Compounds of Silicon and Homologues, 127[1]
Unsaturated Compounds of Silicon and Homologues, 54[2]
Tetrasupersilyl-tristannaallene and -tristannacyclopropene $(tBu_3Si)_4Sn_3$ – Isomers with the Shortest Sn=Sn Double Bonds to Date

Nils Wiberg,*[a] Hans-Wolfram Lerner,[a] Sham-Kumar Vasisht,[a] Susanne Wagner,[a]
Konstantin Karaghiosoff,[a][+] Heinrich Nöth,[a][++] and Werner Ponikwar[a][++]

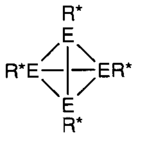
Dedicated to Professor Wolf-Peter Fehlhammer on the occasion of his 60th birthday

Keywords: Double Bonds / NMR Spectroscopy / Silicon / Tin / X-ray structure analyses

The dark blue, air- and moisture-sensitive, thermolabile tristannaallene $R^*_2Sn{=}Sn{=}SnR^*_2$ (**5**) (R^* = Si*t*Bu$_3$) is prepared by reaction of $Sn(OtBu)_2$ or $Sn[N(SiMe_3)_2]_2$ with R*Na in pentane/benzene at –25°C. The dark red-brown, air-sensitive, moisture-insensitive, and thermostable cyclotristannene $R^*_4Sn_3$ (**6**) with a $–R^*Sn{=}SnR^*–$ moiety as part of a Sn_3 ring is obtained from the reaction of $Sn(OtBu)_2$ or $Sn[N(SiMe_3)_2]_2$ with R*Na in pentane at 25°C or from the isomerization of **5** at room temperature ($\tau_{1/2}$ = 9.8 h). According to the result of X-ray structural analyses the Sn_3 framework of chiral **5** is bent (156°) and the terminal Sn atoms have pyramidal surroundings. The SnSn double bonds in **5** (2.68 Å) are shorter than those found for the hitherto structurally investigated distannenes (2.77–2.91 Å). Even shorter is the double bond in **6** (2.59 Å). The unsaturated Sn atoms here have nearly planar surroundings in perfect analogy to the carbon atoms in CC double bonds. The SnSn double bond in **6** can therefore be considered as the first "true" Sn=Sn bond. The structures of **5** and **6** can be deduced also from ^{119}Sn- and ^{29}Si-NMR studies in solution.

The reaction of tin dichloride $SnCl_2$ with supersilyl sodium R*Na ("supersilyl" **R*** = tri-*tert*-butylsilyl Si*t*Bu$_3$) in tetrahydrofuran (THF) attracted our attention for two reasons:

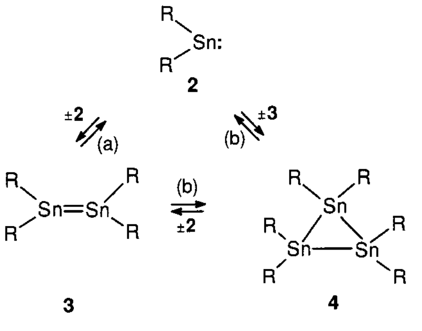
(i) By treating germanium dichloride (in form of its dioxane adduct) with an excess of supersilyl sodium in THF (molar ratio $GeCl_2$ to R*Na of 1:3) we synthesized in 1996 **1b**, the first molecular germanium compound with a Ge_4 tetrahedron[3]. Three years earlier we had already reported **1a**, the first molecular silicon compound with a Si_4 tetrahedron[4]. In continuation of our investigations we attempted the synthesis of **1c**, the first molecular tin compound bearing a Sn_4 tetrahedron by the analogous reaction of $SnCl_2$ with R*Na in THF.



R* = Si*t*Bu$_3$

1a : E = Si
1b : E = Ge
1c : E = Sn

(ii) The reaction of tin dichloride with the twofold molar amount of supersilyl sodium should yield in THF according to $SnCl_2 + 2\ R^*Na \rightarrow R^*_2Sn + 2\ NaCl$ the stannylene R^*_2Sn as the first product. We hoped that it would be possible to isolate or detect the bis(supersilyl)stannylene as the monomer **2** or – less probable – as the dimer **3** or the trimer **4** at low enough temperatures [see Scheme 1, Equations (a) and (b), R = R*].



Scheme 1

In fact, a few distannenes of type **3** with organyl as well as silyl substituents R of *intermediate bulkiness* could be prepared and structurally characterized in the last years (see Table 1 and refs.[5–9]). NMR investigations reveal, however, that in solution these "bis(stannylenes)" **3** are in equilibrium with the corresponding "mono(stannylenes)" **2** and in one case[7] with the "tris(stannylene)" **4**. *Very bulky* organyl as well as silyl substituents (e.g. R = 2,4,6-*t*Bu$_3$C$_6$H$_2$[9] and also R = R* [see below]) prevent the formation of distannenes **2** even in the solid state.

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[a] Institut für Anorganische Chemie der Universität München, Butenandtstraße 5–13 (Haus D), D-81377 München, Germany
[+] NMR studies.
[++] X-ray structure analyses.

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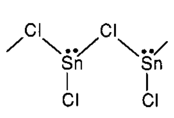
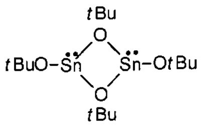
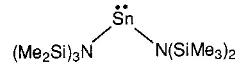
Electronegative substituents R can also stabilize the stannylenes **2**. In such cases with substituents of small, intermediate or large steric demand [e.g. R = Cl,[10] O*t*Bu,[11] or $N(SiMe_3)_2$[12]] they exist as oligomers, dimers, or monomers, respectively. In the oligomers and dimers R acts as a bridge between two tin atoms. As a consequence of the polymeric structure the dichloride **2a** is insoluble in hydrocarbons like pentane and soluble only in ethers like THF in which it forms adducts, whereas the dialkoxide **2b** and the diamide **2c** are soluble also in hydrocarbons.



