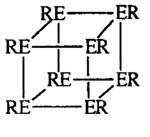
Hexasupersilyl-*triprismo*-hexastannane ($(tBu_3Si)_6Sn_6$)—The First Molecular Tin Compound Containing a Sn_6 Prism[**]

Nils Wiberg,* Hans-Wolfram Lerner, Heinrich Nöth, and Werner Ponikwar

Compounds R_nE_n with cubic (**1**), trigonal-prismatic (**2**), or tetrahedral polyhedra E_n (**3**) of carbon homologues E have only recently (since 1988) become accessible through the use of sterically demanding groups R.[1, 2] Evidently, less sterically demanding substituents do not provide sufficient protection to deter the polyhedral compounds from transforming into less strained compounds.[3, 4] In certain cases, compounds with polyhedral frameworks of type **1** and also types **2** and **3** can be synthesized for E = Si and Ge,[1, 2] whereas for E = Sn only those of type **1**, but not of type **2** and **3** are known. However, for E = Sn, compounds with a pentagonal Sn_{10} prismane and those with a Sn_5 propellane framework also exist,[5] whereas for E = Pb polyhedral compounds R_nE_n are still unknown.



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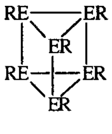

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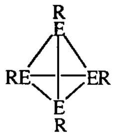
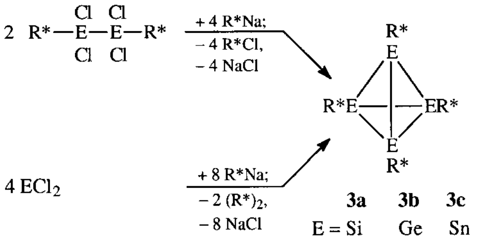


3

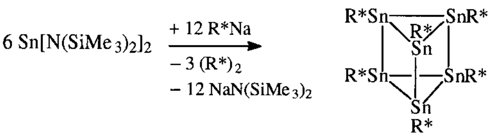
After our successful synthesis of a tetrasilatetrahedrane **3a**[6] along path (1) and then of a tetragermatetrahedrane **3b**[7] (in each case R in **3** is tri-*tert*-butylsilyl R* = Si*t*Bu$_3$ (supersilyl)) along paths (1) and (2) in the last few years, we decided to study the formation of a tetrastannatetrahedrane **3c** along path (2) as a continuation of our work. Accordingly, a solution of tin dichloride $SnCl_2$ in THF was added dropwise to a solution containing two molar equivalents of supersilylsodium tBu_3SiNa in THF cooled to −78 °C. On allowing the reaction mixture to slowly warm to room temperature it becomes dark brown, and a brown-black, insoluble tin compound as well as—according to NMR spectra of the reaction solution—superdisilane $tBu_3SiSitBu_3$[8] and a soluble tin compound, tetrasupersilyltristannacyclopropene $(tBu_3Si)_4Sn_3$[9, 10] are formed. The desired tetrahedrane **3c**, which was expected to be soluble in THF, is thus not obtained by this route.[10] The above-mentioned tristannacyclopropene also forms in reactions of tin di-*tert*-butoxide $Sn(OtBu)_2$ as well as those of tin bis{bis(trimethylsilyl)amide} $Sn[N(SiMe_3)_2]_2$ with tBu_3SiNa in pentane—along the path via isomeric tetrasupersilyltristannaallene $(tBu_3Si)_4Sn_3$[9]—or by dehalogenation of $R^*_2SnCl_2$ with sodium in benzene.[11]



(1)

(2)

The reaction of $Sn[N(SiMe_3)_2]_2$ with tBu_3SiNa (R*Na), proceeds differently when the pentane is replaced by *tert*-butyl methyl ether at −78 °C. After 4 h the dark blue reaction mixture was allowed to warm from −78 °C to −25 °C, and in the course of two days dark violet crystals precipitated from the mixture. According to the X-ray structure analysis[12] the crystals contain hexasupersilyl-*triprismo*-hexastannane (**2a**) in addition to superdisilane[8] and *tert*-butyl methyl ether. Thus again no tetrahedrane **3c** is formed, but instead along path (3) a polyhedral compound of tin with lower strain energy.[3] The crystals can be stored at room temperature in the absence of air, water, and solvents, and decompose in the presence of organic solvents above about −5 °C (formation of dark brown solutions). Remarkably, solutions of the crystals in toluene or THF at −25 °C only give a very weak ^{1}H and ^{29}Si NMR signal, respectively, and no ^{119}Sn NMR signal, which is consistent with the very low solubility of the product at the measurement temperature.



