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Review

Tin derivatives of organosilicon compounds

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Contents

Abstract

This overview covers the development in synthesis and reactivity of tin(IV) and tin(II) silicon derivatives made during the last decade. Attention is directed towards compounds with at least more than one silicon–tin bond, i.e. compounds with Si─Sn─Si, Sn─Si─Sn, Sn─Sn─Si or Si─Si─Sn sequences in the molecule. Some spectroscopic and structural features will be discussed in addition to their preparation and reactivity.

Keywords: Silicon–tin derivatives; Synthesis; Reactivity; Spectroscopy

1. Introduction

The chemistry of organic derivatives containing silicon and tin atoms with direct Si–Sn contacts has been well established for many years. Stannylsilanes are among some of the most useful reagents available to the synthetic organic chemist today. Surprisingly, despite their importance especially in organic chemistry, only a small number of this kind of compounds is commercially available.

Abbreviations: AIBN, azo-*iso*-butyronitrile; Cp, cyclopentadienyl; Cp*, pentamethylcyclopentadienyl; Cy, cyclo; Dcpe, 1,2-bis(dicyclopentanylphosphino)ethane; THF, tetrahydrofuran; LDA, lithiumdi-*iso*-propylamide; Mes, mesityl; 2,4,6-trimethylphenyl; [2.2.2]crypt, 1,10-diaza-4,7,13,16,21,24-hexaoxabicyclo[8.8.8]hexacosan; 18crown6, 1,4,7,10,13,16-hexaoxacyclooctadecane; Hypersilyl, tris(trimethylsilyl)silyl

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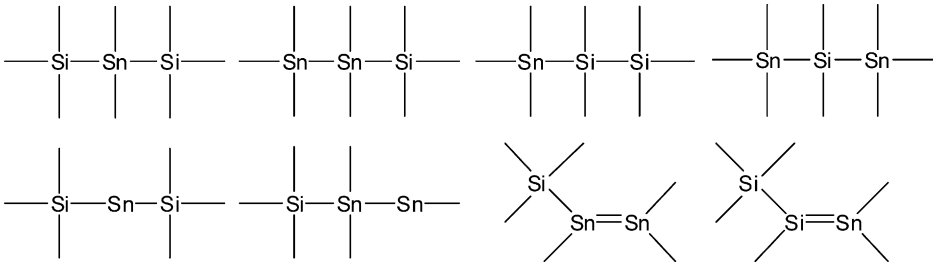
The synthesis and reactivity of Si–Sn derivatives has been reviewed before. Many of the standard reactions in organic chemistry were summarized in a review by Schumann and Schumann at the beginning of the 1990s [1]. Nevertheless, little is known about derivatives containing more than one Si–Sn bond including compounds featuring formal multiple bonding between tin–tin or tin–silicon atoms, for example compounds with sequences in the main chain of the molecule. Therefore this article will focus on work published since the beginning of the 1990s for the latter derivatives, with reference made to earlier work if relevant. This overview consists of two parts, one for the tin(IV) and one for the tin(II) derivatives.

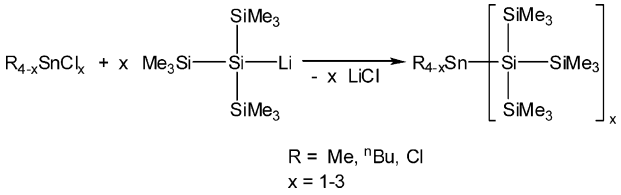


The interest in tin(IV)–silicon compounds has been focused on open chain and cyclic derivatives as potential precursors for novel polymeric materials, catalytic systems or the modification of surfaces as well as on pure scientific aspects such as novel structural behaviour, novel synthetic routes or as reagents in organic synthesis. The chemistry of tin(II)–silicon derivatives mainly concentrates on the investigation of synthesis and reactivity of stannylenes and their structural behaviour.

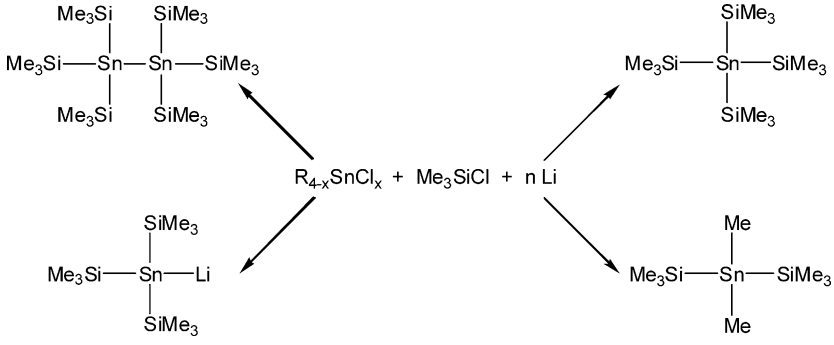
2. The synthesis of tin(IV)–silicon derivatives

2.1. Chain-type compounds

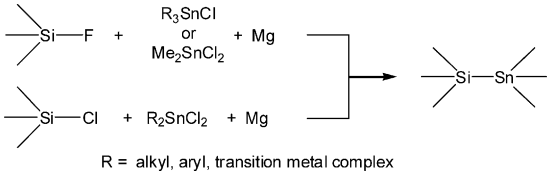
Mallela und Geanangel described reactions of lithium tris(trimethylsilyl)silanide with various organotin(IV) chlorides in the early 1990s [2]. For example, starting from $SnCl_4$ they obtained the first example of a dihalogen substituted Si–Sn–Si derivative, $[(Me_3Si)_3Si]_2SnCl_2$.



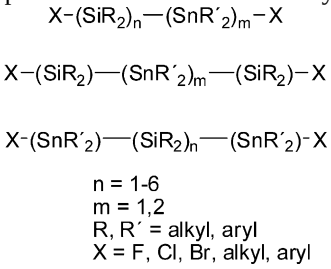
Several groups studied the reaction of $SnCl_4$ with Me_3SiCl/Li. In 1968, Bürger et al. prepared tetrakis(trimethylsilyl)stannane from the reaction in THF at low temperatures [3]. However, under almost identical conditions Mallela and Geanangel obtained hexakis(trimethylsilyl)-distannane $(Me_3Si)_3Sn–Sn(SiMe_3)_3$ in modest yields [4]. In a similar reaction Cardin et al. isolated the lithium derivative $LiSn(SiMe_3)_3$ in 44% yield [5]. $LiSn(SiMe_3)_3$ was previously prepared by reacting $(Me_3Si)_4Sn$ with alkyllithiums in THF [6,36]. Recently a structural study on $(Me_3Si)_3ELi$ (E = Si, Ge, Sn) study was reported [7]. We found that the reaction of dimethyldichlorostannane with Me_3SiCl/Li results in the clean formation of $(Me_3Si)_2SnMe_2$ in excellent yields [25].



In the mid of the 1990s we introduced a convenient one-pot synthesis for the formation of silicon–tin bonds in this field of chemistry. Reacting chlorostannanes and chloro- or fluorosilanes in the presence of magnesium resulted in the formation of a Si–Sn coupled compound. In contrast to lithium mediated coupling reactions, these reactions were generally found to proceed in good yields and nearly without any side reactions [8,9]. Moreover, they were also found suitable for the synthesis of silylated stannanes bearing a transition metal complex group.



In addition, this synthetic approach was successfully applied in the syntheses of a large number of open chain Si–Sn derivatives. Compounds with terminal organotin as well as terminal organosilicon groups (compounds **1**–**3**) were prepared with excellent selectivity and in high yields [10–12].

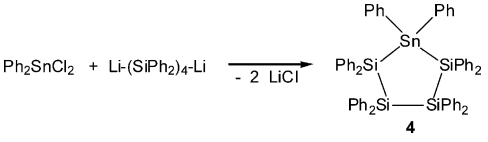


Other synthetic routes towards linear stannasilanes using hydrido-tin substituted Si–Sn derivatives as starting materials as well as classical metathesis reactions are described in the literature [11–14,28,40].

Moreover, cyclic silanes with exocyclic di- and triorganotin units were prepared following a similar reaction pathway [13] but also via salt elimination reactions [14] (Scheme 1).

2.2. Rings and cage like derivatives

For a long period, only one example of a cyclic Si–Sn derivative with more than one Si–Sn bond was known from literature. Back in 1966 Hengge and coworkers described the synthesis of a perphenylated stannatetrasilacyclopentane (**4**) by reacting 1,4-dilithio-octaphenyltetrasilane with diphenyldichlorostannane [15].



4

It took more than 30 years until the next example of such a cyclic Si–Sn derivative was reported in literature. This is in sharp contrast to the chemistry of the corresponding cyclic silanes, which was intensely investigated in the meantime. The lack of examples for cyclic Si–Sn compounds was surprising, especially as they are believed to be potential precursors for ring opening polymerisation reactions due to the lower stability of the Si–Sn bond. During the last years, our group synthesized a large variety of cyclic compounds containing only tin and silicon atoms in the ring skeleton. An overview about these compounds and the substitution pattern obtained so far is given in Scheme 2 [16–24].

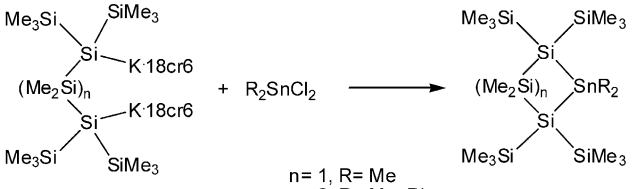
Starting materials, yields, and the ^{119}Sn and ^{29}Si NMR data of some of these derivatives are summarized in Table 1. Nevertheless, due to the small number of known compounds a more general discussion of the spectroscopic properties failed until now. First attempts are presented in Section 2.5.

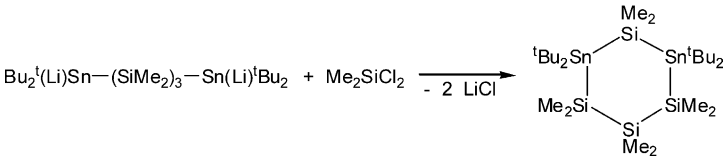
Three general strategies for the synthesis of such compounds proved successful so far. One is a simple one pot synthesis by reacting α,ω-dihaloorganooligosilanes (X–(SiR$_2$)$_n$–X; X = F, Cl; n = 1–6) with diorganodichlorostannanes in the presence of magnesium and THF as solvent. Depending on the steric demand of the substituents on the tin and/or silicon atoms, the ring sizes of the products range from 4 to 8.

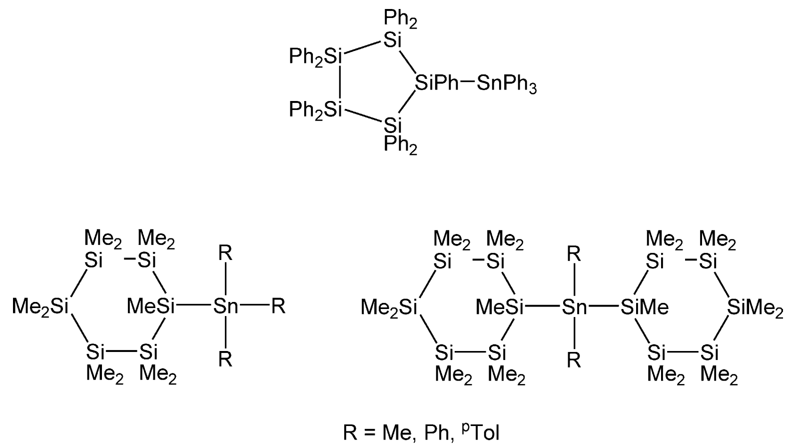
Surprisingly, one of the key steps of the reaction cascade towards these ring compounds is the formation of di- or oligostannanes. For the reaction of dimethyldichlorosilane with di-*tert*-butyldichlorostannane, ClSiMe$_2$(^{t}Bu$_2$Sn)$_2$SiMe$_2$Cl **5** was isolated and fully characterized by NMR spectroscopy as well as by single crystal X-ray analysis [20]. The transformation into the four-membered ring might take place via an insertion of magnesium into the central tin–tin bond. Similar results were observed recently for reactions with Ph$_2$SnCl$_2$ [25] (Scheme 3).