2a: $(SnCl_2)_x$



2b: $[Sn(OtBu)_2]_2$



2c: $Sn[N(SiMe_3)_2]_2$

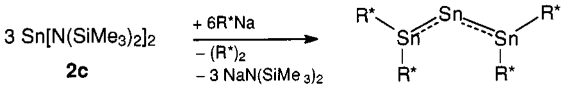
Here we first describe the reactions of the Sn^{II} compounds **2a**−**2c** with supersilyl sodium, which yield together with other products *tetrasupersilyl tristannaallene* **5** and *tetrasupersilyl tristannacyclopropene* **6** (referred to in the following as tristannaallene and cyclotristannene). The subsequent sections deal with the characterization as well as with multinuclear NMR and X-ray studies of the products **5** and **6**.

Preparation of the Tristannaallene 5 and Cyclotristannene 6

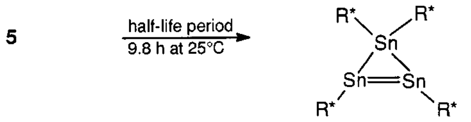
Some years ago[13] we observed that a solution of $SnCl_2$ (**2a**) in THF when added dropwise to a solution of the twofold molar amount of R*Na in THF at −78 °C followed by warming to ambient temperature gives a microcrystalline extremely air-sensitive blackish-brown *insoluble tin compound* (main product) and a dark brown solution. The latter contains a *soluble tin compound* as well as superdisilane $tBu_3Si-SitBu_3$.[14] We had obtained this soluble tin compound already as a product of the dehalogenation of disupersilyltin dichloride $R^*_2SnCl_2$ with sodium metal in benzene.[15] It is also formed from the reaction of $Sn(OtBu)_2$ (**2b**) or of $Sn[N(SiMe_3)_2]_2$ (**2c**) with supersilyl sodium in alkanes like pentane or heptane.

The chemical identity of the insoluble and the soluble tin compounds remained initially obscure. In a communication published recently[16] it is suggested that the insoluble tin compound probably has the tetrasupersilyl *tetrahedro* tetrastannane structure **1c**, whereas for the soluble tin compound a zwitterionic distannene structure $R^*_2Sn{\rightarrow}SnR^*_2$ was proposed. Both presumed structures are inconsistent with our results, however. According to our experience the tetrahedrane **1c** should be soluble in organic solvents and thus cannot account for the insoluble compound (cf. ref.[1]). Our analytical studies reveal that this compound must be a mixture of supersilyl, tin, and sodium containing products.[17] Chemical, NMR, and X-ray studies show the soluble tin compound to be the *cyclotristannene* **6** − a structure, which has been already reported by Sekiguchi et al. for the germanium homologue $R^*_4Ge_3$[18] and by Kira et al. for the silicon homologue $R_3R'Si_3$ ($R' = tBuMe_2Si$; $R = R'_3Si$).[19]

We could gain a deeper insight into the reaction pathway of Sn^{II} compounds with supersilyl sodium by studying the reaction of the diamide **2c** with donor free R*Na in pentane at low temperatures. It yields in the first stage according to Equation (1) together with superdisilane the *tristannaallene* **5** (at first we believed this product to be the expected tetrastannatetrahedrane **1c**[20]). The tristannaallene **5** rearranges at ambient temperature (25 °C), as shown by Equation (2) to the isomeric cyclotristannene **6**. This rearrangement implies the migration of one supersilyl substituent to the supersilyl free central tin atom with concomitant formation of a chemical bond between the outer tin atoms of the tristannaallene. An analogous reaction sequence is observed also for the reaction of **2b** with R*Na in pentane.



5 (1)



6 (2)

The formation of the tristannaallene **5** could proceed according to Equations (3) and (4) via the disupersilyl stannylene R^*_2Sn. The stannylene could subsequently add first one and than a second molecule R^*_2Sn with elimination of supersilyl radicals, which dimerize to give superdisilane. The intermediate formation of R^*_2Sn in pentane at −78 °C is supported by the fact that when the diamide **2c** is allowed to react with an equimolar amount of R*Na half of **2c** remains unchanged. Obviously due to steric reasons the stannylene R^*_2Sn cannot dimerize according to Equation (a) in Scheme 1, but loses, as shown by Equation (4), in the course of its "trimerization" two supersilyl groups. We have no proof for the existence of radicals $R^*_3Sn^{\bullet}_2$, which should form according to the mechanism suggested by Equation (4). We have noted, however, that in the course of the reaction of **2c** with R*Na in pentane at low temperatures the NMR signals of **2c** disappear, while a strong ESR signal appears. As the reaction proceeds further the ESR signal disappears and at the same time the NMR signals of **5** can be detected.

$$Sn[N(SiMe_3)_2]_2 \xrightarrow[-2\,NaN(SiMe_3)_2]{+2\,R^*Na} R^*_2Sn \qquad (3)$$

$$R^*_2Sn \xrightarrow[-R^*]{+R^*_2Sn} [R^*_2Sn{=}SnR^*]^{\bullet} \xrightarrow[-R^*]{+R^*_2Sn} \mathbf{5} \qquad (4)$$

Characterization and Structure of the Tristannaallene 5

From a solution of **5** in 1.7 mL of pentane/0.1 mL of C_6D_6 at −25 °C, prepared from 0.7 mmol of $Sn[N(SiMe_3)_2]_2$ and 0.7 mmol of $t\mathrm{Bu}_3\mathrm{SiNa}$ in 0.7 mL of pentane/0.1 mL of C_6D_6 at −25 °C (cf. Experimental), dark blue crystals of **5** are formed within several days. These are sensitive to air as well as to moisture and slowly thermolyse at room temperature. Hereby, as shown in Equation (2) isomerization with formation of **6** takes place according to a first order reaction with half-life of 9.8 h at 25 °C.

