Terylene, Dacron).



(23-9)

Antifouling Agents

The fouling of ships' hulls by weed, algae, and shellfish increases the weight and roughness of the hull and results in increased fuel consumption, premature drydocking, and the cost of cleaning. The most effective solution is provided by organotin biocides, which came into use in the early 1970s, replacing the Cu_2O that previously had been used.[19–22]

Initially the tributyltin oxide or fluoride antifoulant (TBT) was incorporated into the paint, giving what is termed a “free association” paint. The uncontrolled release of the organotin was initially rapid, then steadily declined, and a paint of this type would typically give 18–24 months’ protection before drydocking was necessary. In 1974, “self polishing” antifouling paints were introduced in which the tin formed part of an acrylic copolymer. This undergoes hydrolysis when the ship is in motion (equation 23-10), releasing tributyltin oxide at a steady and controlled rate of about 1.6 μg (Sn) cm^{-2} per day, which may be equivalent to a total of about 100 g per day for a large ship, and this can give at least 5 years’ protection between drydockings. By 1991, 80% of ships of over 4,000 tons deadweight carried a TBT-based antifoulant, and in 1993, self-polishing paints accounted for 69% of the antifouling market.[23] Copolymer paints were also used for treatment of the nets in fish-farming.

$$\left[\mathrm{CH_2{-}}\underset{\mathrm{CO_2SnBu_3}}{\mathrm{CH}}\right]_n \xrightarrow{\mathrm{H_2O}} \left[\mathrm{CH_2{-}}\underset{\mathrm{CO_2H}}{\mathrm{CH}}\right]_n + \mathrm{(Bu_3Sn)_2O} \qquad (23\text{-}10)$$

However, the TBT that was so effective against the fouling also had an adverse effect on non-target organisms, and caused the collapse of oyster farming in some areas such as Arcachon Bay in south west France (see below), so that the use of the organotin antifoulants is now banned (Section 23.2).

Timber Treatment[1, 20, 24]

Wood is attacked by insects, fungi, and bacteria. Tributyltin compounds are powerful fungicides and bactericides, and tributyltin oxide or naphthenate has been used for wood preservation since the early 1960s. The wood is often impregnated with the organotin compound in an organic solvent by a double-vacuum process. A sealed chamber containing the wood is evacuated to low pressure. The chamber is flooded with the preservative and the vacuum is released so that the preservative is forced into the wood, then the vacuum is restored to remove the excess solution.

It is suggested that the terminal OH groups of the cellulose chain are stannylated and thereby protected from attack.

Agricultural Chemicals[21]

The tributyltin compounds are both fungitoxic and phytotoxic, but other triorganotin compounds show a sufficiently wide separation between the two properties to render them useful in treating fungal diseases in crops. They show good adhesion to the leaf surface, and are rain resistant; there appears to be no evidence for systemic action. Their impact on the environment is reduced as they are degraded by light and microorganisms to environmentally benign monoorganotin or inorganic tin compounds.

Triphenyltin hydroxide (Fentin) and triphenyltin acetate (Brestan) are used to combat potato blight, leaf spot on celery and sugar beet, rice blast, and coffee leaf rust. Tricyclohexyltin hydroxide (Plictran), bis(trineophyltin) oxide (Vendex or Torque), and 1-tricyclohexylstannyl-1,2,4-triazole (Peropal) have also been used for the contol of mites on apples, pears, and citrus fruits.

Glass Coating

Thin films of tin oxide on glass are often applied by exposing the surface at about 600 °C to the vapour of an organotin chloride, usually butyltin trichloride, which is easier to handle, and presents less of a corrosion problem, than does tin tetrachloride. Films of up to 10 nm thickness are used to strengthen glassware so that lighter and cheaper glass containers can be used. Films of greater than 1 μm can be doped to provide a p-type or n-type semiconductor or conductor, which finds applications such as in deicing windscreens, security glass, or display systems. The glass is also finding increasing application in window glazing because of its low heat emissivity, which reduces the heat loss from buildings in winter and the overheating in summer.