In a second synthetic route, cyclic Si–Sn derivatives were obtained in a stepwise manner by starting from α,ω-bis(^{t}butylhydridostannyl)silanes (see Section 2.1) followed by halogenation and a reductive ring closing step with magnesium [17].

A third reaction pathway towards the above-mentioned (Scheme 2) cyclic compounds is a classical salt elimination reaction of silyl alkali metal derivatives [26,27] or α,ω-dilithiostannides [28] with diorganodichlorostannanes or diorganodichlorosilanes, respectively.





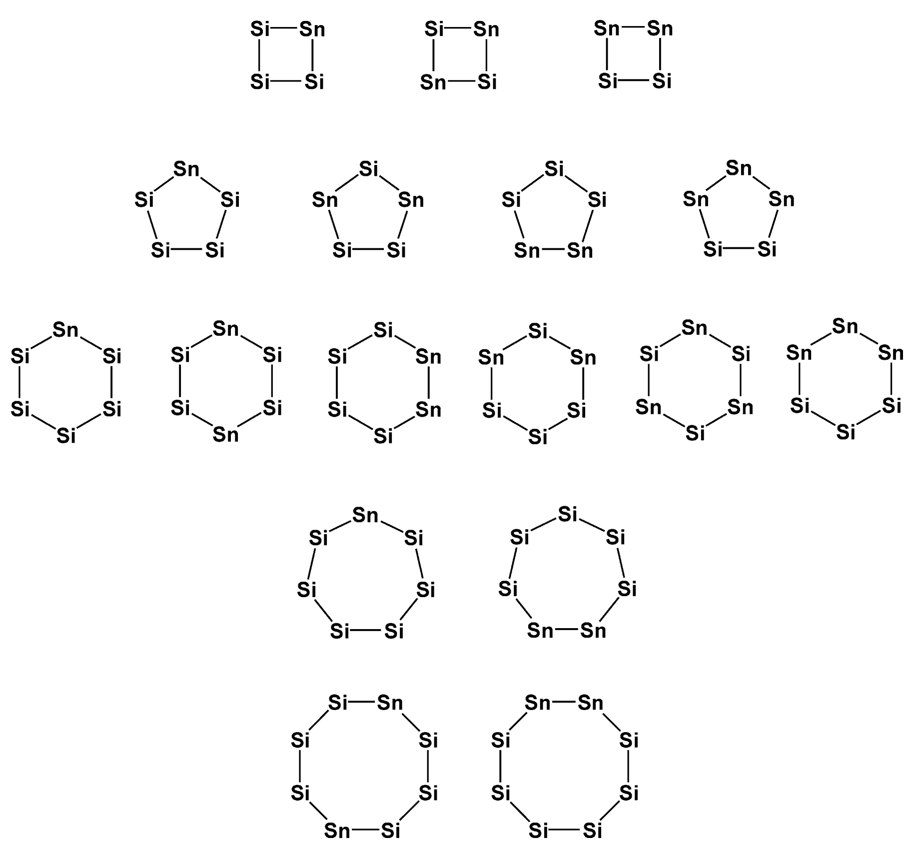


Scheme 1. Cyclohexasilanes with exocyclic tin moieties.

Unfortunately, the reaction of tin hydrides with organoalkali compounds is complex. Frequently, coupling reactions and rearrangement products are obtained and the outcome of the reaction can hardly be forecast. For example, the reaction of the branched derivative **6** with 3 equiv. of LDA did not result in the expected compound with three lithiated terminal tin atoms. Instead, a five-membered ring with a bridging tin–tin unit and one exocyclic dimethylsilyl group was obtained [18]. We were able to confirm this structure by NMR and MS experiments and recently also via X-ray analysis [29] (Scheme 4).

However, until now we failed to use such cyclic compounds in ring opening polymerisations. This is mainly due to the fact that on one hand bulky substituents are able to stabilize the formation of small rings but on the other hand they lower the reactivity of the resulting cyclic systems.

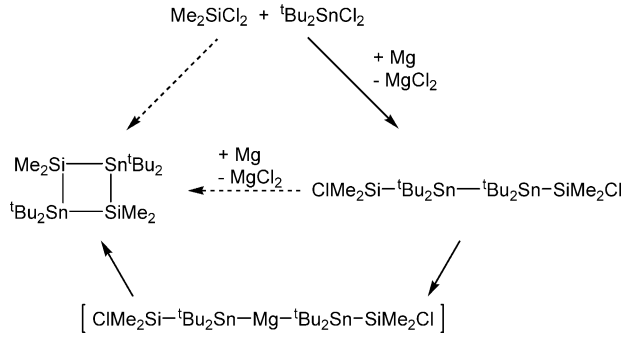
The one-pot synthesis mentioned above can be expanded towards the synthesis of bicyclic Si–Sn derivatives as



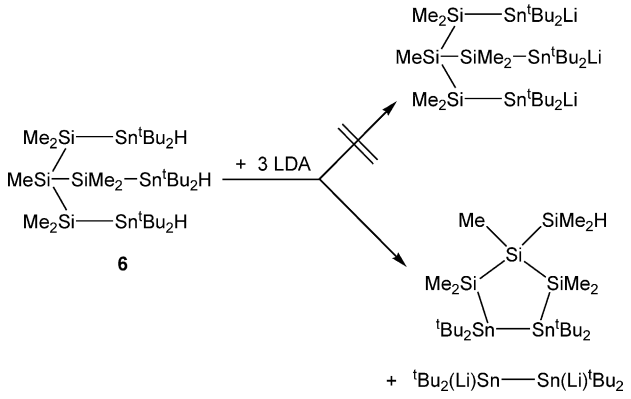
Scheme 2. Substituents at the tin and silicon atoms are omitted for clarity Sn = RR^1Sn; R, R^1 = H, Me, Et, ^{t}Bu, Ph Si = R^2R^3Si; R^2, R^3 = H, Me, Ph.

Table 1
^{119}Sn and ^{29}Si NMR data of selected Si—Sn rings (see Scheme 2)

Product	Starting materials	Yield (%)	δ^{119}Sn (ppm)	δ^{29}Si (ppm)	($J^{117/119}$Sn—^{29}Si) (Hz)	Ref.
Four-membered rings						
[—^{t}Bu$_2$Sn—Me$_2$Si—^{t}Bu$_2$Sn—Me$_2$Si—]	Me$_2$SiCl$_2$ + ^{t}Bu$_2$SnCl$_2$	85	−40.5	−9.1	^1J: 228/239	[20]
[—(Me$_2$Si)$_2$—(^{t}Bu$_2$Sn)$_2$—]	Cl—(Me$_2$Si)$_2$—Cl + ^{t}Bu$_2$SnCl$_2$	84	−19.4	−11.4	^1J: 216/226, ^2J: 249/261	[17]
[—(Me$_3$Si)$_2$SiSiMe$_2$(SiMe$_3$)$_2$Si—Me$_2$Sn—]	K(Me$_3$Si)$_2$SiSiMe$_2$Si(SiMe$_3$)$_2$K + Me$_2$SnCl$_2$	–	−174.0	−7.8, −13.0, −89.0	^2J: 45, ^2J: 52/54, ^1J: 180/188	[27]
Five-membered rings						
[—(Me$_2$Si)$_3$—(^{t}Bu$_2$Sn)$_2$—]	Cl—(Me$_2$Si)$_3$—Cl + ^{t}Bu$_2$SnCl$_2$	82	−98.5	−33.9, −37.4	^1J: 207/217, ^2J: 66, ^2J: 67	[17]
[—(Me$_2$Si)$_2$—(^{t}Bu$_2$Sn)$_3$—]	Br^{t}Bu$_2$Sn(Me$_2$Si)$_2$Sn^{t}Bu$_2$Br + ^{t}Bu$_2$SnCl$_2$	84	−28.2, −95.3	−30.8	^1J: 196/206, ^2J: 62	[17]
[—(Me$_2$Si)$_2$—^{t}Bu$_2$Sn—Me$_2$Sn—^{t}Bu$_2$Sn—]	^{t}Bu$_2$Sn(H)—(Me$_2$Si)$_2$Sn(H)^{t}Bu$_2$ + Me$_2$Sn(NEt$_2$)$_2$	80	−117.6, −253.1	−32.3	^1J: 243/254, ^2J: 97/93, ^{2+3}J: 59/62	[22]
[—(Me$_3$Si)$_2$Si(SiMe$_2$)$_2$(SiMe$_3$)$_2$Si—Me$_2$Sn—]	K(Me$_3$Si)$_2$Si(SiMe$_2$)$_2$Si(SiMe$_3$)$_2$K + Me$_2$SnCl$_2$	55	−118.6	−5.4, −22.2, −137.5	^2J: 44, ^2J: 61, ^1J: 186/192	[26,27]
[—(Me$_3$Si)$_2$Si(SiMe$_2$)$_2$(SiMe$_3$)$_2$Si—Ph$_2$Sn—]	K(Me$_3$Si)$_2$Si(SiMe$_2$)$_2$Si(SiMe$_3$)$_2$K + Ph$_2$SnCl$_2$	48	−85.9	−3.6, −21.2, −132.0	^2J: 48, ^2J: 71, ^1J: 176/184	[26,27]
[—(Me$_2$Si)$_4$—(^{t}Bu$_2$Sn)—]	^{t}Bu$_2$Sn(H)—(Me$_2$Si)$_4$Sn(H)^{t}Bu$_2$ + LDA	54	−151.0	−38.0, −36.8	^2J: 73, ^1J: 261/276	[28]
[—(Me$_2$Si)$_2$—^{t}Bu$_2$Sn—Me$_2$Si—^{t}Bu$_2$Sn—]	^{t}Bu$_2$Sn(Li)—(Me$_2$Si)$_2$Sn(Li)^{t}Bu$_2$ + Me$_2$SiCl$_2$	25	−147.6	−32.3, −31.1	^1J: 281/294, ^2J: 90, ^1J: 212/228	[28]
[—(Me$_2$Si)$_2$—^{t}Bu$_2$Sn—Ph$_2$Si—^{t}Bu$_2$Sn—]	^{t}Bu$_2$Sn(Li)—(Me$_2$Si)$_2$Sn(Li)^{t}Bu$_2$ + Ph$_2$SiCl$_2$	20	−152.3	−31.5, −11.7	^1J: 265/274, ^2J: 67, ^1J: 182/190	[28]
[—Me$_2$Si(H)MeSi—(Me$_2$Si—^{t}Bu$_2$Sn)$_2$—]	MeSi(Me$_2$Si—^{t}Bu$_2$Sn(H))$_3$ + LDA, [—Me$_2$Si(Cl)MeSi—(Me$_2$Si—^{t}Bu$_2$Sn)$_2$—] +LAH	25, 85	−97.1	−28.1, −33.4, −76.0	^1J: 200/209, ^2J: 76, ^3J: 23, ^2J: 52	[18,29]
[—Me$_2$Si(Cl)MeSi—(Me$_2$Si—^{t}Bu$_2$Sn)$_2$—]	MeSi(Me$_2$Si—Cl)$_3$ + ^{t}Bu$_2$SnCl$_2$	90	−98.3	−29.2, 32.3, −71.9	^1J: 199/209, ^2J: 72, ^3J: 31, ^2J: 55/57	[29]
Six-membered rings						
[—Ph$_2$Sn—Me$_2$Si—]$_3$	Me$_2$SiCl$_2$ + Ph$_2$SnCl$_2$	87	−212.2	−35.0	^1J: 345/361	[20]
[—(Me$_2$Si)$_4$—(Me$_2$Sn)$_2$—]	F—(Me$_2$Si)$_4$—F + Me$_2$SnCl$_2$	35	−252.0	−36.4, −39.9	^1J: 349/365, ^2J: 94/98, ^2J: 92/96	[22,23]
[—(Me$_2$Si)$_4$—(Ph$_2$Sn)$_2$—]	F—(Me$_2$Si)$_4$—F + Ph$_2$SnCl$_2$	30	−222.6	−37.2, −38.3	^1J: 352/369, ^2J: 97/102, ^2J: 107/112	[22,23]
[—(Me$_2$Si)$_4$—(^{t}Bu$_2$Sn)$_2$—]	Cl—(Me$_2$Si)$_4$—Cl + ^{t}Bu$_2$SnCl$_2$	76	−99.7	−34.0, −38.1	^1J: 204/214, ^2J: 54, ^2J: 89, ^3J: 62	[17]
[—(Me$_2$Si)$_5$—(Me$_2$Sn)—]	F—(Me$_2$Si)$_5$—F + Me$_2$SnCl$_2$	45	−242.6	−38.8, −39.2, −42.1	^1J: 370/387, ^2J: 88/93, ^3J: not obs.	[16]
[—(Me$_2$Si)$_5$—(Ph$_2$Sn)—]	F—(Me$_2$Si)$_5$—F + Ph$_2$SnCl$_2$	40	−223.1	−34.9, −38.4, −41.5	^1J: 350/368, ^2J: 94/99, ^3J: 24	[16]
[—(Me$_2$Si)$_5$—(^{t}Bu$_2$Sn)—]	^{t}Bu$_2$Sn(Cl)—(Me$_2$Si)$_5$Sn(Cl)^{t}Bu$_2$ + Mg	35	−28.7	−29.5, −31.0, −38.3	^1J: 172/181, ^2J: 60, ^3J: not found	[24]
[—(Me$_2$Si)$_3$—^{t}Bu$_2$Sn—Me$_2$Si—^{t}Bu$_2$Sn—]	^{t}Bu$_2$Sn(Li)—(Me$_2$Si)$_3$Sn(Li)^{t}Bu$_2$ + Me$_2$SiCl$_2$	70	−156.2	−38.2, −37.0, −30.7	^2J: 72, ^1J: 261/273, ^2J: 95, ^1J: 218/229	[28]
[—(Me$_2$Si)$_2$—(Ph$_2$Sn)—]$_2$	F—(Me$_2$Si)$_2$—F + Ph$_2$SnCl$_2$	45	−223.0	−31.8	^1J: 356/372, ^2J: 98/102	[22,23]
[—(Me$_2$Si)$_2$—(MePhSn)—]$_2$	F—(Me$_2$Si)$_2$—F + MePhSnCl$_2$	56	−238.4 (isomer A), −239.7 (isomer B)	−32.5, −32.7	^1J: 368/385, ^2J: 100/105, ^1J: 368/386, ^2J: 99/104	[22,23]
[—(Me$_2$Si)$_2$—(^{t}Bu$_2$Sn)—]$_2$	^{t}Bu$_2$Sn(H)—(Me$_2$Si)$_2$Sn(H)^{t}Bu$_2$ + LDA	25	−164.2	−33.6	^1J: 260/272, ^2J: 80	[28]
[—(Me$_2$Si)$_3$—^{t}Bu$_2$Sn—Me$_2$Sn—^{t}Bu$_2$Sn—]	^{t}Bu$_2$Sn(H)—(Me$_2$Si)$_3$Sn(H)^{t}Bu$_2$ + Me$_2$Sn(NEt$_2$)$_2$	75	−125.0, −268.0	−33.3, −36.9	^1J: 228/239, ^2J: 93/97, ^2J: 58/60, ^3J: 13	[22,23]
[—(Me$_2$Si)$_3$—(Ph$_2$Sn)$_3$—]	Cl—(Me$_2$Si)$_3$—Cl + Ph$_2$SnCl$_2$/Mg	20	−213.2, −230.1	−30.6, −36.8	^1J: 349/364, ^2J: 92/95, ^2J: 88/92, ^3J: 14	[22,23]
Seven- and eight-membered rings						
[—(Me$_2$Si)$_6$—(Me$_2$Sn)—]	F—(Me$_2$Si)$_6$—F + Me$_2$SnCl$_2$	15	−243.6	−38.5, −39.1, −41.5	^1J: 373/390, ^2J: 88/92, ^3J: not obs.	[16]
[—(Me$_2$Si)$_6$—(Ph$_2$Sn)—]	F—(Me$_2$Si)$_6$—F + Ph$_2$SnCl$_2$	32	−224.1	−34.4, −38.7, −41.4	^1J: 354/370, ^2J: 90/94, ^3J: 30	[16]
[—(Me$_2$Si)$_6$—(MePhSn)—]	F—(Me$_2$Si)$_6$—F + MePhSnCl$_2$	20	−240	−36.6, −38.9, −41.5	^1J: 364/381, ^2J: 91/95, ^3J: not found	[23]
[—(Me$_2$Si)$_6$—(^{t}Bu$_2$Sn)—]	^{t}Bu$_2$Sn(Cl)—(Me$_2$Si)$_2$Sn(Cl)^{t}Bu$_2$ + Mg	45	−30.6	−30.4, −31.7, −34.4	^1J: 178/185, ^2J: 62, ^3J: 16	[24]
[—(Me$_2$Si)$_3$—(Ph$_2$Sn)—]$_2$	F—(Me$_2$Si)$_6$—F + Me$_2$SnCl$_2$	15	−222.4	−28.2, −34.7	^1J: 320/335, ^3J: 33, ^2J: 39	[23]
[—(Me$_2$Si)$_3$—(Me$_2$Sn)—]$_2$	F—(Me$_2$Si)$_6$—F + Ph$_2$SnCl$_2$	20	−238.2	−33.1, −36.1	^1J: 341/355, ^3J: 36, ^2J: 40	[23]
[—(Me$_2$Si)$_3$—(MePhSn)—]$_2$	F—(Me$_2$Si)$_6$—F + MePhSnCl$_2$	10	−232.2	−30.2, −35.2	^1J: 329/345, ^3J: 36, ^2J: 37	[23]



