Compounds of Germanium and Tin, 25[◇]

A Zwitterionic Distannene and Two $(RSnX)_4$ Cages with an Unusual Arrangement of the Sn_4X_4 Cluster Atoms ($R = t\text{Bu}_3\text{Si}$, X = Se, Te)[☆]

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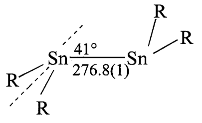
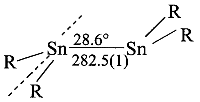
Reaction of tin(II) chloride with $RNa(THF)_2$ ($R = t\text{Bu}_3\text{Si}$) in THF at –30 °C led to a complex reaction mixture, from which the compounds $R_4Sn_4(THF)_2$, R_2SnSnR_2 (**5**), R–R (**7**), and a brownish black compound **6** were isolated. In toluene as solvent, the zwitterionic distannene **5** was obtained together with **7** and **6** which upon treatment with Et_3PX, furnished the cluster compounds $(RSnX)_4$ (**10**: X = Se; **11**: X = Te). The X-ray structure analyses of the isotypic compounds **10** and **11** revealed that the tin atoms occupy the corners of an undistorted tetrahedron with weak tin–tin interactions. The chalcogen atoms form a plane which bisects the Sn_4 tetrahedron.

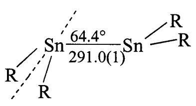
Lappert's distannene **1** was the first molecule with a formal homonuclear double bond between the heavier elements of group 14 to be prepared.[2][3] Although compound **1** was prepared in 1976 and characterized by X-ray crystallography almost twenty years passed before the compounds **2**[4] and **3**[5] could be isolated as further examples of this class of compound.



1, R = $CH(SiMe_3)_2$



2, R = $Si(SiMe_3)_3$

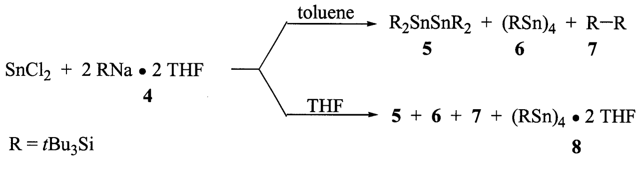


3, R = 2-*t*Bu-4,5,6-Me_3C_6H

The three crystalline distannenes possess widely differing structures. While the centrosymmetrical compound **1** exhibits an undistorted *trans*-bent arrangement of its substituents with a fold angle of 41° – which closely approaches the theoretically predicted fold angles of 46–51° for the parent compound $[Sn_2H_4]$[3][5] – the sterically overloaded compound **2** avoids interactions between its substituents by adopting a twist angle of 63.2° and a fold angle of 28.6°.[4] The behavior of compound **3** is even more surprising. The markedly lengthened tin–tin bond length and the differing environments of the two tin atoms possibly suggest that merely an interaction between the fully occupied 5s orbital of one tin atom with the empty 5p orbital of the other tin atom is operative. The zwitterionic structure of **3** that could be deduced from this assumption, however, is not supported by the ^{119}Sn CP-MAS NMR spectrum in which only one signal at $\delta_{\text{iso}} = 819$ is observed.[6] Similar to **1**, the recently described heteroleptic distannene RR′Sn=SnRR′ [$R = Si(SiMe_3)_3$, $R' = 2,4,6\text{-}(CF_3)_3C_6H_2$] exhibits a centrosymmetric structure with an Sn–Sn bond length of 283.3(1) pm and a fold angle of 41.5°.[7]

The distannenes **1–3** decompose in solution to the respective stannylene molecules R_2Sn:. We have now examined whether a distannene that is stable both in the solid state and in solution can be obtained by use of other substituents R. Our first choice of substituent was the tri-*tert*-butylsilyl group with its extremely high steric requirements for which we reported a simple access more than 20 years ago[8] and which in the mean time has been used successfully by Wiberg et al. in the syntheses of many interesting compounds including the tetrahedral molecules $(RSi)_4$ and $(RGe)_4$.[9]

We now report on a zwitterionic distannene as well as a tin cluster compound for which, however, characterization was only possible on the basis of the products of subsequent reactions.