The *structure* of the tristannaallene **5** results unambiguously from the $^{119}Sn\{^1H\}$- and $^{29}Si\{^1H\}$-NMR spectra, as well as from an X-ray structure analysis. In the *$^{119}Sn\{^1H\}$-NMR spectrum* (cf. Figure 1) two signals at low field (δ = 503, 2233, intensity ratio 2:1) are observed, which result from the isotopomers with ^{119}Sn in terminal and central position, respectively. The chemical shift of the terminal three-coordinate Sn atoms in **5** compares well with that of the distannene **3** with R = 2,4,6-$i\mathrm{Pr}_3C_6H_2$ (δ = 427.3[7]) − the only distannene known so far to be stable in solution at ambient temperature. In contrast, the NMR signal of the central two-coordinate Sn atom appears at much lower field in the same region where also the signals of the symmetrically and unsymmetrically substituted stannylenes **2** with $R_2 = (Me_3Si)_2C{-}CH_2{-}CH_2{-}C(SiMe_3)_2$ (δ = 2323[21]) as well as $[CH(SiMe_3)_2]_2$ (δ = 2328[22]) and R/R = 2,4,6-$i\mathrm{Pr}_3C_6H_2$/2,4,6-$[(Me_3Si)_2CH]_3C_6H_2$ (δ = 2208[23]) are found. This similarity suggests for the central tin atom in **5** a considerable stannylene character with a stereochemically active lone pair of electrons − a fact which is further supported by the bent Sn−Sn−Sn arrangement resulting from the X-ray structure analysis for the solid state (see below). Thus, the bonding situation in **5** is best described by the resonance formulae shown in Equation (5).

(5)

The ^{119}Sn-NMR signals of the central and terminal tin atoms are each accompanied by two pairs of satellites, which arise from the isotopomers having either one ^{119}Sn and one ^{117}Sn or two ^{119}Sn nuclei in one of the terminal positions and in the central position (Figure 1). The signal of the terminal tin atoms exhibits an additional pair of satellites, which results from the two-bond ^{119}Sn,^{117}Sn coupling of the isotopomer having one ^{119}Sn and one ^{117}Sn in the terminal positions. The observed value for the one-bond tin,tin coupling of 4302 Hz for $^1J(^{119}Sn,^{119}Sn)$ and 4117 Hz for $^1J(^{119}Sn,^{117}Sn)$ is considerably larger than $^1J(^{119}Sn,^{117}Sn)$ in the distannenes **3** with R = 2,4,6-$i\mathrm{Pr}_3C_6H_2$ (2930 Hz[24]) and R = $CH(SiMe_3)_2$ (1340 Hz, from the ^{119}Sn CPMAS spectrum[22]). This is in accord with the shorter Sn=Sn distance in **5** (2.68 Å) relative to the Sn=Sn distances reported so far for distannenes (2.76−2.94 Å; cf. Table 1). $^2J(^{119}Sn,^{117}Sn)$ is with 1679 Hz also remarkably large.[25]

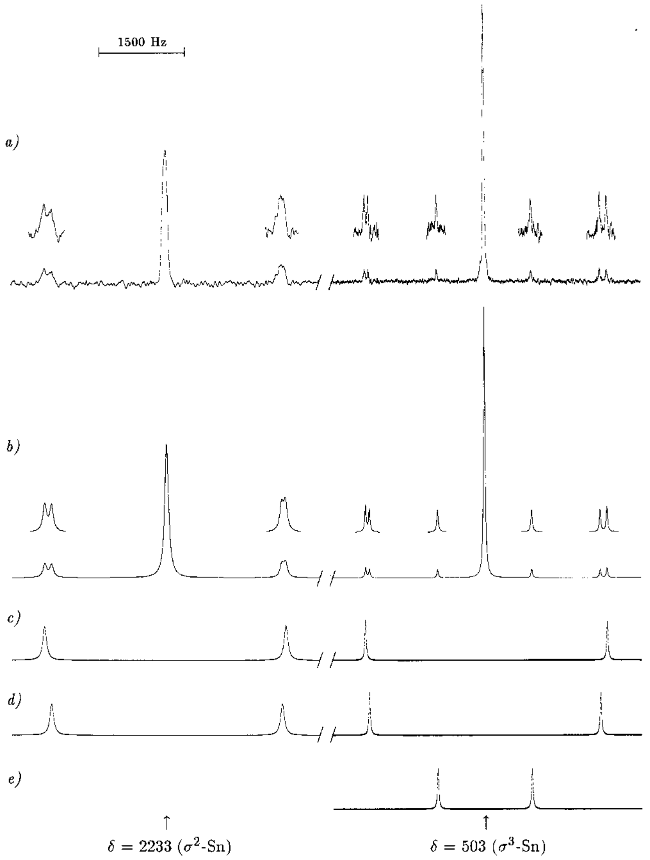


Figure 1. $^{119}Sn\{^1H\}$-NMR spectrum of the tristannaallene **5**: *a)* Observed spectrum at 100.7 MHz and −20 °C (ca. 0.1 M solution in $[D_8]$toluene, 10000 scans with 0.7 s repetition time). − *b)* Calculated total spectrum (Program DSYMPC, G. Hägele, R. Spiske, S. Goudetsidis, F. Mistry, University of Düsseldorf, **1994**), representing the sum of the spectra of all isotopomers with ^{119}Sn, and ^{119}Sn together with ^{117}Sn, weighted according to their natural abundances. The tin satellites of the low field signal originate from the superposition of the signals of the σ^2−Sn atom in the isotopomers with one additional ^{119}Sn (14.3% rel. intensity, $^1J(^{119}Sn,\ ^{119}Sn)$ = 4302 Hz) and ^{117}Sn (12.7% rel. intensity, $^1J(^{119}Sn,\ ^{117}Sn)$ = 4117 Hz) in the terminal positions. (cf. *c* and *d*) For the signal of the σ^3-Sn atoms the tin satellites result from the superposition of the signals of the isotopomers with one additional ^{119}Sn (7.2% rel. intensity) and ^{117}Sn (6.3% rel. intensity) in the central position, as well as ^{117}Sn (6.3% rel. int, $^2J(^{119}Sn,\ ^{117}Sn)$ = 1679 Hz) in the other terminal position (cf. *c*, *d*, and *e*).

The *$^{29}Si\{^1H\}$-NMR spectrum* of **5** shows only one signal at δ = 77.3. It is accompanied by three pairs of satellites, arising from the isotopomers with one ^{119}Sn or ^{117}Sn nucleus in the three possible positions. From the satellites the values of 109 Hz for ^1J(Sn,Si), of 54 Hz for ^2J(Sn,Si), and of 12 Hz for ^3J(Sn,Si) can be estimated.