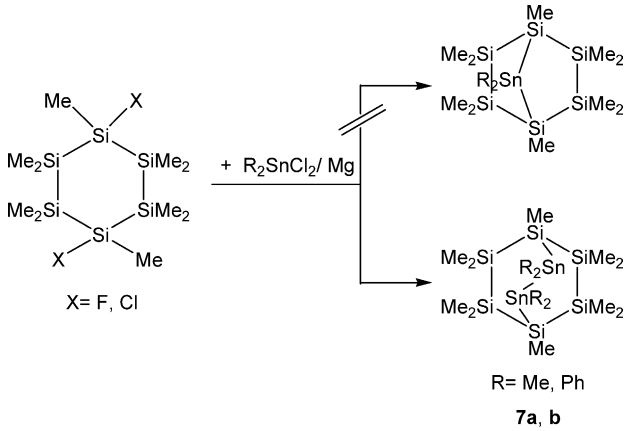
Scheme 3. Possible reaction mechanism for the formation of a four-membered Si—Sn ring.



Scheme 4. Reaction of the branched compound **6** with 3 equiv. of LDA.

well. Therefore, the reaction of equimolar amounts of 1,4-dihalodecamethylcyclohexasilanes Me(X)Si($Me_2SiSiMe_2$)$_2$ Si(X)Me; (X = F; Cl) and diorganodihalostannanes R_2SnCl_2 (R = Me, Ph) with magnesium provided access to the 1,2,3,4,5,6-hexasila-7,8-distannabicyclo[2.2.2]octanes **7a** and **7b** in moderate yields (Scheme 5) [30].

Reactions in a 1.5:1 molar ratio of silane:stannane: magnesium increased the yields of the bicyclic compounds to up to 35%. When exact stoichiometric amounts

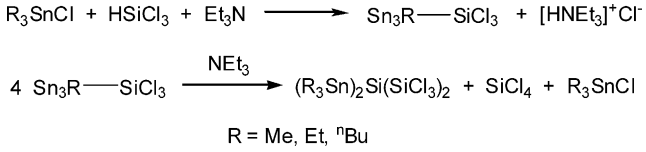


Scheme 5. Reaction of the 1,4-dihalocyclohexasilanes with R_2SiCl_2 in the presence of magnesium.

of 2:1 were used, unidentified byproducts without Si–Sn moieties were observed, preventing the isolation of bicyclic derivatives from the reaction mixtures. There is no evidence for the formation of a thermodynamically less favored, more strained bicyclo[2.2.1]heptane derivative (Scheme 5), but the reactions are well suited for the formation of thermodynamically favored bicyclo[2.2.2]octane systems.

2.3. Miscellaneous

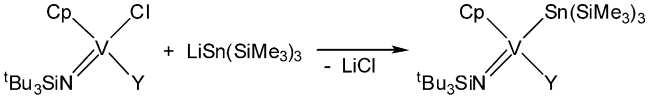
du Mont et al. reported on a number of trihalosilyl substituted compounds as trifunctional precursors for the synthesis of highly functionalized and branched Si-derivatives. Trichlorosilylstannanes or -germanes are described as most desirable precursors for further transformations [31,32]. The modified Benkeser reaction of a chlorotriorganostannane (R_3SnCl; R = Me, Et, ^{n}Bu) with trichlorosilane/triethylamine yielded only small amounts of the expected R_3Sn–$SiCl_3$ species. Instead, $(R_3Sn)_2Si(SiCl_3)_2$ was obtained. Moreover, for R = ^{n}Bu another Si–Sn derivative, $Bu_3SnSi(SiCl_3)_3$, was observed as well.



Surprisingly, only a limited number of transition metal complexes containing Si and Sn groups with a direct silicon–tin contact are known from literature. Heyn and Tilley described such compounds for the first time in 1990 [33]. It was hoped that these derivatives would undergo a Si–Sn bond cleavage to provide access to base free silylene complexes which could be used in chemical transformations, respectively. The starting point of their investigations was the synthesis of the $(THF)_3LiSi(SnMe_3)_3$ which was used to generate complexes of early and late transition metals (first complex [33], second complex [34] and third complex [35]).

$[Et_4N][(Me_3Sn)_3SiM(CO)_5]$	$Cp_2M(Si(SnMe_3)_3)Cl$	$[L(L')M(Si(SnMe_3)_3)]$
M = Cr, Mo, W	M = Ti, Zr, Hf	M = Pt, Ru L = Cp*, dcpe L´ = Me_3P, Cl
[33]	[34]	[35]

Transition metal compounds with a $(Me_3Si)_3Sn$ unit instead of the $(Me_3Sn)_3Si$ derivatives discussed above were synthesized by Preuss et al. in 1992 for the first time. The reaction of [^{t}Bu$_3$SiN=V(Cp)(Y)Cl] (Y = NHSi^{t}Bu$_3$, O^{t}Bu) with $LiSn(SiMe_3)_3$ yielded the corresponding vanadium complexes with a tris(trimethylsilyl)stannyl group [36].



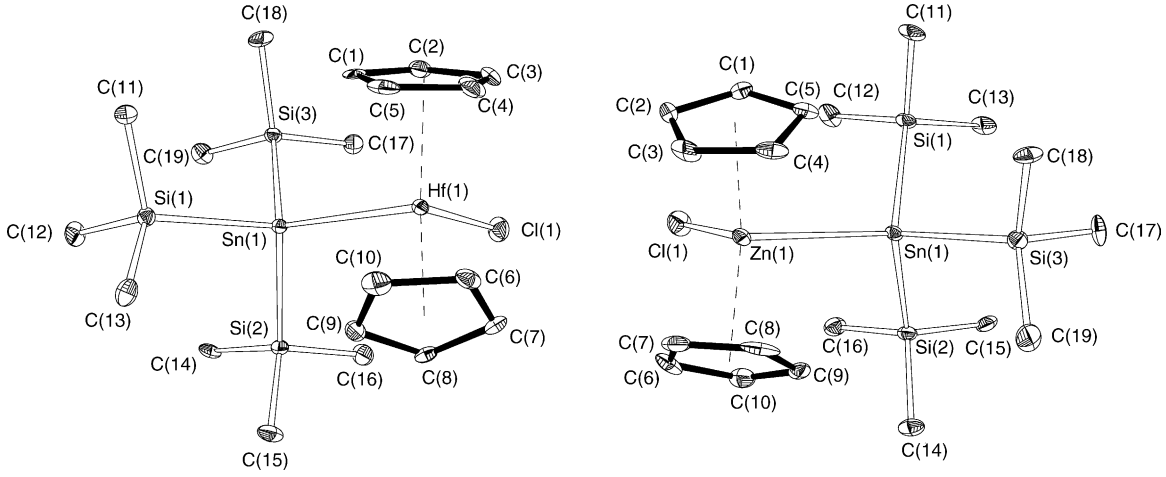


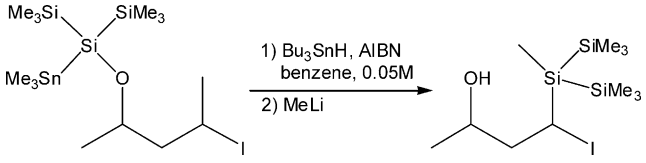
Fig. 1. Molecular structure of the $[Cp_2M(Sn(SiMe_3)_3Cl]$ species (M = Zr, Hf).