23.2 Environmental Issues[25, 26]

The effectiveness of organotin compounds as industrial and agricultural biocides carries with it the hazard of their toxicity to higher life forms. This was headlined in 1954 when a preparation for the treatment of boils containing triethyltin iodide was marketed in France under the name of Stalinon, and which caused the death of 102 people, and a recent incident in China involving industrial lard contaminated with Me_2SnCl_2 which caused the death of two people.[27]

Some approximate values for mammalian toxity expressed in mmol Sn per kg body weight are given in Table 23-2. These should be taken as indicative only; figures for individual compounds are given in Sax's Dangerous Properties of Industrial Materials,[28] in the Registry of Toxic Effects of Chemical Substances (RTECS),[29] and the Dictionary of Substances and Their Effects (DOSE).[30] The general trend is that the toxicity decreases for compounds R_nSnX_{4-n} in the sequence $n = 3 > 2 > 1$, and as the size of R increases, though ethyl compounds are often more toxic than methyl compounds. The tetraalkylstannanes ($n = 4$) apparently exert their toxicity through the trialkyltin compounds ($n = 3$) that they form on rapid dealkylation.

Table 23-2 Mammalian toxicity of organotin compounds R_nSnX_{4-n}[a].

R	$n =$ 4	3	2	1
Me	1.5	0.07	0.7	4
Et	0.6	0.04	0.3	< 0.008
Bu	> 12	0.7	0.5	8
Oct	> 7	> 8	> 10	9
Ph		0.3		

[a] LD_{50} in mmol/kg for rats, by oral administration.

Control of the manufacture and marketing of organotin compounds has largely removed the human hazard, but the problems associated with the accumulation of organotin, particularly tributyltin, residues in the environment have been a subject of major concern and have resulted in much legislation,[31–33] an extensive literature,[25, 26, 34] and the establishment of an organisation, the ORTEP (Organotin Environmental Programme), which have the aim of disseminating the relevant technical and scientific information.[20]

This arose from the use of organotin compounds as antifouling paints (Section 23.1). In harbours or marinas, or near dockyards and slipways where boats' hulls are cleaned, the concentration of tributyltin could be up to 500 ng Sn L^{-1}.[35] Its degradation in marine water by dealkylation to the less-toxic dialkyl- and monoalkyl-tin compounds, and the non-toxic inorganic tin, has a half-life of one or two weeks. Unlike most other organometallic contaminants, however, tributyltin compounds concentrate in the sediment by a factor of 4.5×10^3 to 2×10^5, and under these conditions the degradation is considerably slower, with a half-life of a few years.[36] These ambient concentrations of TBT can have lethal or irreversible sublethal physiological effects on molluscs and cretaceans, with the local extinction of some species, including farmed oysters.[20, 37]

Legislation to restrict the use of organotin compounds in antifouling paints began in France in 1982 in order to protect the oyster culture industry, and this lead was followed by most of the industrialised countries.[32] The present position is that the International Maritime Organisation (IMO) has agreed a resolution that there should be a global prohibition on the application of organotin antifoulants by 1 January 2003, and that no ships should carry such compounds on their hulls by January 1 2008. At the time of writing (December 2002), however, no country appears to have ratified the treaty.

23.3 Analysis

This concern about organotin compounds in the environment has stimulated a great deal of work on the analysis of organotin compounds.[38]

The classical method for elemental analysis for tin when sufficient of the sample is available is by ashing by combustion in oxygen or by wet ashing and ignition to give SnO_2 which is weighed;[39, 40] alternatively, the product can be reduced to Sn(II) and determined by titration. A simple procedure involving wet ashing with HNO_3/H_2SO_4 then weighing the product as SnO_2 is described by Luijten and van der Kerk.[40, 41]

Most recent work, however, has been focussed on the speciation of trace amounts of organotin compounds in the air or in waters, sediments, or tissues, at amounts down to a few ng Sn.[42–44]

The organotin compounds R_nSnX_{4-n} are extracted then converted into the hydrides R_nSnH_{4-n} with $NaBH_4$, or, more usually, are alkylated to $R_nSnR'_{4-n}$ with a Grignard reagent or with $NaBEt_4$. These volatile, relatively non-polar, compounds are then separated by GLC or HPLC and analysed by techniques such as atomic absorption, flame photometry, or mass spectrometry.[43, 45] At the moment GLC-FP or GLC-MS appear to give the best performance, but of the four steps that are involved in the analysis, namely extraction, derivatisation, separation, and detection, it is not the analysis itself, but rather the extraction and derivatisation that are the major source of errors and are most in need of improvement.

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