Reaction of tin(II) chloride with the tri-*tert*-butylsilylsodium · THF adduct **4**[10] in toluene furnished a black-brown

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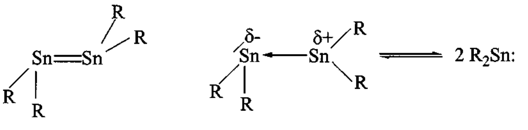
solution from which three products were isolated by fractional crystallization. First of all, a black-brown, finely crystalline precipitate was obtained but its constitution could not be determined neither by analytical nor spectroscopic means, an account of its poor solubility and extreme sensitivity to air. Only the subsequent reactions described below allowed conclusions to be drawn about the structure of this compound **6**. Colorless needles of the known hexa-*tert*-butyldisilane (**7**)[11] were obtained as a second fraction. Finally, upon longer standing of the solution at −25°C, dark brown, fibrous crystals separated, complete elemental analysis data of which are indicative of the distannene **5** or the corresponding stannylene R_2Sn:.



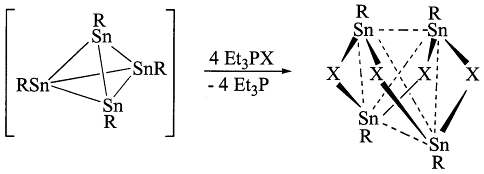
5a, R = *t*Bu$_3$Si **5b** **9**

Since we have not yet been able to obtain crystals of **5** suitable for X-ray diffraction analysis, its structural elucidation is based on NMR examinations of all nuclei present in **5** (C, H, Si, Sn). The presence of two singlet signals of equal intensity in the ^{1}H-NMR spectrum as well as the presence of two signals each for the primary and quaternary carbon atoms in the ^{13}C-NMR spectrum clearly show that two sorts of differently bonded *tert*-butyl groups are present. This is supported by the observation of two signals with different $^1J(^{29}Si,^{119}Sn)$ coupling constants in the ^{29}Si-NMR spectrum. Unambiguous information about the structure of **5** is provided by the ^{119}Sn-NMR spectrum in which two signals with chemical shifts of $\delta = -690$ and $+413$ and a coupling constant of $^1J(^{119}Sn,^{117}Sn) = 2135$ Hz demonstrate the presence of two tin atoms bonded to each other but having widely differing electronic environments.

It would seem that neither the stannylene **9** nor the centrosymmetric distannene **5a** exists in the solution. The data rather support the zwitterionic structure **5b** with the tin atom producing the ^{119}Sn signal shifted to low field acting as an electron donor from its doubly occupied 5s orbital to the unoccupied 5p orbital of the electron-accepting tin atom giving rise to the ^{119}Sn-NMR signal shifted to high field. An adduct of tin(II) chloride and a four-coordinated stannylene was recently reported;[12] the X-ray crystallographic analysis and ^{119}Sn-NMR spectrum of this adduct are, in spite of the different bonding partners and coordination numbers, suggestive of a bonding situation similar to that in **5b**.

The behavior of **5** as well as that of the $SnCl_2$ adduct is not self-evident since the distannenes **1**,[13] **2**,[4] and **3**[6] − which are stable in the solid state − do not give rise to any ^{119}Sn-NMR signals in solution at room temperature. This is assumed to be due in all cases to the rapid equilibrium distannene $\rightleftharpoons$ stannylene. In order to determine whether **5** is also subject to a similar equilibrium the molecular mass of **5** was determined in dilute solution (dilution from 4 g/100 ml to 0.6 g/100 ml). The measured value of 520 g · mol^{-1} was in good agreement with the calculated value of 517.5 for the stannylene **9**. The appearance of only one ^{1}H-NMR signal at $\delta = 1.35$ and of two ^{13}C-NMR signals at $\delta = 27.74$ (C_p) and 32.12 (C_q) is a further indication for the equilibrium **5** $\rightleftharpoons$ 2 **9**; ^{29}Si-and ^{119}Sn-NMR signals could not be recorded from this dilute solution.

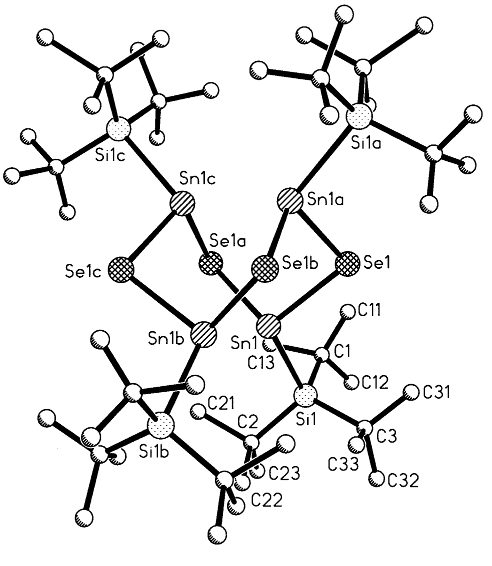
When the reaction of tin(II) chloride with **4** was performed in THF instead of toluene a dark-blue, fine crystalline solid was isolated in addition to compounds **5**−**7**. The analytical and spectroscopic data of this solid are indicative of the THF adduct **8**. However, the broad signals in the ^{1}H-NMR spectrum and the failure to observe ^{29}Si- and ^{119}Sn-NMR signals suggest that, like compounds **1**, **2**, and **3**, rapid exchange processes are in operation. Spectroscopic measurements at lower temperatures did not furnish a different result.