Similar reactions of potassium tris(trimethylsilyl)stannide were described by our group recently for the early transition metal complexes of zirconium and hafnium $[Cp_2M(Sn(SiMe_3)_3Cl]$ (M = Zr, Hf) [37]. The ^{119}Sn chemical shifts of these derivatives are −415 ppm for the zirconium and −392 ppm for the hafnium compound. Fig. 1 displays the molecular structure of the $[Cp_2M(Sn(SiMe_3)_3Cl]$ species.

2.4. Reactivity

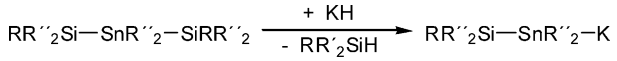
2.4.1. Radical reactions

As discussed in the introduction, stannasilanes are widely used as reagents in organic synthesis. One example for the use of stannasilanes containing larger group 14 skeletons was reported by Studer and Stehen in 1999 [38]. They used open chain bis(trimethylsilyl)(trimethylstannyl)silyl substituted alkoxysilanes in a novel synthesis for the preparation of linear and cyclic alkoxysilanes under mild radical conditions.



2.4.2. Metallation of stannasilanes

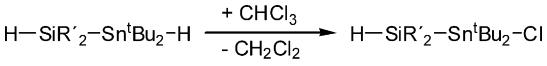
As shown above, under defined conditions it is possible to convert hydrido-tin substituted stannasilanes into the corresponding lithium derivatives [28]. A simpler access towards alkali metal stannides containing at least one additional Si–Sn bond was reported recently by our group [39].

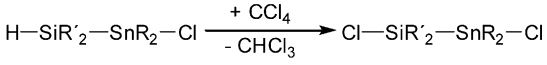


R, R´ = Me, Ph, R´´ = Ph, ^{t}Bu, Me_3Si

2.4.3. Chlorination of stannasilanes

Treatment of stannasilanes bearing hydrido-substituents on silicon and tin centers with $CHCl_3$ results in a selective chlorination of the tin center. Subsequent reaction with CCl_4 allows for the chlorination of the silicon site, leaving the tin–silicon bond intact [1,12,40].





R, R´= alkyl, aryl

2.4.4. Oxidation of stannasilanes

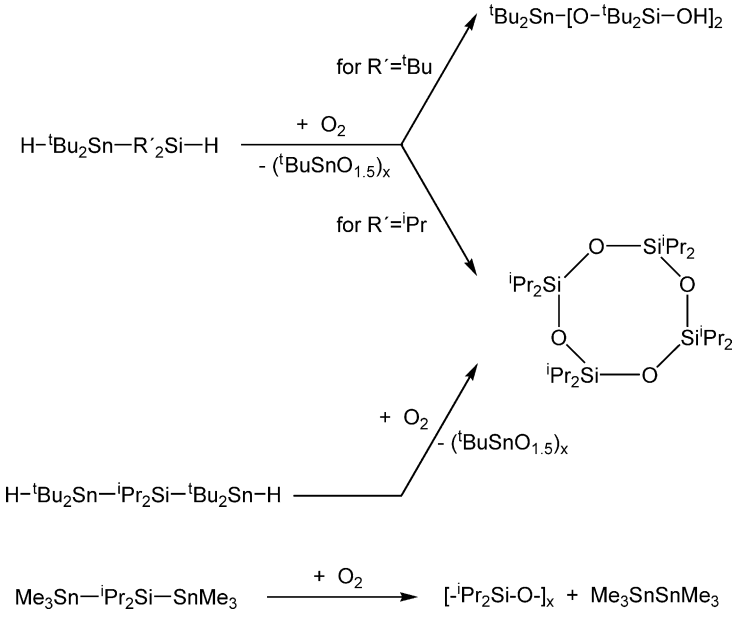
The hydrido and triorganostannyl substituted stannasilanes decompose on contact with air to distannanes and siloxanes. Depending on the steric demand of the organyl groups, alternatively linear (^{t}Bu$_2$Sn(–O–^{t}Bu$_2$Si–OH)$_2$) and cyclic ((–^{t}Bu$_2$Sn–O–^{i}Pr$_2$Si–O–)$_2$) stannasiloxanes [40] are formed (Scheme 6).

2.4.5. Transition metal compound mediated rearrangements

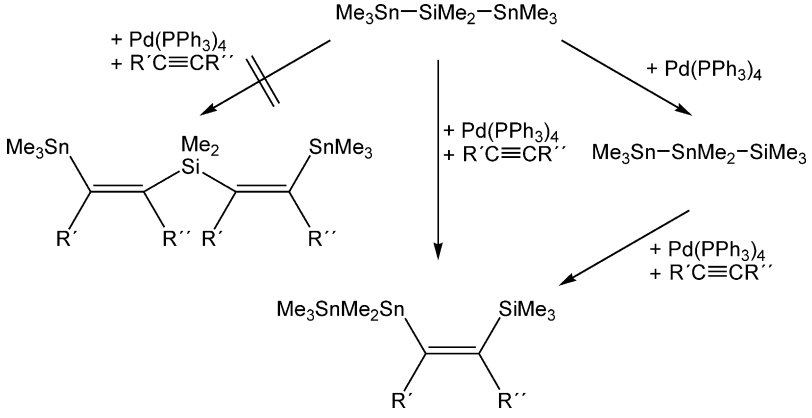
Unexpected rearrangements of compounds containing Sn–Si–Sn sequences are encountered when reacting them with tetrakis(triphenylphosphine)palladium yielding a Sn–Sn–Si sequence [12] (Scheme 7).

2.5. Spectroscopic features of tin(IV)-substituted silicon compounds

Although ^{119}Sn and ^{29}Si NMR spectroscopy find widespread application in the characterization of Si–Sn compounds, too little data is available for a detailed understanding of trends in coupling constants and chemical

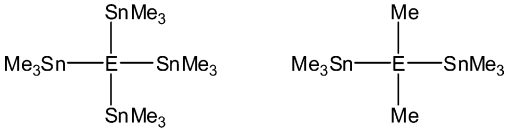


Scheme 6. Chemical reactivity of stannasilanes towards oxygen.



Scheme 7. Rearrangement reactions of stannasilanes in the presence of $Pd(PPh_3)_4$.

shifts. Some structurally closely related Si–Sn compounds were investigated spectroscopically in order to obtain a better knowledge of the tin–silicon interaction and their influence on ^{29}Si or ^{119}Sn chemical shifts. Nevertheless, the limited number of such articles does not allow general conclusions about this topic. Systematic investigations are reported by Wrackmeyer and Bernatowicz [41] for $(Me_3Sn)_4E$ and $(Me_3Sn)_2EMe_2$ (E = C, Si, Ge, Sn) (Table 2) and by Uhlig and Marsmann [42] for some cyclic derivatives (Scheme 8).

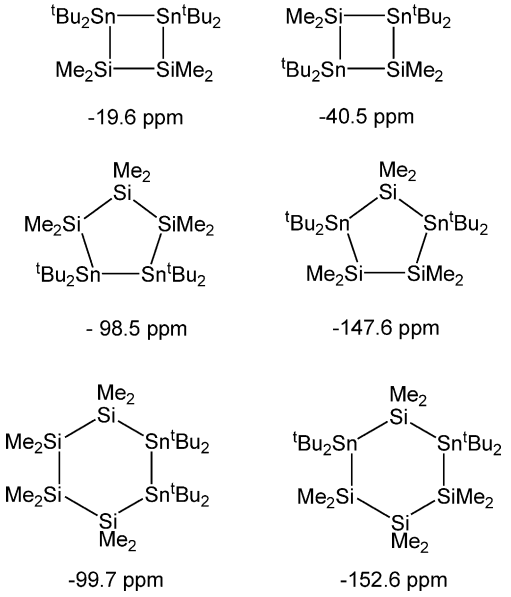


E = C, Si, Ge, Sn

Compounds containing one or two silyl substituents at one tin atom display ^{119}Sn chemical shifts that are similar to those of the corresponding tin hydrides (±30 ppm). Bulky substituents (^{t}Bu, ^{i}Pr) at the tin and/or the silicon atoms cause

Table 2
^{119}Sn NMR data of Me_3Sn-substituted group 14 derivatives

$(Me_3Sn)_4E$	δ^{119}Sn (ppm)	Ref.	$(Me_3Sn)_2EMe_2$	δ^{119}Sn (ppm)	Ref.
$(Me_3Sn)_4C$	49.3	[41]	$(Me_3Sn)_2CMe_2$	−30.2	[41]
$(Me_3Sn)_4Si$	−34.1	[41]	$(Me_3Sn)_2SiMe_2$	−99.0/−97.6	[41]/[43]
$(Me_3Sn)_4Ge$	−25.1/−25.2	[41]/[43]	$(Me_3Sn)_2GeMe_2$	−79.5	[41]
$(Me_3Sn)_4Sn$	−81.5	[41]	$(Me_3Sn)_2SnMe_2$	−99.5	[41]



Scheme 8. ^{119}Sn NMR chemical shifts of tin-modified cyclosilanes [42].

slightly higher deviations [42].

$\delta_{^{119}Sn}$: $R_3SnH \approx R_3Sn{-}Si$,

$\delta_{^{119}Sn}$: $R_2SnH_2 \approx Si{-}R_2Sn{-}Si$

Exceptions are compounds with a relatively high ring strain and therefore smaller bond angles such as, for example, four-membered Si–Sn rings. The ^{119}Sn resonance is shifted significantly to lower field and this effect is in accordance with results shown for rings that contain carbon [44] instead of silyl moieties. Similar effects are observed for the ^{29}Si NMR chemical shifts, however the differences are much smaller, probably due to the smaller chemical shift range of silicon in comparison to tin.

In contrast to carbon and tin containing rings, the differences between the ^{119}Sn chemical shifts of five- and six-membered Si–Sn rings are much smaller, probably due to the larger Si–Si and Si–Sn bond lengths, atomic radii and therefore to a less distorted tetrahedral geometry.

Comparative studies of $(Me_3M)_4M'$ (M, M′ = Si, Ge, Sn) derivatives include vibrational and electronic spectra [45] and X-ray powder diffraction investigations [46], as well as Raman investigations of linear $Me_3Sn{-}(SiMe_2)_n{-}SnMe_3$ (n = 2–6) compounds [47].