The dark-blue crystals of the tristannaallene, obtained from pentane/benzene at −25°C, contain according to the result of an *X-ray structure analysis* in the unit cell two independent molecules of **5**, which form an axially chiral pair of enantiomers. The structure of one of the molecules of **5** in the unit cell is displayed in Figure 2 together with selected bond lengths and angles for both molecules **5**. Figure 3 shows Newman projections of both enantiomeric molecules **5** viewed in direction of the outer tin atoms of the Sn_3 chain together with selected fold and torsion angles.

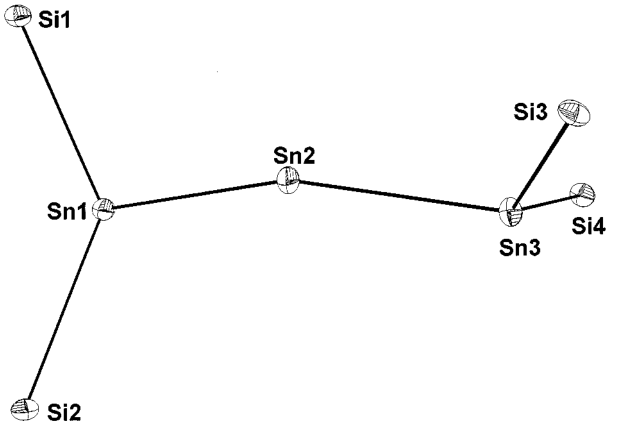


Figure 2. View of the crystal structure of one of the two enantiomers **5** in the unit cell (ORTEP, 25% thermal probability ellipsoide, tert-butyl groups omitted for clarity). Selected bond lengths [Å] and angles [°] (in brackets corresponding data of the other enantiomer **5** in the unit cell with Sn6/Sn5/Sn4/Si7/Si8/Si6/Si5 instead of Sn1/Sn2/Sn3/Si1/Si2/Si3/Si4; for folding and torsion angles see Figure 3): Sn1−Sn2 2.684 (1) [2.682(1)], Sn2−Sn3 2.675(1) [2.675(1)], Sn1−Si1 2.692(3) [2.694(3)], Sn1−Si2 2.689(3) [2.687(3)], Sn3−Si3 2.683(3) [2.701(3)], Sn3−Si4 2.696(3) [2.697(3)]. − Sn1−Sn2−Sn3 156.01(3) [155.81(3)], Si1−Sn1−Si2 134.29(9) [133.96(9)], Si1−Sn1−Sn2 100.58(7) [101.16(7)], Si2−Sn1−Sn2 109.39(7) [108.69(7)], Si3−Sn3−Si4 133.61(10) [134.38(10)], Si3−Sn3−Sn2 100.48(7) [99.94(6)], Si4−Sn3−Sn2 112.79(8) [113.01(8)].

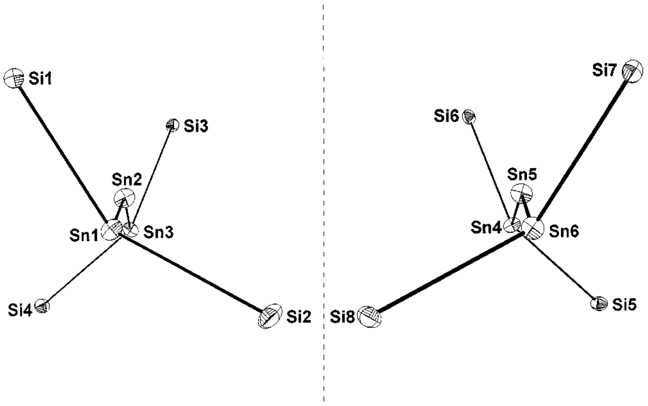
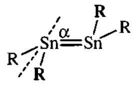


Figure 3. Newman projection of the two tristannaallene enantiomers **5** in the unit cell, viewed in direction Sn1−Sn3 and Sn6−Sn4. Folding angles [°] between the bisector b-Sn of the SiSnSi angles and the SnSn bonds as well as torsion angles [°] between the SiSn bonds of the two $R^*{}_2Sn$ groups in **5** (for bond lengths and angles see Figure 2): b-Sn1/Sn1−Sn2 48.5, b-Sn3/Sn3-Sn2 43.4, b-Sn6/Sn6−Sn5 48.9, b-Sn4/Sn4−Sn5 43.3. − Si1−Sn1−Sn3−Si3 53.0, Si1−Sn1−Sn3−Si4 98.0, Si2−Sn1−Sn3−Si3 97.1, Si2−Sn1−Sn3−Si4 111.8, Si7−Sn6−Sn4−Si6 52.5, Si7−Sn6−Sn4−Si5 99.6, Si8−Sn6−Sn4−Si6 98.9, Si8−Sn6−Sn4−Si5 111.1.

The most striking feature of the structure of **5** are the short SnSn distances, for which an avarage value of 2.683 Å is found. The SnSn distances in **5** are thus shorter than all SnSn distances observed for distannenes so far (2.77−2.91 Å; cf. Table 1), but longer than the one found for the Sn=Sn bond in **6** (2.59 Å, see below). This suggests, in accordance with the resonance formulae (5), a bond order between one and two for the SnSn bonds in **5**; in contrast, a bond order of nearly one for the "distannenes" is listed in Table 1 (cf. 2.85 Å for the Sn−Sn single bond length in **6**), as indicated by the resonance formulae

$$[R_2Sn{\rightarrow}SnR_2 \leftrightarrow R_2Sn{\leftarrow}SnR_2]. \qquad (5)$$

Table 1. Double bond lengths *d*(SnSn), fold angles α (cf. formula in the Table), and dihedral angles δ(**R**Sn**SnR**) of distannenes **3** studied by X-ray structure analyses to date

R/R in 	*d* (SnSn)	α	δ(**R**SnSn**R**)	Ref.
$CH(SiMe_3)_2$ / $CH(SiMe_3)_2$	2.77 Å	41°	0°	[5]
R'_4C_6H / R'_4C_6H[a]	2.91 Å	21/64°	33/55°	[6]
Tip/Tip[b]	[b]			[7]
$Si(SiMe_3)_3$ / $Si(SiMe_3)_3$	2.83 Å	29°	63°	[8a]
$Si(SiMe_3)_3$ / 2,4,6-$(CF_3)_3C_6H_2$	2.83 Å	42°	0°	[8b]
Tristannaallene **5**[c]	2.68 Å	24/46°	—	present
Cyclotristannene **6**[c]	2.59 Å	< 5°		paper

[a] R'_4C_6H = 2-*t*Bu-4,5,6-Me_3C_6H. − [b] From solutions that contain 3 $(Tip_2Sn)_2 \rightleftharpoons 2\,(Tip_2Sn)_3$ with Tip = 2,4,6-*i*$Pr_3C_6H_2$ only $(Tip_2Sn)_3$ crystallizes.[7] − [c] Mean values.