6, R = *t*Bu$_3$Si **10**, X =Se; **11**, X = Te

In order to obtain information about the structure of the practically insoluble and highly sensitive compound **6** we attempted to convert it to better characterizable products by treatment with the heavier chalcogenes. Although no rections with selenium or tellurium were observed, treatment of **6** with triethylphosphane selenide or telluride furnished the compounds **10** or **11**, respectively, in a smooth reaction. NMR data of these products indicate the existence of highly symmetrical molecules.

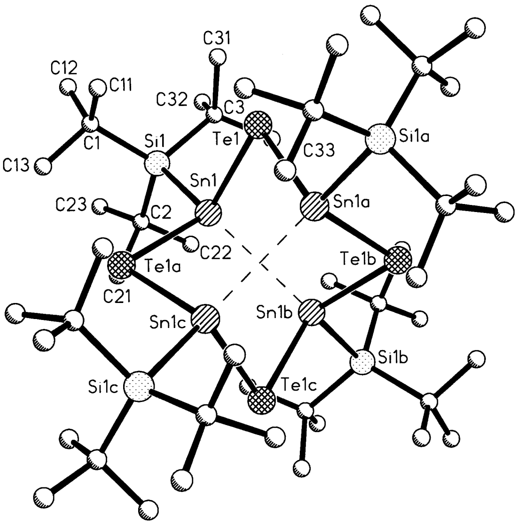
Figure 1. Molecular structure of **10** in the crystal (hydrogen atoms omitted)[a]



[a] Selected bond lengths [pm] and angles [°]: Sn−Se 255.2(2), Sn−Sn 301.8(3), Sn−Si 265.6(5); Sn−Se−Sn 94.8(1), Se−Sn−Se 101.5(1), Se−Sn−Si 108.0(1), Se−Sn−Sn 100.2(1).

The X-ray crystallographic analysis of **10** (Figure 1) confirmed the deductions from the NMR data and additionally provided some noteworthy details. In the crystal the asymmetrical unit contains a quarter of the molecule. The equivalent positions are designated by the letters a, b, and c in the figure. Accordingly, the respective Sn−Se, Sn−Si, and also Sn−Sn bond lengths are the same. The structure of **10** is not only unusual but also without precedent in the chemistry of tin chalcogenides. The four tin atoms form an undistorted tetrahedron that is divided into two equal parts by a quadratic layer of selenium atoms. The structure resembles that of the arsenic sulfide mineral realgar in which the arsenic and chalcogen atoms have a similar arrangement.[14] The tin−tin separations of 301.8 pm markedly exceed the normal value of 278 pm for the single bond in the reference substance hexamethylditin.[15] The long tin−tin bonds become reasonable upon simple electron counting. Merely four electrons are available for a total of six Sn−Sn bonds (one from each tin atom) within the tetrahedron so that the existence of a delocalized electron system with bond orders of markedly less than one may be assumed.

Figure 2. Molecular structure of **11** in the crystal (hydrogen atoms omitted)[a]



[a] Selected bond lengths [pm] and angles [°]: Sn−Te 274.2(1), Sn−Sn 328.1(2), Sn−Si 265.2(3); Sn−Te−Sn 95.1, Te−Sn−Te 101.8(1), Te−Sn−Si 109.1(1), Fe−Sn−Sn 100.3(1).

These structural peculiarities are even more pronounced in **11**, which is isotypical with **10** and is shown in a different perspective in Figure 2 in order to emphasize the unusual atomic arrangement. The tin−tin separation in **11** of 328.1(2) pm is even larger than that in **10** and again supports a low bond order for the Sn−Sn bonds.