3. The synthesis of tin(II)–silicon derivatives

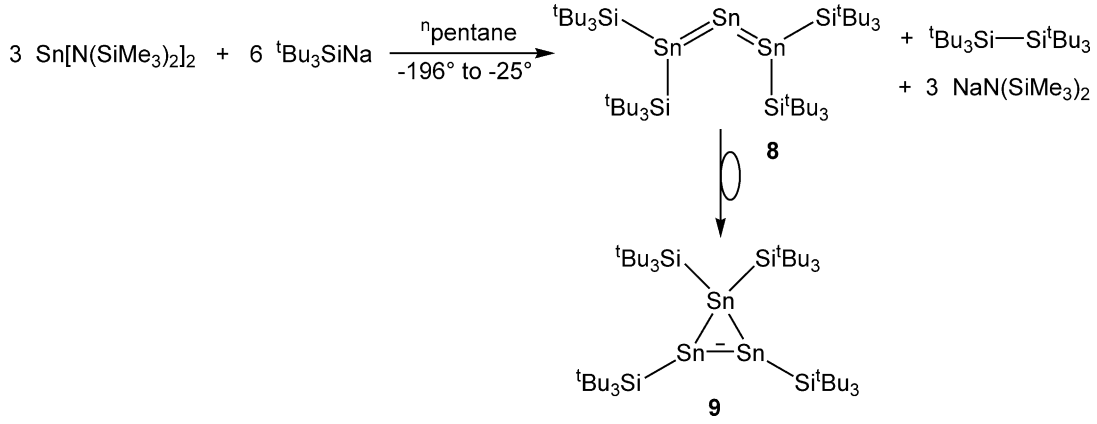
3.1. Synthesis

Despite the fact that "Lappert's distannene" $[(Me_3Si)_2CH]_2Sn{=}Sn[CH(SiMe_3)_2]_2$ [48] was prepared and characterized in 1976, almost 20 years passed before Klinkhammer and Schwarz were able to describe the first distannene with silyl substituents only [64]. Nevertheless, such Sn–Sn double bond systems carrying more or less bulky Si groups are now more common in tin chemistry.

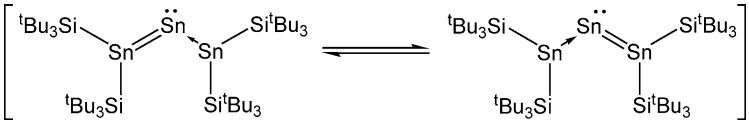
Wiberg et al. investigated the reactions of supersilyl sodium ^{t}Bu$_3$SiNa with tin(II) electrophiles under several conditions. Reaction of ^{t}Bu$_3$SiNa with $SnCl_2$ in THF did not afford the desired tetrastannatetrahedrane $(^tBu_3SiSn)_4$, but **8** and **9** were obtained, in contrast to similar experiments with $GeCl_2$, where the $(^tBu_3SiGe)_4$ was isolated [49]. Similar reactions were investigated by Weidenbruch et al. [50].

Soluble and insoluble compounds containing tin were obtained from reactions with tin(II) chloride but the true constitution remained obscure. Detailed studies of the chemical reactivity, involving the tin(II) diamide $Sn[N(SiMe_3)_2]_2$ or tin(II) di-^{t}butoxide $Sn(^tBuO)_2$ instead of $SnCl_2$ and using solvent free ^{t}Bu$_3$SiNa in hydrocarbon solvents, finally revealed that a tristannaallene is initially formed and is slowly converted into a tristannacyclopropene [51] (Scheme 9).

Both compounds **8** and **9** were characterized by multinuclear NMR spectroscopy and single crystal X-ray diffraction analysis. In ^{119}Sn NMR spectrum of **8**, two resonances were found at 503 and 2233 ppm with a ratio of 2:1, respectively. The signal at 2233 ppm was assigned to the central tin atom. The strong low-field shift compared to the other resonance is indicative for a strong stannylene



Scheme 9. Formation of stannaallene **8** and stannacyclopropene **9**.

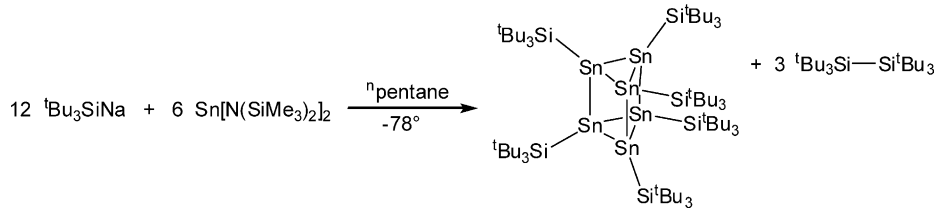


Scheme 10. Resonance forms for compound **8**.

like character and compares well to other stannylenes R_2Sn, $R_2 = (Me_3Si)_2CCH_2CH_2C(SiMe_3)_2$ ($\delta = 2323$ ppm), [52] $R = CH(SiMe_3)_2$ ($\delta = 2328$ ppm) [53] R/R = C_6H_2-2,4,6-^{i}Pr$_3$/C_6H_2-2,4,6-[$(Me_3Si)_2CH]_2$ ($\delta = 2208$ ppm) [54]. The other signal however was observed in the shift range typical for distannenes R_2SnSnR_2 (R = C_6H_2-2,4,6-^{i}Pr$_3$ ($\delta = 427.3$ ppm)) [55] and compares well to a silastannene [79]. $^1J_{119Sn-119Sn}$ and $^1J_{117Sn-119Sn}$ coupling constants are remarkably large with 4302 and 4117 Hz, respectively. The $^2J_{117Sn-119Sn}$ coupling constant was determined as 1679 Hz. The ^{29}Si NMR spectrum showed one signal at 77.3 ppm with three pairs of satellites for $^1J_{29Si-117/119Sn}$ (~109 Hz), $^2J_{29Si-117/119Sn}$ (~54 Hz) and $^3J_{29Si-117/119Sn}$ (~12 Hz). Single crystal X-ray diffraction analysis revealed very short tin–tin bond lengths from 2.675(1) to 2.684(1) Å and silicon–tin bond lengths within the range of expectations from 2.683(3) to 2.701(3) Å. The bond angle spanned by the three tin atoms is close to 156° and torsion angles between silicon atoms on different tin atoms were determined to be 98.0–111.8°, and are therefore substantially larger than 90°. Judging from these data and ^{119}Sn NMR shifts, **8** is not really an allene analogue but is better described by the resonance structures given in Scheme 10.

Structural characterization of the cyclotristannene **9** also revealed unusual aspects. ^{119}Sn NMR resonances were found at −694 ppm ((^{t}Bu$_3$Si)$_2$Sn) and 412 ppm (^{t}Bu$_3$SiSn). The $^1J_{117Sn-119Sn}$ coupling constant between the two three-coordinate tin atoms is 2110 Hz, $^1J_{117Sn-119Sn}$ and $^1J_{119Sn-119Sn}$ coupling constants between the three- and four-coordinate tin atoms are 2123 and 2223 Hz, respectively. Two signals with equal intensity at 58.0 ppm (Sn(Si^{t}Bu$_3$)$_2$, $^1J_{29Si-117/119Sn}$ = 12 Hz) and 35.6 ppm (Sn(Si^{t}Bu$_3$), $^1J_{29Si-117/119Sn}$ = 84 Hz) were observed in the ^{29}Si NMR spectrum. Results of single crystal X-ray diffraction analysis showed the presence of two independent molecules per unit cell. The formal tin–tin double bond is exceptionally short with only 2.582(4) and 2.601(3) Å. Tin–tin single bond lengths are somewhat elongated with values between 2.841(3) and 2.859(3) Å. Angles within the triangle were all found close to 60°.

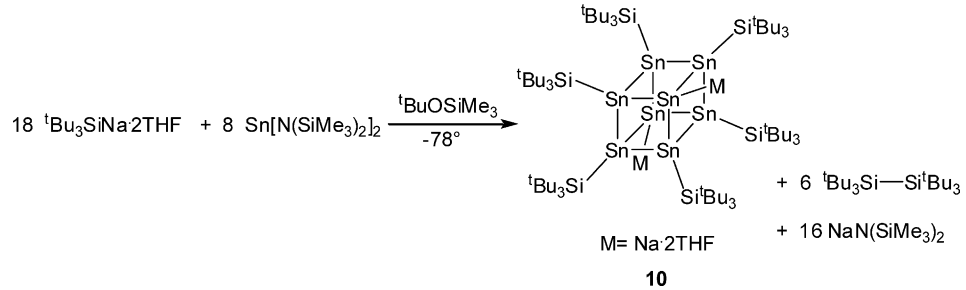
Wiberg et al. were also successful in isolating a hexastannaprismane from the reaction of Sn[N(SiMe$_3$)$_2$]$_2$ and ^{t}Bu$_3$SiNa in cold pentane and subsequent change of the solvent to ^{t}BuOMe prior to warming to −25°.



By X-ray crystallography, all tin–tin bonds were found to be elongated compared to the sum of covalent radii. Tin–tin bonds constituting the triangles are 2.907(1)–2.941(1)–Å, and tin–tin bonds linking them are 2.903(1)–2.907(1) Å. Bond angles are close to 60° and 90°, respectively, building an almost perfect prismane. Decomposition in solution was found to occur above −5 °C and above 80 °C in solid state [56].

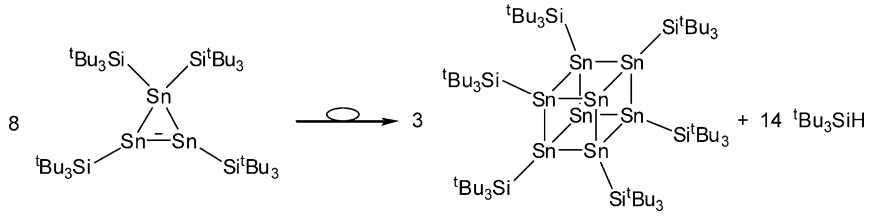
However, when the reaction of Sn[N(SiMe$_3$)$_2$]$_2$ was carried out in cold ^{t}BuOMe with the THF adduct of ^{t}Bu$_3$SiNa, a dimetallated stannacubane was isolated. ^{119}Sn NMR resonances were found at −767 and −2045 ppm, where the latter signal was assigned to the SnNa centers. ^{29}Si NMR spectroscopy showed one signal at 41.3 ppm with $^1J_{29Si-117/119Sn}$ 577/569 Hz and $^2J_{29Si-117/119Sn}$ 333 Hz.

Single crystal X-ray diffraction analysis revealed **10** to exist in the solid state as a slightly distorted cubane with tin–tin bond distances between 2.871(2) and 2.908(2) Å. All angles within the cubane moiety were found close to 90° (88.06(3)–91.62(3)°) [57].

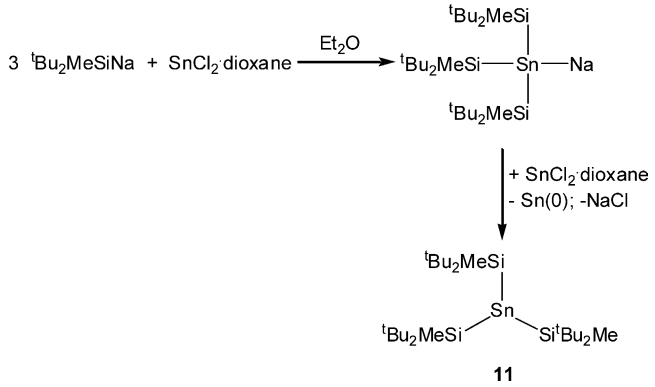


10

A very similar octastannacubane was obtained upon thermal rearrangement of cyclotristannene **9**. In this case, two tin centers along a space diagonal remain unsubstituted as indicated by X-ray crystallographic results.

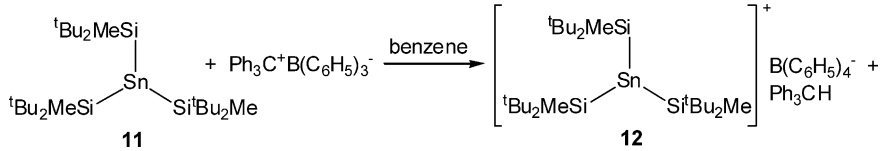


Sekiguchi et al. studied the reactions of $^{t}Bu_2MeSiNa$, which is less bulky than $^{t}Bu_3SiNa$, with $SnCl_2$.dioxane. A persistent stannyl radical (**11**) was obtained directly in a reaction where $SnCl_2$ is both the electrophile and oxidizing agent. The in situ prepared triorganosilylstannyl anion is converted into the radical by a single electron oxidation.