Another interesting feature, which becomes evident from Figure 2, is − as already mentioned − the bent rather than linear Sn_3 chain in **5**. This is again in accordance with the resonance formulae (5), and consequently **5** does not represent a "real" homologue of an allene. Indeed, the observed SnSnSn bond angle of 155.9° is quite large (cf. NSnN angle in crystalline **2c**[12], 104.7°) − a consequence of the steric interactions of the supersilyl groups and perhaps also a consequence of a small participation of the lone pair of electrons at the central tin atom in the bond system of the Sn_3 fragment.

The two outer tin atoms of the Sn_3 chain in **5** have no planar surroundings, as is the case with the corresponding carbon atoms in allenes; they are located each at the top of a flat pyramid, the base of which is formed by two supersilyl groups and the inner Sn atom (sum of the angles at the outer Sn atoms on average 345.6°). The "folding angle" between the bisecting line of the SiSnSi angle and the bond axis between the outer and the central tin atoms falls with an average value of 46.0°, in the same range as the folding angles observed for distannenes (21−64°, cf. Table 1).

As a consequence of the steric pressure of the two Sn-bonded supersilyl groups the SiSnSi bond angle in the two $R^*{}_2Sn$ groups of compound **5** is quite large and clearly exceeds 120° (on average 134.1°; cf. SiSnSi angle in $R^*{}_2SnCl_2$, 145.0°,[26] and in **6**, 131°, see below). The $R^*{}_2Sn$ groups in **5** adopt − as the R_2C groups in allenes − a *gauche* configuration (cf. Figure 3). The four supersilyl groups in compound **5** occupy in close approximation the edges of a bisphenoid (cf. Figure 3). They cover the Sn_3 chain almost completely and prevent undesired reactions between the Sn_3 groups of different molecules. The SnSi distances (2.68−2.70 Å) are larger than the sum of the atomic radii $r_{Sn} + r_{Si}$ (1.40 + 1.17 = 2.57 Å[10]) − obviously a consequence of the mutual steric repulsion of the supersilyl groups.

Characterization and Structure of the Cyclotristannene 6

From a solution of **6** in 30 mL of *tert*-butyl methyl ether at −25 °C, prepared from 12 mmol of $Sn(OtBu)_2$ and 24 mmol of $tBu_3SiNa(THF)_2$ in 60 mL of pentane at −78 °C and 25 °C (cf. Experimental), dark red-brown crystals of **6** are formed within several days. These are sensitive to air, but stable to moisture at room temperature. As a solid, **6** decomposes at 166 °C; in benzene solution it slowly thermolyses at 100 °C with the formation of hexasupersilyl-*hexahedro*-octastannane $R^*_6Sn_8$.[17]

The *structure* of **6** − an isomere of tristannaallene **5** − with a distannene unit integrated in a Sn_3 ring is suggested by the $^{119}Sn\{^1H\}$- and the $^{29}Si\{^1H\}$-NMR spectra as well as by an X-ray structure analysis. The *$^{119}Sn\{^1H\}$-NMR spectrum* (cf. Figure 4) exhibits a signal at high field (δ = −694) together with a second signal at low field (δ = 412) with double intensity. The position of the low-field signal corresponds to that observed for the distannene **3** with R = 2,4,6-$iPr_3C_6H_2$ (δ = 427.3[7]) and for the terminal tin atoms in the tristannaallene **5** (s. above). Thus it can be unambiguously assigned to the three-coordinate tin atoms of the distannene unit in **6**. The high-field signal appears in the same region as the signals of the only cyclotristannanes **4** known so far with R = 2,6-$Et_2C_6H_3$ (δ = −416.5[6]) and with R = 2,4,6-$iPr_3C_6H_2$ (δ = −378.9[24]) and has to be assigned to the tetracoordinate tin atom in **6**.

The $^{119,117}Sn$ satellites originate from the isotopomer with two anisochronic ^{119}Sn nuclei and from the isotopomers with one ^{119}Sn and one ^{117}Sn nucleus and are clearly observable (Figure 4). The observed relative intensity of the tin satellites (22% for the low field signal and 28% for the high field signal) proves the presence of three tin atoms in the molecule and at the same time clearly excludes the zwitterionic distannene structure suggested in ref.[16]. The striking unsymmetrical arrangement of the satellites (Figure 4) is caused by the AX spectrum of the isotopomer with two anisochronous ^{119}Sn nuclei, which already slightly deviates from the first order. $^1J(^{119}Sn,^{117}Sn)$ between the two three-coordinate tin atoms of the distannene unit is 2110 Hz, almost half the coupling observed for **5** (see above), and roughly comparable to the Sn,Sn coupling constant in the distannene **3** with R = 2,4,6-$iPr_3C_6H_2$ (2930 Hz[7]). On the other hand the observed value is definitely larger than the one reported for the distannene **3** with R = $CH(SiMe_3)_2$ (1340 Hz[22]), for which an exceptionally weak Sn,Sn bond is discussed. The coupling constants $^1J(^{119}Sn,^{119}Sn)$ and $^1J(^{119}Sn,^{117}Sn)$ between the three- and the tetracoordinate Sn atoms in **6** of 2223 and 2123 Hz, respectively, are of the same order of magnitude as $^1J(^{119}Sn,^{117}Sn)$ in the cyclotristannanes **4** with R = 2,6-$Et_2C_6H_3$ (2285 Hz[6]) and with R = 2,4,6-$iPr_3C_6H_2$ (3017[24]).