The isolation of compounds **10** and **11** allows the conclusion, albeit with some reservations, that compound **6** could be a representative of the long sought *tetrahedro*-tetrastannane system and that chalcogen insertion into four of the six Sn−Sn bonds has given rise to these unequivocally characterized cage compounds. Wiberg et al. also obtained a product from similar reactions that they held to be **6** but which could not, on account of its above-mentioned properties, be characterized further.[9][16]

The various products arising from the action of **4** on tin(II) chloride can be most simply explained in terms of the primary formation of the stannylene **9** which either dimerizes to give the zwitterionic distannene **5** or reacts further with cleavage of tBu$_3$Si radicals[9] to furnish **7** and **6** (or **8** in THF). Hexaarylcyclotristannanes also behave similarly: their pyrolyses furnish, by suitable choice of the aryl groups, a wide variety of tin cluster compounds.[17]

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Experimental Section

All manipulations were performed by using standard Schlenk techniques under dry argon. − ^{1}H and ^{13}C NMR: Bruker AM 300. − ^{29}Si and ^{119}Sn NMR (inverse gated, ^{1}H-decoupled, Me$_4$Sn external): Bruker AMX 300. − MS: Varian MAT 212. − Elemental analyses: Analytische Laboratorien, D-51789 Lindlar, Germany.

Reactions of Tin(II) Chloride with **4**: A solution of anhydrous tin(II) chloride (2.11 g, 11.8 mmol) in 25 ml of THF was added dropwise to a solution of **4** (7.70 g, 22.4 mmol) in 50 ml of toluene at −30°C over a period of 3 h with stirring. The brownish black reaction mixture was stirred for an additional 1 h at −20°C and the insoluble compound **6** (0.38 g, 11% yield), m.p. 182°C, was filtered off. The solvents were removed and the residue redissolved in 30 ml of *n*-hexane. Precipitated NaCl was filtered off and the solution cooled to −50°C. After 12 h at this temperature, colorless crystals of **7** (1.0 g, 24% yield) were isolated and identified by comparison with literature data.[11] Concentration of the solution to a volume of 20 ml and cooling at −24°C for 3 d yielded dark brown, fibrous crystals of **5** (1.2 g, 21% yield).

Tetrakis(tri-tert-butylsilyl)distannene (**5**): M.p. 104°C. − ^{1}H NMR (C$_6$D$_6$, 25°C): δ = 1.40 [s, 54 H, $^4J(^1\text{H},^{119}\text{Sn})$ = 17.7 Hz], 1.51 [s, 54 H, $^4J(^1\text{H},^{119}\text{Sn})$ = 17.9 Hz]. − ^{13}C NMR (C$_6$D$_6$, 25°C): δ = 26.27 (C$_q$), 28.90 (C$_q$), 32.42 (C$_p$), 34.54 (C$_p$); C$_p$ and C$_q$ refer to primary and quaternary carbon atoms. − ^{29}Si NMR (C$_6$D$_6$, 25°C): δ = 24.99 [s, $^1J(^{29}\text{Si},^{13}\text{C})$ = 35 Hz, $^1J(^{29}\text{Si},^{119}\text{Sn})$ = 85.5 Hz], 54.49 [s, $^1J(^{29}\text{Si},^{13}\text{C})$ = 42.1 Hz, $^1J(^{29}\text{Si},^{119}\text{Sn})$ = 11.6 Hz]. − ^{119}Sn NMR (C$_6$D$_6$, 25°C): δ = 412.6 [s, $^1J(^{119}\text{Sn},^{117}\text{Sn})$ = 2135 Hz], − 689.9. − MS (CI, isobutane); *m/z* (%): 1037 (1) [MH$^+$], 519 (16) [MH$^+$ − SnR$_2$]. − C$_{48}$H$_{108}$Si$_4$Sn$_2$ (1035.1): calcd. C 55.70, H 10.52, Sn 22.93; found C 55.34, H 10.36, Sn 23.20.

A similar reaction in which toluene was replaced by THF led to the same products in comparable yields. However, in addition to compounds **5**, **6**, and **7**, 0.29 g of the dark blue, microcrystalline compound **8**, m.p. 76°C was isolated.

(tBu$_3$Si)$_4$Sn$_4$(THF)$_2$ (**8**): ^{1}H NMR ([D$_8$]toluene, 243 K): δ = 1.31 (br. s, 54 H), 1.43 (br. s, 54 H), 1.89 (m, 8 H), 3.57 (m, 8 H). − ^{13}C NMR ([D$_8$]toluene, 243 K): δ = 25.84 (C$_q$), 26.09 (C$_q$), 31.89 (C$_p$), 33.16 (C$_p$). − The ^{29}Si- and ^{119}Sn-NMR signals could not be observed. − C$_{56}$H$_{124}$O$_2$Si$_4$Sn$_4$ (1179.1): calcd. C 47.48, H 8.82; found C 47.40, H 8.91.