11

The solid state structure was established by X-ray crystallography. The three coordinate tin center is almost perfectly planar (sum of angles = 359.9°) with in-plane configuration of all methyl groups at the silyl substituents. The values found for the tin–silicon bond lengths of **11** are between 2.6146(5) and 2.6193(5) Å. In hexane, the radical showed one EPR signal at room temperature with a *g*-value of 2.0482. The signal showed only one pair of tin satellites with a coupling constant of 32.9 mT. However, isotopic splitting to ^{117}Sn and ^{119}Sn was not observed, presumably due to the broad lineshape. The small hyperfine coupling constant compared to other tin radicals and the planar geometry in solid state are evidence for the fact that **11** is a π-radical in both solid state and solution.



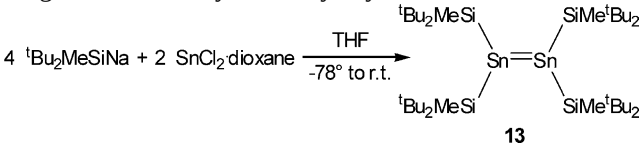
11 **12**

Reaction of **11** with one equivalent $Ph_3C^+B(C_6F_5)_4^-$ resulted in the formation of stannylium ion **12**. The stannylium ion is perfectly planar with a sum of angles of exactly 360°. Again, methyl groups are found in the plane of silyl and tin atoms which reduces steric strain. Silicon–tin bond lengths range from 2.6792(8) to 2.6930(7) Å and are somewhat longer than in the parent radical. The cationic tin center and the closest fluorine atom of the counterion are more than 5 Å apart, which is more than the sum of van der Waals radii. The ^{119}Sn chemical shift of the free cationic tin atom was found at 2653 ppm being a measure for the high degree of deshielding caused by the separation of the ion pair [58].

On the other hand, tin radical **11** was converted into the corresponding stannyl anion upon one electron reduction with alkali metals. Reduction with lithium in THF produced $(^{t}Bu_2MeSi)_3SnLi{\cdot}2THF$. Reaction with potassium in the presence of one equivalent [2.2.2]cryptand yielded the respective potassium stannide that exists as a completely separate ion pair in the solid state. However, upon reduction with lithium in heptane, a dimeric $[(^{t}Bu_2MeSi)_3Sn(\mu\text{-}Li)]_2$ species was isolated. Reduction with lithium in benzene yielded a monomeric lithium stannide with an η^6 coordination mode between a benzene molecule and lithium cation. Both, ^{119}Sn and ^{7}Li NMR spectroscopy of the latter species showed the coupling pattern between tin and lithium one would expect when the covalent character is also preserved in solution [59] (Scheme 11).

Sekiguchi et al. also investigated the reaction of $^{t}Bu_2MeSiNa$ with $SnCl_2$ dioxane in THF. In this case, the outcome of the reaction is different to results obtained in Et_2O where the radical **11** is formed. In contrast to earlier experiments, the reaction was found to produce tetrakis(di-*tert*-butylmethylsilyl)distannene. This compound is the first example of a distannene that preserves its dimeric nature in solution. ^{119}Sn NMR resonance was observed at 630.7 ppm. The crystal structure was determined by X-ray crystallography. The tin–tin bond is very short, 2.6683(10) Å. Interestingly, the geometry around the tin atoms is essentially planar with a bend angle of only 1.22(5)°. All other structurally characterized distannenes adopt a *trans*-bent configuration of the substituents with bending angles between 21.4° and 64.4°.

Compound **13** is highly twisted in the solid state (twist angle = 44.62(7)°), a finding that was ascribed to the large steric congestion caused by the bulky silyl substituents.



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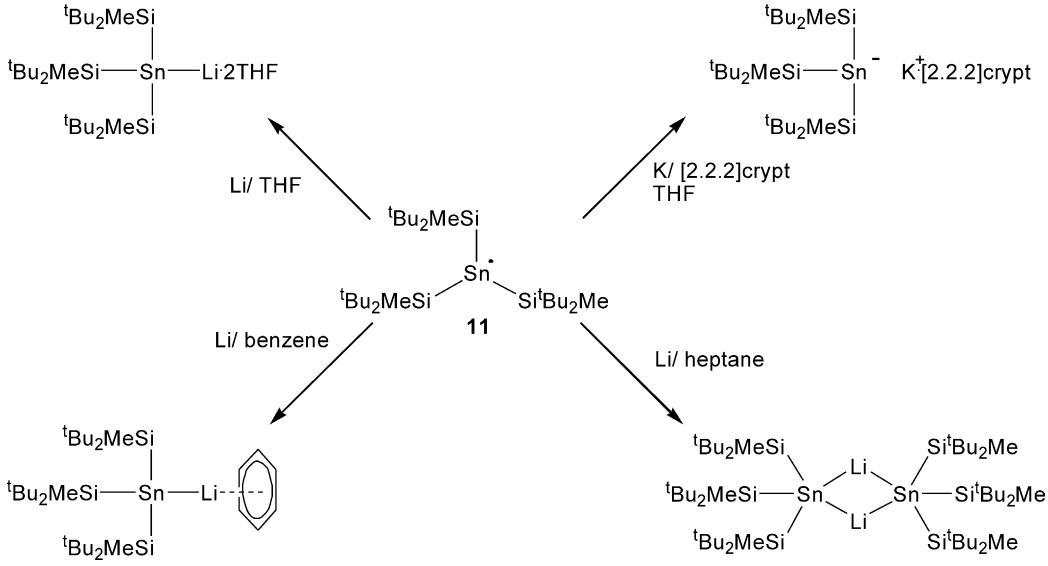


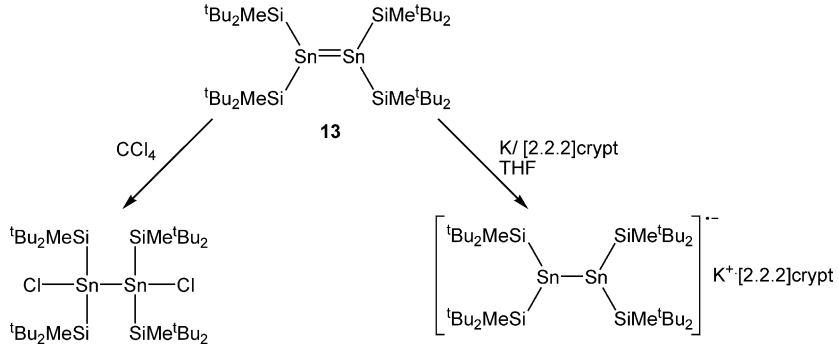
Scheme 11. Metallation of radical **11**.

Compound **13** readily reacts with CCl_4 to yield a 1,2-dichlorodistannane (Scheme 12). Single electron reduction with potassium/[2.2.2]cryptand in THF yields a radical anion that was also structurally characterized. The two tin atoms strongly differ in geometry. One adopts a pyramidal configuration (sum of bond angles 323.16°, *trans* bent angle 60.05(4)°), but the other one is almost planar (sum of bond angles 355.39°, *trans* bent angle 19.50(4)°), suggesting a clear separation between negative charge and unpaired electron. The central tin–tin bond distance increases to 2.8978(3) Å. The charge–electron separation is also intact in solution as demonstrated by EPR spectroscopy. The EPR spectrum showed a central signal ($g = 2.0517$) with two pairs of $^{117/119}$Sn satellites and hyperfine coupling constants of 34.0 and 18.7 mT. The two hyperfine coupling constants arise from the existence of two distinct tin atoms [60].

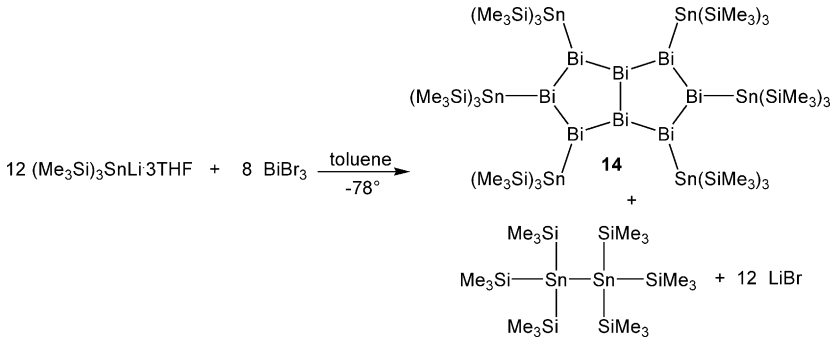
Due to the kinetic stabilization imposed by the steric demand, as well as their stabilizing electronic properties, tris(trimethylsilyl)silyl- and tris(trimethylsilyl)stannyl groups find widespread application in the synthesis of novel main group element clusters [61]. Reaction of $(Me_3Si)_3SiLi{\cdot}3THF$ or $(Me_3Si)_3SnLi{\cdot}3THF$ with $BiBr_3$ in cold toluene in the dark produced $[(Me_3Si)_3Sn]_6Bi_8$, the first example of a structurally characterized molecule with tin–bismuth bonds in addition to the respective oxidative coupling product $(Me_3Si)_3EE(SiMe_3)_3$ (E = Si, Sn), a novel cyclotetrabismuthane $[(Me_3Si)_3SiBi]_4$ and a bicyclo-[3.3.0]-octabismuthane [62] (Scheme 13).

The bicyclic ring-system of **14** adopts a strongly folded conformation in the solid state with an all-*trans*-configuration of the tris(trimethylsilyl)stannyl groups. Bond lengths are within the range of expected values with Bi–Bi distances from 2.972(2) to 3.019(2) Å. The bond length between the 'naked' bismuth bridgeheads is 2.991(2) Å. Tin–bismuth bond lengths are 2.897(3)–2.961(3) Å with an average of 2.926(3) Å which is consistent with the covalent radii of the elements.

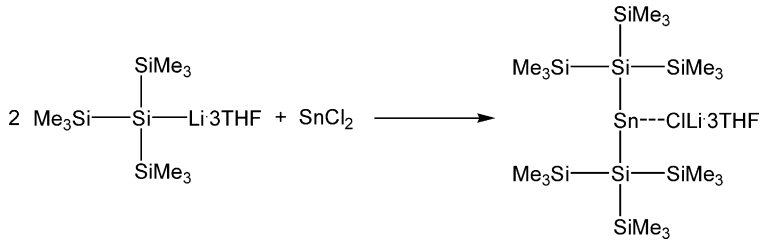
First reports on the reaction of bulky silyl anions with tin(II) chloride to produce a bis(silylated) tin(II) derivative were made by Cowley and coworkers [63]. The reaction of $(Me_3Si)_3SiLi{\cdot}3THF$ in *n*-hexane at −78 °C yielded $[(Me_3Si)_3Si]_2SnLi(\mu\text{-}Cl)(THF)_3$ (Scheme 14). The product was characterized by ^{29}Si NMR spectroscopy and single crystal X-ray diffraction analysis.



Scheme 12. Reactions of distannene **13**.



Scheme 13. Formation of bicyclo-[3.3.0]-octabismuthane **14**.



Scheme 14. Formation of $[(Me_3Si)_3Si]_2SnLi(\mu\text{-}Cl)(THF)_3$.

The bond angles around tricoordinate tin atom add up to 301.9°, in other words the low coordinate tin atom is highly pyramidalized. The average tin–silicon bond length is 2.673(12) Å which is slightly longer compared to the sum of covalent radii (2.52 Å) for these elements. ^{29}Si NMR spectroscopic resonances were found at −6.2 ppm for the trimethylsilyl groups and at −22.1 ppm for the central silicon atom.

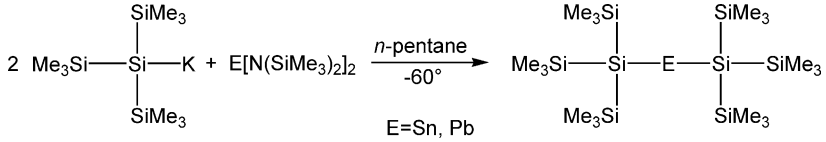
In 1995 Klinkhammer and Schwarz reported on the synthesis of bis(hypersilyl)tin and lead. Reaction of ether free $(Me_3Si)_3SiK$ with $E[N(SiMe_3)_2]_2$ (E = Sn, Pb) in cold *n*-pentane cleanly yielded the expected bis-silylated stannylenes and plumbylenes (Scheme 15) [64].