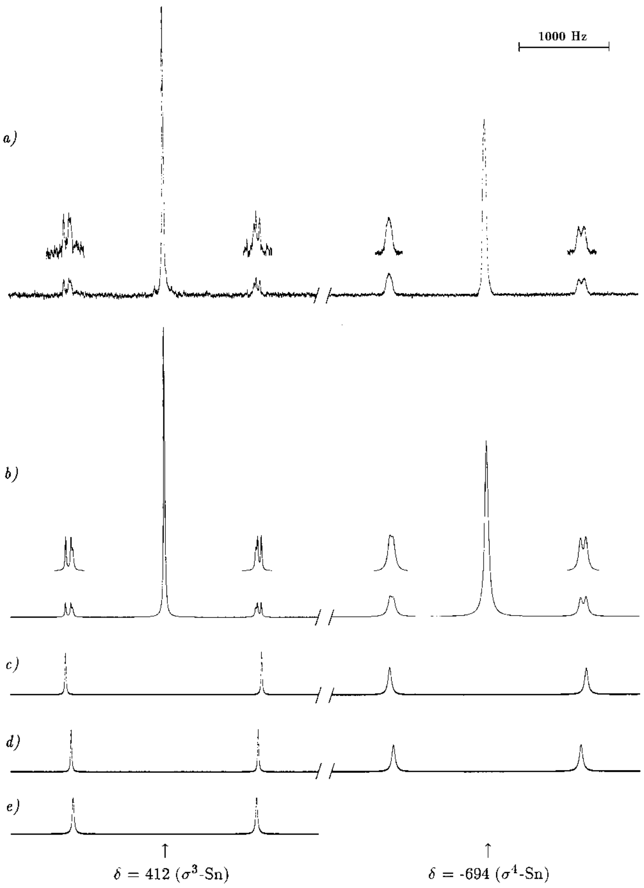


Figure 4. $^{119}Sn\{^1H\}$-NMR spectrum of the cyclotristannene **6**: *a)* Observed spectrum at 100.7 MHz (ca. 0.1 M solution in C_6D_6, 70000 scans with 0.7 s repetition time). − *b)* Calculated total spectrum (Program DSYMPC, G. Hägele, R. Spiske, S. Goudetsidis, F. Mistry, University of Düsseldorf, **1994**), resulting from the addition of the spectra of all isotopomers containing ^{119}Sn, and ^{119}Sn together with ^{117}Sn, weighted according to their natural abundances. The Sn satellites of the low-field signal originate from the superposition of signals of the σ^3-Sn atoms in the isotopomers with one additional ^{119}Sn in 3-position [7.2% rel. intensity, $^1J(^{119}Sn,^{115}Sn)$ = 2223 Hz], ^{117}Sn in 3-position (6.3% rel. intensity, $^1J(^{119}Sn,^{117}Sn)$ = 2123 Hz) and ^{117}Sn in 1(2)-position (6.3% rel. intensity, $^1J(^{119}Sn,^{117}Sn)$ = 2110 Hz) (cf. *c*, *d*, and *e*). For the high field signal the Sn satellites arise from the signals of the σ^4-Sn atom of the isotopomers with one additional ^{119}Sn (14.3% rel. intensity) and ^{117}Sn (12.7 rel. intensity) in 1(2)-position (cf. *c* and *d*).

The *$^{29}Si\{^1H\}$-NMR spectrum* of **6** shows, in accordance with the cyclotristannene structure, two signals of equal intensity at δ = 58.0 (for $Sn(SitBu_3)_2$) and at δ = 35.6 (for $SnSitBu_3$). Each of the two signals is accompanied by one pair of satellites, resulting from the isotopomers with one ^{119}Sn or ^{117}Sn directly bonded to the ^{29}Si nucleus. A $^1J(Sn,Si)$ of 81 Hz for the $SitBu_3$ groups at the distannene unit falls into the usual range. In contrast, an unusually small value[25] of $^1J(Sn,Si)$ = 12 Hz is observed for the $SitBu_3$ groups bonded to the tetracoordinate tin atom.

The dark red-brown crystals of the cyclotristannene, obtained from *tert*-butyl methyl ether at −25 °C, contain according to the result of an *X-ray structure analysis* two independent molecules **6** in the unit cell. Figure 5 shows the structure of one of the molecules **6**, as well as selected bond lengths and bond angles for both molecules. However, due to the poor quality of the crystals obtained from *t*BuOMe (no crystals could be obtained from heptane or benzene), only the positions of the Sn and Si atoms could be determined with sufficient accuracy.

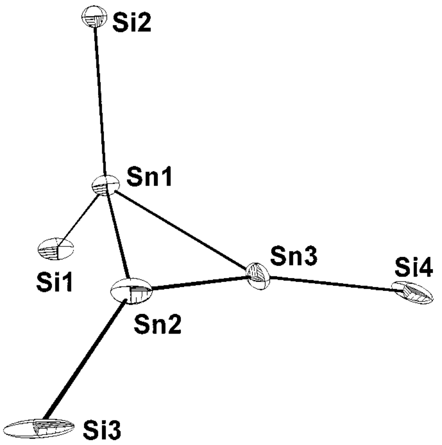


Figure 5. View of the molecular core of one of the two crystallographically independent cyclotristannene molecules **6** in the unit cell (ORTEP plot, 25% thermal probability ellipsoids, *tert*-butyl groups omitted for clarity). Selected bond lengths [Å] and angles [°] (in brackets corresponding data of the second molecule **6** in the unit cell with Sn4/Sn5/Sn6 instead of Sn1/Sn2/Sn3): Sn1−Sn2 2.852(2) [2.841(3)], Sn1−Sn3 2.859(3) [2.846(2)], Sn2−Sn3 2.601(3) [2.582(4)]. − Sn2−Sn1−Sn3 54.19(7) [53.99(8)], Sn1−Sn2−Sn3 63.05(7) [63.07(8)], Sn2−Sn3−Sn1 62.76(6) [62.94(7)]. − Angle sum at Sn2/Sn3 350.8/355.8, at Sn5/Sn6 359.6/360.0.