Formation of the Cluster Compound **10**: A solution of triethylphosphane selenide (0.32 g, 1.62 mmol) in 10 ml of *n*-hexane was added dropwise to a suspension of **6** (0.51 g, 0.40 mmol) in 100 ml of toluene at ambient temperature over a period of 30 min. The reaction mixture was stirred for 3 d in the dark. All insoluble components were filtered off and the solvents removed. The residue was redissolved in 10 ml of DME. Cooling of the yellow, light-sensitive solution to −24°C afforded 0.42 g (66% yield) of pale yellow, rectangular crystals of **10**, m.p. 115°C. − ^{1}H NMR (C$_6$D$_6$, 25°C): δ = 1.38 (s). − ^{13} C NMR (C$_6$D$_6$, 25°C): δ = 31.87 (C$_q$), 32.48 (C_p). − ^{119}Sn-NMR (C_6D_6, 25°C): $\delta = 120.21$. − MS (CI, isobutane); *m/z* (%): 1112 (8) [$t\mathrm{Bu}_3\mathrm{Sn}_3\mathrm{Se}_3$]. − $C_{48}H_{108}Se_4Si_4Sn_4 \cdot 2$ DME (1768.6): calcd. C 38.03, H 7.29; found C 38.80, H 7.43.

Formation of the Cluster Compound **11**: A solution of triethylphosphane telluride (0.98 g, 3.99 mmol) in 10 ml of *n*-hexane was added dropwise to a suspension of **6** (0.80 g, 0.63 mmol) in 60 ml of toluene over a period of 30 min. The reaction mixture was stirred in the dark for 3 d at room temperature. The solvents were removed and the residue was dissolved in 10 ml of *n*-hexane. All insoluble components were filtered off and the remaining red solution was stored for 4 d at 4°C. Excess triethylphosphane telluride was filtered off, the solvent removed and the residue redissolved in 8 ml of DME. Cooling to −24°C for 4 d furnished 0.64 g (57% yield) of air- and light-sensitive red crystals of **11**, m.p. 183°C. − ^{1}H NMR (C_6D_6, 25°C): $\delta = 1.37$ (s). − ^{13}C NMR (C_6D_6, 25°C): $\delta = 32.03$ (C_q), 34.02 (C_p). − ^{119}Sn NMR (C_6D_6, 25°C): between $\delta = +300$ and -500 no signal could be observed. − $C_{48}H_{108}Si_4Sn_4Te_4$ (1782.9): calcd. C 32.34, H 6.11; found C 33.43, H 6.62.

X-ray Structure Analyses of **10 and 11**: Crystal data and numerical data of the structure determinations are given in Table 1. Crystals were obtained by cooling a solution of **10** in diethyl ether to −24°C (**10**) or by cooling a DME solution of **11** to 4°C. In each case, the crystal was mounted in a thin-walled glas capillary. The structures were solved by direct phase determination using the SHELXTL PLUS program system and refined by full-matrix least-squares techniques. Hydrogen atoms were placed in the calculated positions, and all other atoms were refined anisotropically.[18]

Table 1. Crystallographic data of **10** and **11**

	10	**11**
Formula	$C_{48}H_{108}Se_4Si_4Sn_4$	$C_{48}H_{108}Si_4Sn_4Te_4$
Mol. mass	1588.32	1782.88
Cryst. dimensions [mm]	0.45 × 0.55 × 0.30	0.4 × 0.45 × 1.35
Cryst. system	tetragonal	tetragonal
Space group	$I\bar{4}2d$	$I\bar{4}2d$
a [pm]	2371.1(1)	2388.0(3)
c [pm]	1420.3(1)	1455.8(2)
V [× 10^6 pm^3]	7958	8302
Z	16	16
$d_{\mathrm{calcd.}}$ [g cm^{-3}]	1.982	2.140
Diffractometer	Siemens P4	Siemens P4
Radiation (graphite-monochromated) [pm]	Mo-K_α 71.073	Mo-K_α 71.073
T [K]	296(2)	296(2)
μ [mm^{-1}]	3.14	2.65
Scan method	ω	ω
$2\theta_{\max}$ [°]	55	55
No. of unique reflections	2666	2767
No. of observed reflections	1702	2133
F_o/parameter ratio	12.51	14.03
R (R_w) [$F > 3\sigma$ (F)]	0.066 (0.060)	0.064 (0.065)

☆ Dedicated to Professor *Bernt Krebs* on the occasion of his 60th birthday.

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[18] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101345. Copies of the data can be obtained free of charge on applications to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax. (internat.) + 44(0)1223/336-093; E-mail: deposit@ccdc.cam.ac.uk].

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