Although ^{1}H and ^{13}C NMR signals were observed, ^{29}Si or ^{119}Sn NMR signals were not detected for the tin and lead derivatives in a temperature range from −60° to +30°. Single crystal X-ray diffraction analyses revealed a monomeric nature of the lead compound in the solid state whereas the tin derivative was found to form the dimer $((Me_3Si)_3Si)_2Sn{=}Sn(Si(SiMe_3)_3)_2$. For the latter molecule, a *trans*- bent configuration was observed with the hypersilyl groups being 28.6° out of plane. For the interatomic tin–tin distance a value of 2.82 Å was determined which is close to the values observed for tin–tin single bonds.

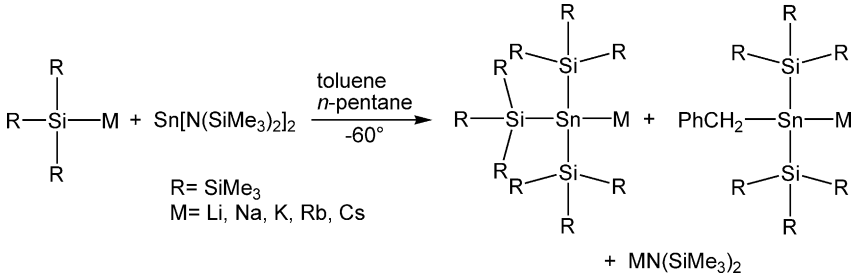
de Lima et al. subjected Cp_2Sn to the reaction with $(Me_3Si)_3SiLi{\cdot}3THF$ and found NMR spectroscopic evidence for the formation of $Sn[Si(SiMe_3)_3]_2$ [65]. However, when the reaction of ether free $(Me_3Si)_3SiM$ (M = Li, Na, K, Rb, Cs) with $Sn[N(SiMe_3)_2]_2$ was carried out at temperatures below −40° in toluene/*n*-pentane mixtures instead of neat *n*-pentane, an interesting anionic product was obtained (Scheme 16), which can formally be considered as an $(Me_3Si)_3SiM$ adduct of the bis(hypersilyl)stannylene [66]. The tolyl-adduct $MSn(CH_2Ph)[Si(SiMe_3)_3]_2$ was formed as a side product. Reactions with $Pb[N(SiMe_3)_2]_2$ were found to produce only $MPb(CH_2Ph)[Si(SiMe_3)_3]_2$ and $MPb[Si(SiMe_3)_3]_3$ was not obtained.

3.2. Reactions of stannylenes

Reaction of two distinct stannylenes R_2Sn and R'_2Sn (R = $SiMe_3$, R′ = 2,4,6-$(CF_3)_3C_6H_2$) with different tendency towards dimerization was found to result in ligand exchange processes and formation of mixed distannenes. A similar scrambling of ligands was observed for the reaction of R_2Pb and R'_2Sn (R = $SiMe_3$, R′ = 2,4,6-$(CF_3)_3C_6H_2$). However, fractional crystallization gave only the distannene and diplumbene, and mixed tetrel dimers were not isolated [67].



Scheme 15. Formation of $(Me_3Si)_3Si{-}E{-}Si(SiMe_3)_3$ (E = Sn, Pb).

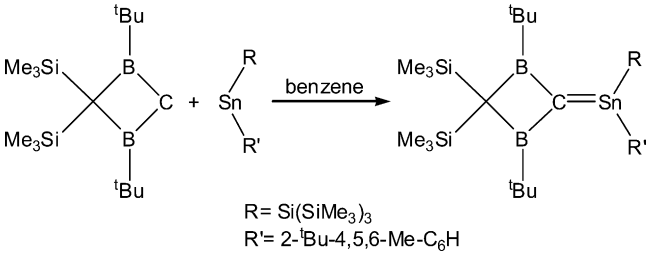


Scheme 16. Formation of tris(hypersilyl)- and bis(bishypersilyl)tolyl stannides.

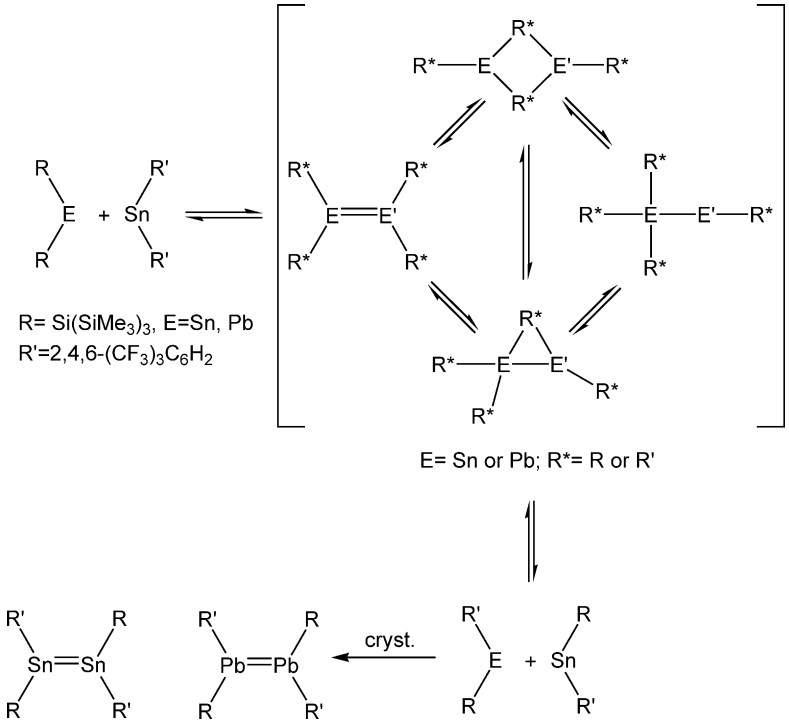
The proposed mechanism is depicted in Scheme 17, and may also be valid for isomerization processes found with the chemistry of disilenes, digermenes or other distannenes.

Similar scrambling of ligands was observed for the reaction of $[(Me_3Si)_3Si]_2Sn$ and Ar^*_2Sn ($Ar^* = 2$-^{t}Bu-4,5,6-Me_3C_6H). Upon crystallization, the mixed distannene $Ar^*[(Me_3Si)_3Si]SnSn[(Me_3Si)_3Si]Ar^*$ was isolated as the sole product. In solution however, only the stannylene $Ar^*[(Me_3Si)_3Si]Sn$ is present as confirmed by multinuclear NMR spectroscopy. Again, the resonance for the central silicon atom was not observed [68].

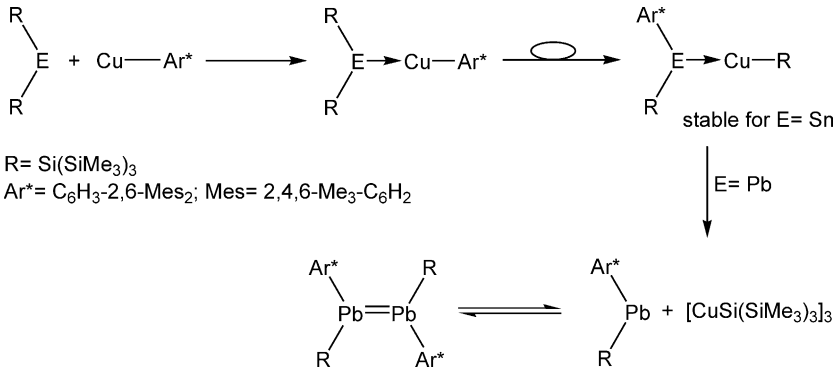
Reaction of the heteroleptic stannylene $Ar^*[(Me_3Si)_3Si]Sn$ ($Ar^* = 2$-^{t}Bu-4,5,6-Me_3C_6H) with the carbene $(Me_3Si)_2C(^t$BuB$)_2C$ yielded the stannaethene $(Me_3Si)_2C(^t$BuB$)_2CSn[(Me_3Si)_3Si]SnAr^*$. The respective germaethene was obtained from the reaction of $(Me_3Si)_2C(^t$BuB$)_2C$ and the germylene Ar^*_2Ge [69].



The homoleptic tetrylenes $[(Me_3Si)_3Si]_2E$ were also found to undergo ligand exchange reactions with Ar^*Cu ($Ar^* = C_6H_3$-2,6-Mes_2; Mes = 2,4,6-Me_3-C_6H_2). In this case the product can be considered a donor–acceptor complex between $[(Me_3Si)_3Si]Cu$ and $Ar^*[(Me_3Si)_3Si]E$ (E = Sn, Pb). However, the lead derivative was found to be unstable under the conditions and decomposed to finally yield the previously described heteroleptic diplumbene and $[(Me_3Si)_3SiCu]_3$ (Scheme 18). Similar decomposition



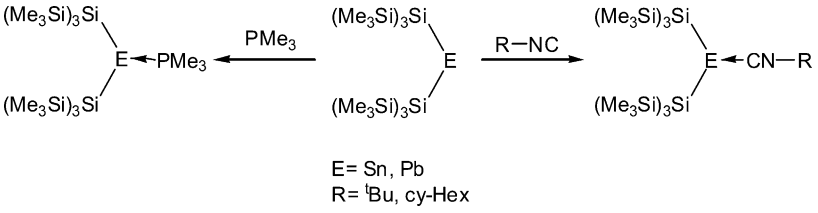
Scheme 17. Formation of heteroleptic distannenes and diplumbenes.



Scheme 18. Ligand exchange of $[(Me_3Si)_3Si]_2E$ with Ar^*Cu.

products were obtained when less bulky aromatic moieties were used. Reaction with MesCu, instead of Ar^*Cu, was reported to yield mixtures of hypersilyl substituted compounds from which only the mixed alkene homologues $Mes[(Me_3Si)_3Si]EE[Si(Me_3Si)_3]Mes$ were identified unambiguously [70].

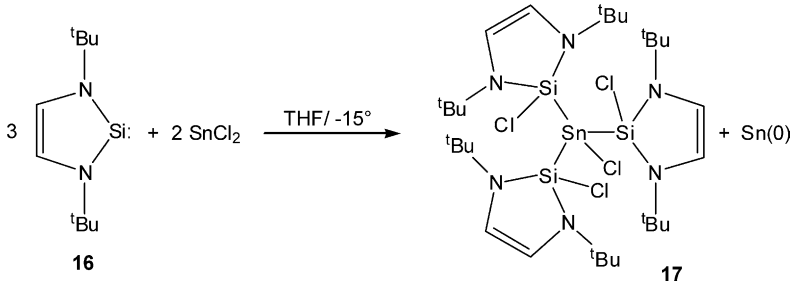
In addition to the Lewis base character, bis(hypersilyl)-tetrylenes may also act as strong Lewis acids as exemplified by the reactions with isonitriles and phosphines. The isonitrile adducts were isolated in almost quantitative yields and characterized by means of single crystal X-ray diffraction analyses. In solution the lead derivatives decomposed with formation of Pb(0), $(Me_3Si)_3SiSi(SiMe_3)_3$ and the respective isonitrile. The tin derivative however is stable in solution under exclusion of light [71].



Reaction of two equivalents of silylene with $E[N(SiMe_3)_2]_2$ (E = Ge, Sn, Pb) and $E(OAr^*)_2$ ($Ar^* = C_6H_3$-2,6-^{t}Bu$_2$ for E = Sn, Pb; $Ar^* = C_6H_2$-2,6-^{t}Bu$_2$-4-Me for E = Ge) was investigated by Gehrhus and Lappert. The respective stannylene and plumbylene were obtained for tin and lead. However, for germanium, a cyclic, tetravalent derivative was isolated that was obviously formed via a C–H insertion reaction.

When an Ar^* substituted stannylene or a mixed $Ar^*[(SiMe_3)_2N]Sn$ species is used in the reaction with the silylene, instead of the amido- or phenoxy substituted compounds from Scheme 19, a stable heteroleptic silylstannylene is obtained (Scheme 20). The formation of the silylstannylene probably proceeds via the formation of a transient silastannene and a subsequent 1,2-shift of an Ar^*- or a $N(SiMe_3)_2$-group [72].