The most striking feature in the structure of **6** is the SnSn double bond length in the Sn_3 rings, for which an average value of only 2.59 Å is found. The cyclotristannene **6** exhibits thus the shortest Sn=Sn bond of all structurally investigated distannenes so far (cf. Table 1). The Sn=Sn moiety has a nearly planar surrounding, formed by the directly attached Si atoms and by the tetracoordinate Sn atom. Thus the "distannene" **6** is the first compound with a Sn=Sn bond analogous to C=C bonds. As in the case of other analogous of the C=C bond, the length of a "true" Sn=Sn bond can be calculated as the sum of the atom radii, each reduced by 0.1 Å ($2 \times r_{Sn} - 0.2 = 2 \times 1.40 - 0.2 = 2.60$ Å[10]). The SnSn single bond lengths in the Sn_3 rings are with an average value of 2.85 Å somewhat longer than the sum of the Sn atom radii (2.80 Å).

The four supersilyl groups in compound **6** occupy roughly the edges of a tetrahedron, thus adopting a close packing. They cover the Sn_3 ring almost completely and prevent it from reacting with the Sn_3 ring of another molecule. The distances between the Si atoms and the attached unsaturated Sn atoms in **6** of 2.57−2.60 Å fall within the usual range ($r_{Sn} + r_{Si} = 1.40 + 1.17 = 2.57$ Å). On the other hand the distances of the Si atoms bonded to the saturated Sn atom in the cyclotristannene (2.72−2.76 Å) are clearly elongated as a consequence of the steric interactions between the two supersilyl groups.

Experimental Section

All experiments were carried out in flame-dried glass apparatus with the Schlenk technique under dry argon atmosphere. During all manipulations air and moisture were strictly excluded. tBu$_3$SiNa (in pentane),[27] tBu$_3$SiNa (in THF),[27] Sn(O*t*Bu)$_2$,[11] and Sn[N(SiMe$_3$)$_2$]$_2$[12] were prepared according to literature procedures. The solvents (pentane, benzene, tetrahydrofuran) were distilled from sodium/benzophenone immediately before use. − The NMR spectra were recorded with a JEOL GSX-270 (^{1}H/^{13}C/^{29}Si/^{119}Sn: 270.17/67.94/53.67/100.75 MHz) and a JEOL EX-400 (^{1}H/^{13}C/^{29}Si/^{119}Sn: 399.78/100.54/79.43/149.08 MHz) spectrometer. The ^{29}Si-NMR spectra were recorded with the INEPT pulse sequence using empirically optimized parameters for polarization transfer from the *t*Bu substituents. For the ^{119}Sn-NMR spectra an acquisition time of 0.3−0.4 s and a repetition rate of ca. 0.6 s were used; for 0.1 m solutions of the tin compounds typically 5000 scans were necessary to obtain spectra with satisfactory signal to noise ratio.

Formation of 5 from Sn[N(SiMe$_3$)$_2$]$_2$: A solution of 0.311 g (0.708 mmol) of Sn[N(SiMe$_3$)$_2$]$_2$ in 0.7 mL of pentane and 0.1 mL of C_6D_6 was added dropwise to 0.152 g (0.685 mmol) of solid tBu$_3$SiNa at −196 °C. The resulting reaction mixture was warmed to −25 °C. At this temperature the reaction solution contains, according to the ^{119}Sn-NMR spectrum, **5** (see below), **6** (see below), Sn[N(SiMe$_3$)$_2$]$_2$,[12] and a still unidentified tin compound **7** bearing tBu$_3$Si as well as Me$_3$Si groups and two equivalent tin atoms [integral ratio of the ^{119}Sn NMR signals of **5** (1 + 2 Sn atoms), **6** (1 + 2 Sn atoms), **7** (2 Sn atoms) = (7 + 14):(1/2 + 1):5].[28] In the ^{29}Si-NMR spectrum of the reaction solution at −25 °C in addition to **5**, **6**, Sn[N(SiMe$_3$)$_2$]$_2$, and **7**, as well as tBu$_3$Si−Si*t*Bu$_3$ (δ = 35.2) and tBu$_3$SiH (δ = 17.4) can be identified. The reaction solution was separated at −25 °C from the precipitate formed, which was then washed with pentane (1 mL). The combined pentane solutions are kept at −25 °C for several days during which time dark blue crystals of *tetrakis(tri-tert-butylsilyl)tristannaallene* (**5**) (0.040 g, 0.035 mmol, 20%) are formed. − ^{1}H NMR (C_6D_6, −25 °C, TMS internal reference (int.)): δ = 1.40 (s, 4 Si*t*Bu$_3$). − ^{29}Si NMR (C_6D_6, −25 °C, TMS external reference (ext.)) and ^{119}Sn NMR ($C_6D_5CD_3$, −20 °C, SnMe$_4$ ext.): Cf. general part and Figure 1. − X-ray structure analysis. Cf. Figure 2 and 3.

Formation of 5 from Sn(O*t*Bu)$_2$: In an NMR tube 0.055 g (0.207 mmol) of Sn(O*t*Bu)$_2$ and 0.046 g (0.207 mmol) of tBu$_3$SiNa are dissolved in 0.6 mL of C_6D_6 and the solution was immediately cooled to −25 °C. The reaction mixture instantly adopts a black color. The ^{29}Si-NMR spectrum of the reaction solution shows after warming to ambient temperature the signals of tBu$_3$Si−Si*t*Bu$_3$, tBu$_3$SiH, and **5**.