(3)

2a

Figure 1 shows the molecular structure of **2a** in the crystal. Compound **2a** comprises a near equilateral Sn_6 prismane framework with almost parallel Sn_3 faces that are only slightly twisted away from each other (see Figure 2; angle between the angle bisector of the upper and lower Sn_3 faces is 5.1°). Thus, both with respect to the Sn_6 structure as well as with respect to the $6 \times 3(Sn) = 18$ framework electrons (two electrons per bond), compound **2a** is classified as electron-precise; in contrast, the $[Sn_6\{Cr(CO)_5\}_6]^{2-}$ ion, which has been known for some time, is classified as a *closo* compound[13] both with respect to the Sn_6 structure (octahedron) as well as with respect to the $6 \times 2(Sn) + 2(e^-) = 14 = 2n + 2$ framework electrons present (n = number of Sn atoms). The three Sn–Sn distances between the Sn_3 faces of the Sn_6 prismane are each 2.91 Å, and within the Sn_3 faces two of the Sn–Sn distances are also 2.91 Å and one is 2.94 Å; they are thus—for steric reasons—slightly longer than the sum of the radii of two Sn atoms (2.80 Å[14]). Through the twisting of the Sn–Si bonds from the two Sn_3 units in opposite directions, the supersilyl groups achieve staggered (octahedral) packing (Figure 2). The Si–Sn distances are on average 2.71 Å and are thus longer than the sum $r_{Sn} + r_{Si} = 2.57$ Å,[14] but similar to the Si–Sn distances in $(tBu_3Si)_2SnCl_2$ (2.70 Å[15]).

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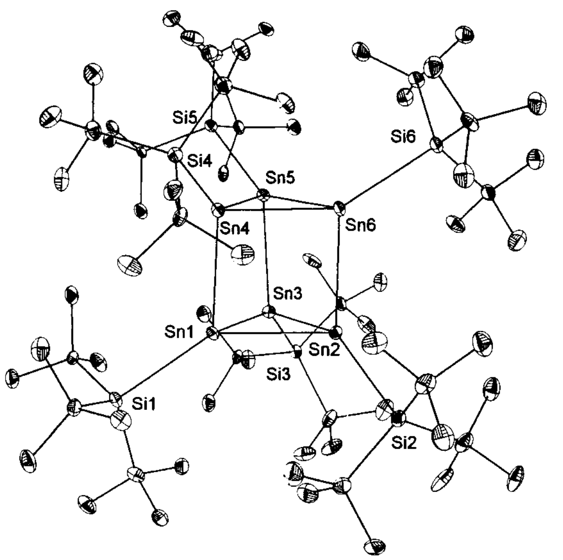

Figure 1. Side view of the molecular structure of $R^{*}_{6}Sn_{6}$ in the crystal (ORTEP plot; 25 % thermal probability ellipsoids; for clarity hydrogen atoms are not shown) and atom numbering scheme. Selected bond lengths [Å] and angles [°]: Sn1–Sn2 2.910(1), Sn1–Sn3 2.939(1), Sn1–Sn4 2.907(2), Sn2–Sn3 2.907(1), Sn2–Sn5 2.907(1), Sn3–Sn6 2.903(1), Sn4–Sn5 2.907(1), Sn4–Sn6 2.916(1), Sn5–Sn6 2.941(1), Si1–Sn1 2.743(3), Si2–Sn2 2.687(3), Si3–Sn3 2.700(3), Si4–Sn4 2.683(3), Si5–Sn5 2.752(3), Si6–Sn6 2.724(3), Si–C 1.940 (av); Sn_3 ring angles at Sn1/Sn2/Sn3 and Sn4/Sn5/Sn6 59.59(3)/60.70(3)/59.71(3) and 60.67(3)/59.82(3)/59.51(3), respectively, Sn_4 ring angles at Sn1/Sn2/Sn5/Sn4, Sn2/Sn3/Sn6/Sn5, and Sn1/Sn3/Sn6/Sn4 89.39(5)/90.22(5)/89.44(5)/90.29(5), 92.42(5)/88.01(5)/91.80(5)/87.28(5), and. 86.69(5)/92.64(5)/87.18(5)/93.05(5), respectively, Si1-Sn1-Sn2 114.74(6), Si1-Sn1-Sn3 145.25(6), Si1-Sn1-Sn4 128.05(6), analogous Si-Sn-Sn angles (see Figure 2) at Sn2 115.56(6)/146.29(6)/123.32(7), at Sn3 115.74(6)/147.11(7)/124.70(7), at Sn4 119.31(7)/144.81(6)/123.79(6), at Sn5 117.77(6)/146.21(7)/126.23(7), and at Sn6 117.74(6)/144.28(7)/127.91(6), C-Si-C 111.1 (av).