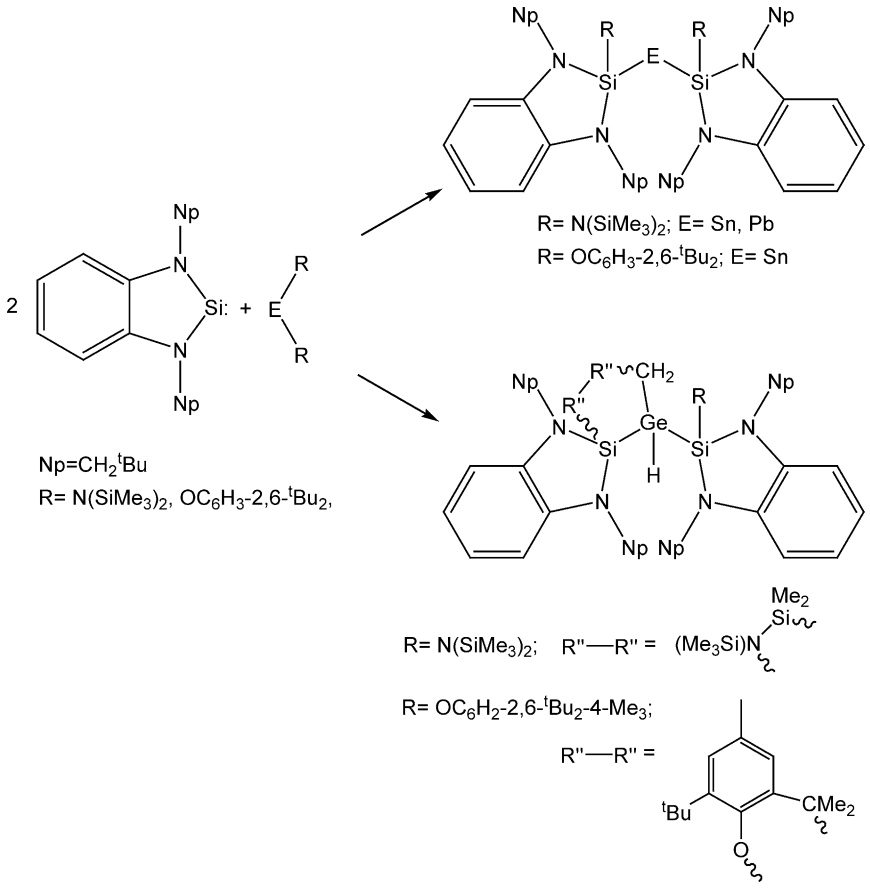
However, the use of $SnCl_2$ instead of tin(II) diamides in the reaction with silylene **16** [73] causes a disproportionation of the tin(II) species and formation of a triply silylated tin chloride **17** and elemental tin [74].



16 **17**

Compound **17** is thermally and photolytically unstable, resulting in cleavage of silicon–tin bonds and formation of elemental tin (Δ), or a mixture of elemental tin and $SnCl_2$ ($h\nu$). Under thermolytic conditions, silylene **16**, dichlorosilane **18** and dichlorodisilane **19** were formed. However, photolytic decomposition cleanly leads to **19** as the only silicon containing product (Scheme 21).

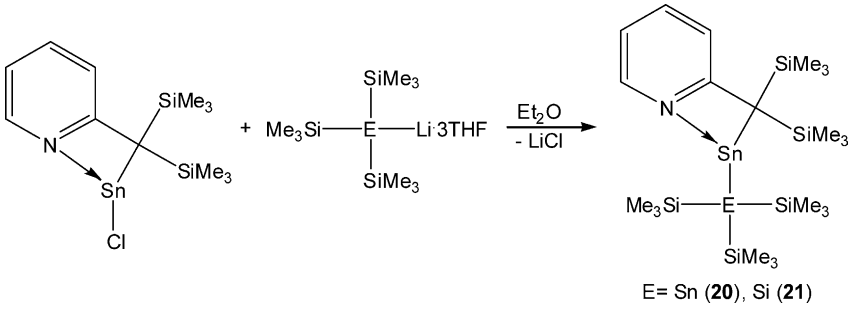
The first compound containing a bond between divalent and tetravalent tin **20** was prepared by the reaction of



Scheme 19. Reaction of a silylene with germylenes, stannylenes and plumbylenes.

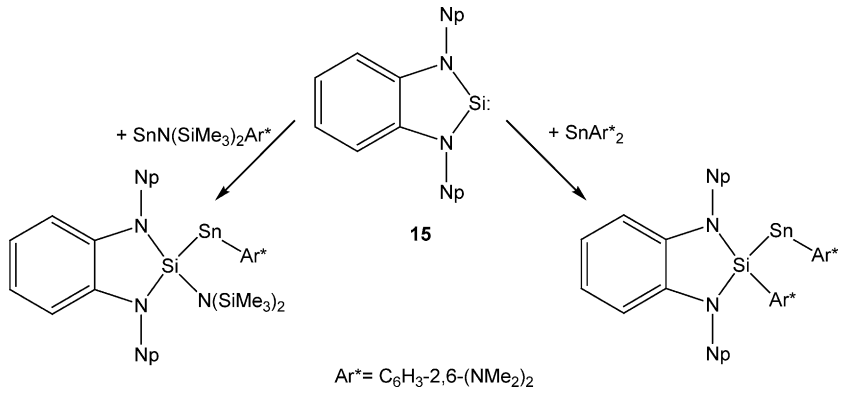
ClSn[2-(SiMe)$_2$C–C$_5$H$_4$N] with (Me$_3$Si)$_3$SnLi·3THF [75]. The tin–tin bond length was determined at 2.8689(5) Å. Angles around the strongly pyramidalized three-coordinated tin center sum up to 259.3°. The nitrogen atom of the pyridino ligand is strongly coordinated to the divalent tin atom with an interatomic distance of 2.228(2) Å.

Reaction of the pyridyl substituted chlorostannane with (Me$_3$Si)$_3$SiLi·3THF yielded the respective silylsubstituted stannylene **21**. In this case, the ^{119}Sn NMR resonance was found at 876 ppm. Again, a signal for central silicon atom of the (Me$_3$Si)$_3$Si group was not detected by ^{29}Si NMR spectroscopy. Results from single crys-

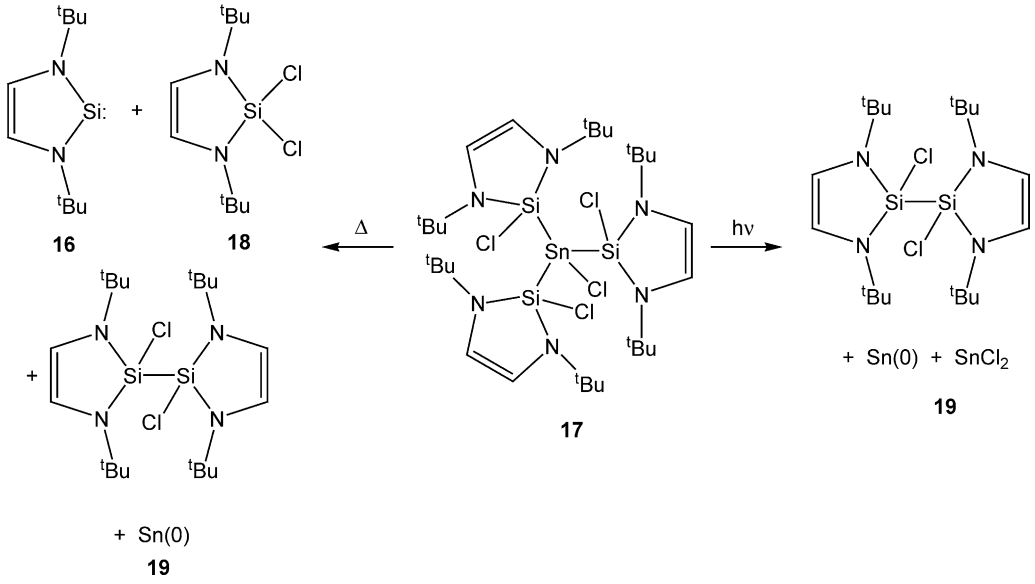


NMR spectroscopic investigations in solution revealed that the two trimethylsilyl groups at the (Me$_3$Si)$_2$CSn center remain inequivalent, indicating that coordination persists in solution. Two sharp resonances were found in the ^{119}Sn spectrum, one located at 897 ppm and the other at −502 ppm mutually coupled by 6746 Hz ($^1J_{119Sn-119Sn}$) and 6451 Hz ($^1J_{119Sn-117Sn}$) with the expected roof-effect [76].

tal diffraction analysis were almost identical to those for **20**. Angles around the three-fold coordinate, divalent tin atom were determined to sum up to 268.3° and the tin–silicon bond is 2.7236(18) Å, which is considerably elongated compared to [(Me$_3$Si)$_3$Si]$_2$Sn (2.6667(11) and 2.678(11) Å) [64], [(Me$_3$Si)$_3$Si]$_2$Sn(μ-Cl)Li (2.681(2) Å) [63] or for [Sn{C$_6$H$_3$-2,6-(NMe$_2$)$_2$}(Si{(–NCH$_2$^{t}Bu-1,2-C$_6$H$_4$)}{C$_6$H$_3$-2,6-(NMe$_2$)$_2$)}] (2.636(2) Å) [72,77].

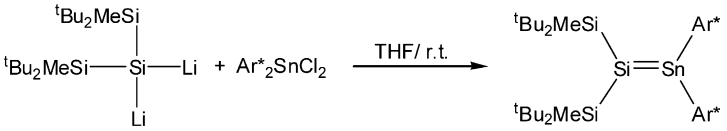


Scheme 20. Reaction of silylene **15** with bulky stannylenes.



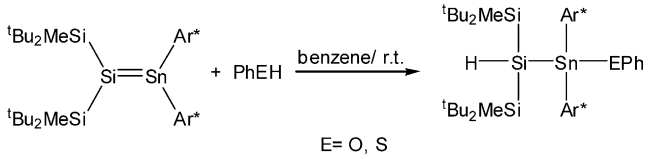
Scheme 21. Decomposition of derivative **17**.

The rare example of a geminally dilithiated silane [78] was used in the directed synthesis of a mixed silastannene. Reaction of $[Me^tBu_2Si]_2SiLi_2$ with bulky $Ar^*_2SnCl_2$ ($Ar^* = C_6H_2$-2,4,6-^{i}Pr$_3$) gave, in 50% yield, the first compound containing a silicon–tin double bond [79].



A signal was detected at 516.7 ppm in the ^{119}Sn NMR spectrum and two resonances at 27.4 and 27.6 ppm were found with a ratio of 1:2 in ^{29}Si NMR spectra. Single crystal X-ray diffraction analysis revealed a central bond length of 2.4188(14) Å, which is about 7% less than Si–Sn single bonds (2.60 Å). The substituents at the tin and the silicon centers both acquire a *trans*-bent configuration. The bending angle at the silicon center of 26.2° is about three times as large as the one at the tin atom (9.6°), which is surprising as disilenes usually prefer a rather planar geometry. However, distannenes usually exhibit quite large bending angles [80]. A possible explanation may be found in bond polarity induced by substituents. Electropositive silyl groups at silicon and electronegative aryl groups attached to tin cause a polarity of the double bond, $Si^{\delta-} = Sn^{\delta+}$. Generally speaking, the *trans*-bent structure arises from donor-acceptor interactions. In the presence of substituents with different electronegativity, the donor–acceptor interaction is no longer symmetrical forcing the negatively charged center to acquire a more bent structure than the positively charged center. Calculations on $(H_3Si)_2SiSnPh_2$ as model compound at the B3LYP/DZd level strongly support this explanation.

Bond polarization also becomes evident in chemical reactivity. Addition of PhEH (E = O, S) to the double bond was found to proceed via protonation of the nucleophilic silicon center and the PhE-moiety is transferred to the positively charged tin atom.



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