Formation of 6 from Sn(O*t*Bu)$_2$: A solution of 3.179 g (12.00 mmol) of Sn(O*t*Bu)$_2$ in 20 mL of pentane was added dropwise at −78 °C to a solution of 8.799 g (24.00 mmol) of tBu$_3$SiNa(THF)$_2$ in 60 mL of pentane. After stirring for 3 d at −78 °C and for further 2 d at ambient temperature the reaction solution contains, according to the ^{1}H-NMR spectrum, in addition to supersilane tBu$_3$SiH (formed from the hydrolysis of tBu$_3$SiNa) practically only tBu$_3$Si−Si*t*Bu$_3$ and **6** in a molar ratio of 1.1 (in the case the formation of **6** would proceed exclusively via (1) and (2) the molar ratio should amount to 1.0). The solvent and all volatile components are removed in vacuo, the remaining brown residue was stirred with 50 mL of *n*-heptane, and the insoluble materials (mainly NaO*t*Bu and small amounts of an insoluble tin compound) are separated by filtration. The solvent was removed from the filtrate in vacuo and the residue left dissolved in 20 mL of pentane. In the course of 2 weeks at −23 °C one part of the dissolved superdisilane crystallizes from the pentane solution and was separated by filtration. The pentane filtrate was subjected to flash chromatography on an Al_2O_3 column with *n*-heptane as mobile phase. The heptane was removed in vacuo and the residue dissolved in 30 mL of *t*BuOMe. After several days *1,2,3,3-tetrakis(tri-tert-butylsilyl)cyclotristannene* (**6**; 1.244 g, 1.080 mmol, 27%) crystallizes from this solution at −25 °C as dark red-brown rods. − ^{1}H NMR (C_6D_6, TMS int.): δ = 1.409 (s; 2 SnSi*t*Bu$_3$), 1.515 [s; Sn(Si*t*Bu$_3$)$_2$]. − ^{13}C{^{1}H} NMR ($C_6D_5CD_3$, TMS int.): δ = 29.05/34.66 (*C*Me$_3$/C*Me*$_3$ of 2 SnSi*t*Bu$_3$), 26.42/32.55 [*C*Me$_3$/C*Me*$_3$ of Sn(Si*t*Bu$_3$)$_2$]. − ^{29}Si (C_6D_6, TMS ext.) and ^{119}Sn NMR (C_6D_6, SnMe$_4$ ext.): Cf. General part and Figure 4. − X-ray structure analysis: Cf. Figure 5.

Thermolysis of 5: A solution of 0.152 g (0.306 mmol) of Sn[N(SiMe$_3$)$_2$]$_2$ in 0.6 mL of C_6D_6 was added to 0.059 g (0.265 mmol) of *t*Bu$_3$SiNa and the resulting blue reaction solution was investigated by ^{1}H and ^{29}Si NMR. Every 24 min a ^{1}H-NMR spectrum (16 scans, PD = 2.5 s) was recorded at 25 °C for a total of 27 ^{1}H-NMR spectra. Between every two ^{1}H experiments a ^{29}Si-NMR spectrum was recorded in order to control the course of the reaction. The first recorded ^{1}H-NMR spectrum showed the following signals: δ = 1.407 (**5**, rel. intensity 2.69), 1.476 and 1.378 (**6**, rel. intensity of both signals together 2.19), 1.365 (*t*Bu$_3$Si−Si*t*Bu$_3$, rel. intensity 1.67), 1.118 (*t*Bu$_3$SiH, rel. intensity 2.65), 1.343 and 0.456 (**7**, rel. intensity of both signals together 2.76), 0.274 {Sn[N(SiMe$_3$)$_2$]$_2$, rel. intensity 11.5}. The intensities of the ^{1}H-NMR signals as resulting from the evaluation of the integrals, are assumed to correspond to the relative concentrations of the single compounds in the reaction solution. To determine the reaction order ln(signal region **5** + signal region **6**/signal region **5**) was plotted against the time *t*, where signal regions **5** and **6** are the relative intensities of the ^{1}H-NMR signals of **5** and **6** (both signals of **5** as well as **6** together), respectively. The half-life of the first-order isomerization was determined to be 9.8 h at 25 °C.

X-ray Structure Determination of 5: Siemens P4 diffractometer, Mo-K_α radiation, graphite monochromator, CCD area detector, crystal dimensions 0.2 × 0.15 × 0.1 mm. The crystal was mounted in perfluoro ether oil, T = 183(2) K, $C_{48}H_{108}Si_4Sn_3$, M_r = 1153.77, deep purple prism, orthorhombic, a = 28.7513(6), b = 12.1963(2), c = 33.3574(2) Å, $\alpha = \beta = \gamma = 90°$, V = 11697.1(4) Å^3, Z = 8; space group *Pca*2(1), ρ_{cacd} = 1.310 Mg m^{-3}, μ = 1.381 mm^{-1}, F(000) = 4816. *Data collection*: 2 θ from 2.44 to 58.38°, $-38 \le h \le 30$, $-15 \le k \le 15$, $-41 \le l \le 41$; of 64648 reflections 22638 were independent (R_{int} = 0.1221) and 14134 were observed [$F > 4\sigma(F)$], semiempirical absorption correction with SADABS (max./min. transmission 0.9765/0.8571), R_1 = 0.0708, wR_2 = 0.0801 [$F > 4\sigma(F)$], GOOF (F^2) = 0.989; maximum residual electron density 1.226 eÅ^{-3}. *Structure determination:* The structure was solved by direct methods (SHELXL-97). The absolute structure could not be determined. Three C atoms could only be refined with isotropic displacement parameters. The structure has not been completely refined until now.[29]

X-ray Structure Determination of 6: Siemens P4 diffractometer, Mo-K_α radiation, graphite monochromator, CCD area detector. It was extremely difficult to select a suitable crystal from the almost brown-black solution, and a large number of crystals were tested. The crystals were mounted in perfluoro ether oil, T = 183(2) K, $C_{48}H_{108}Si_4Sn_3$, M_r = 1153.77, deep red-brown plates. The best crystal 0.2 × 0.15 × 0.1 mm, gave the following monoclinic cell: a = 13.133(3), b = 29.956(6), c = 16.752(3) Å, β = 95.365(8)°, V = 6561.4 Å, Z = 4. In spite of absorption correction (SADABS), it was difficult to find an acceptable space group. For the best crystal it was space group *P*2(1). Structure solution by the heavy atom method revealed clearly the Sn_3Si_4 core of the molecule. The Sn−Si atom distances covered the range from 2.567(7) to 2.763(7) Å. Almost all *tert*-butyl groups showed rotational disorder. Therefore, the R_1 value of the "best" solution is only 17%. This is of course rather unsatisfactory; however, the data for the Sn−Sn distances are reliable if the esd′s are considered.

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[28] Compound **7** is formed in much better yield from the reaction of 0.381 g (1.713 mmol) of tBu$_3$SiNa with 0.369 g (0.840 mmol) of Sn[N(SiMe$_3$)$_2$]$_2$ in 15 mL of pentane at −78 °C, followed by complete evaporation of the pentane in vacuo, dissolution of the remaining residue in 10 mL of benzene and stirring of the benzene solution for several days.

[29] Crystallographic data (excluding structure factors) for compound **5** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-117961. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223/ 336-033; E-mail: deposit@ccdc.cam.ac.uk].

Received April 9, 1999
[I99105]