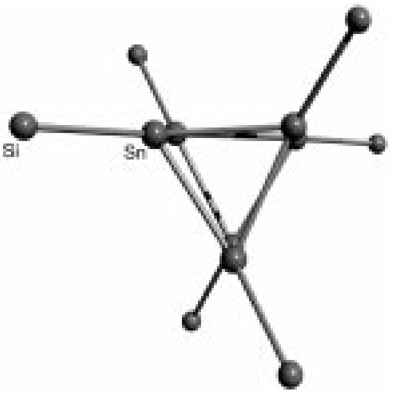

Figure 2. View of the structure of $R^{*}_{6}Sn_{6}$ in the crystal (SCHAKAL plot; atoms with arbitrary radii, for clarity *t*Bu groups are not shown).

Dark violet $(R^{*}Sn)_6$ is after orange-colored $(RSn)_{10}$ with a pentagonal Sn_{10} framework and ruby $(RSn)_8$ with a square Sn_8 prismane framework ($R = 2,6\text{-}Et_2C_6H_3$ in each case)[5] a further molecular Sn_n prismane compound of tin. It is based for the first time on a trigonal Sn_6 prismane framework. Thus, whereas the 2,6-diethylphenyl substituent leads to the formation of less strained[3] Sn_n prismanes, the sterically more demanding supersilyl substituent results in the formation of the more strained Sn_6 prismane. Evidently the faces in the Sn_{10} and in the Sn_8 prismane—unlike those in the Sn_6 prismane—do not offer sufficient space for one Si*t*Bu_3 group per Sn atom.[16] However, the Si*t*Bu_3 substituents cover the faces of the Sn_4 tetrahedrane of **3c**—unlike those of the Ge_4 or Si_4 tetrahedrane **3b** and **3a**,[6, 7] respectively—although not completely. Consequently, this polyhedral framework is not formed when *t*Bu_3Si substituents are used owing to its particularly high strain:[3] substituents more sterically demanding than supersilyl groups are necessary for the stabilization of a Sn_4 tetrahedrane.

To date very little is known about the mechanism of the formation of $R^{*}_{6}Sn_{6}$ (or of $R^{*}_{4}Sn_{3}$[9]) from $Sn[N(SiMe_3)_2]_2$ and R*Na in *t*BuOMe (or pentane). It proceeds possibly by an initial substitution of the amide groups by supersilyl groups with formation of the stannylene $R^{*}_{2}Sn$, the dimerization of which to give the distannene $R^{*}_{2}Sn{=}SnR^{*}_{2}$, however, does not take place for steric reasons. On the other hand, the composition of the reaction products obtained—$R^{*}_{6}Sn_{6}$ as well as $R^{*}_{4}Sn_{3}$ in addition to R*R*—indicate that the oligomerization of $R^{*}_{2}Sn$ proceeds by elimination of supersilyl radicals R*, which subsequently dimerize; the path of this oligomerization is determined by the nature of the reaction medium used.

Experimental Section

$Sn[N(SiMe_3)_2]_2$[17] (0.710 g, 1.45 mmol) in pentane (5 mL) was added dropwise to a solution of *t*Bu_3SiNa (0.660 g, 2.97 mmol) in pentane (10 mL) at −78 °C. The reaction mixture was maintained at −78 °C for one day and then at −90 °C for three days. Then the solution cooled to −90 °C was decanted off from insoluble material ($NaN(SiMe_3)_2$). After the pentane had been condensed off at −78 °C, the remaining residue was dissolved in *t*BuOMe at −78 °C and the dark blue solution was allowed to warm to −25 °C. Dark violet crystals (0.107 g, 0.045 mmol; 18 %) of the composition $(tBu_3Si)_6Sn_6$(**2a**)·0.4$(tBu_3Si)_2$·2*t*BuOMe (confirmed by the X-ray structure analysis) crystallized from this solution in the course of two days. The crystals decomposed in the absence of solvent at about 80 °C and in the presence of a solvent at about −5 °C. In [D_8]toluene cooled to −25 °C the crystals display ^{1}H NMR signals at $\delta = 1.373$ (s; 18*t*Bu from **2a**?), 1.383 (s; 6*t*Bu from $(tBu_3Si)_2$), and 1.057/3.017 (s/s; *t*Bu/Me from *t*BuOMe). The determined ratio of areas of the *t*Bu signals is 3.56:1.00:5.79. In THF or [D_8]toluene cooled to −25 °C the crystals display ^{29}Si NMR signals at $\delta = 35.4$ ($tBu_3SiSitBu_3$) and 61.0 (**2a**?). Since for the latter ^{29}Si NMR signal no $^{119/117}$Sn satellites were observed owing to its low intensity, this cannot be assigned unambiguously to the prismane $(tBu_3Si)_6Sn_6$. At room temperature the above-mentioned ^{1}H and ^{29}Si NMR signals assigned to compound **2a** disappear. In THF or [D_8]toluene cooled to −20 °C, compound **2a** displays an ESR signal without fine structure, which could not been assigned to date.

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[3] According to ab initio calculations[1, 2, 4] the strain energy of E_nH_n polyhedrons of the carbon homologues for a given element (E = constant) decreases in the order tetrahedrane, trigonal prismane, cubane framework (R = H in **3**, **2**, **1**; the pentagonal prismane framework is even less strained) and for the given polyhedron type

($n=$ constant) decreases in the order $(SiH)_n$, $(GeH)_n$, $(SnH)_n$, $(PbH)_n$; it is, however, about 250 kJ mol^{-1} even for $(PbH)_8$.

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[10] According to our detailed studies the insoluble tin compound is not the tetrahedrane **3c** and the soluble tin compound is not a zwitterionic distannene $R^*_2Sn \rightarrow SnR^*_2$, as proposed by others (M. Weidenbruch, A. Stilter, H. Marsmann, K. Peters, H. G. von Schnering, *Eur. J. Inorg. Chem.* **1998**, 1333).

[11] According to X-ray structure analyses,[9] in tristannallenes $R^*_4Sn_3$ the Sn–Sn bond lengths and the Sn-Sn-Sn bond angles are 2.68 Å and 156°, respectively, in the isomeric cyclotristannenes $R^*_4Sn_3$ the lengths of the Sn–Sn single and double bonds are 2.86 and 2.61 Å, respectively.[9]

[12] Crystal structure analysis of $(t\mathrm{Bu}_3\mathrm{Si})_6\mathrm{Sn}_6 \cdot 0.4\,(t\mathrm{Bu}_3\mathrm{Si})_2 \cdot 2\,t\mathrm{BuOMe}$: Siemens P4 diffractometer, $\mathrm{Mo}_{K\alpha}$ radiation, graphite monochromator, CCD area detector, crystal dimensions $0.03 \times 0.15 \times 0.14$ mm^3. The crystal was mounted in perfluoroether oil, $T = 163(2)$ K, $C_{90.6}H_{204.6}O_2Si_{6.8}Sn_6$, $M_r = 2229.54$, black-red prisms, triclinic, $a = 16.86(1)$, $b = 17.229(9)$, $c = 21.64(1)$ Å, $\alpha = 89.17(1)$, $\beta = 67.15(2)$, $\gamma = 84.25(2)^\circ$, $V = 5764(6)$ Å^3, $Z = 2$; space group $P\bar{1}$, $\rho_{\mathrm{calcd}} = 1.287$ Mg m^{-3}, $\mu = 1.391$ mm^{-1}, $F(000) = 2280$. Data collection: 2θ from 2.38 to 58.26° in $-20 \leq h \leq 20$, $-22 \leq k \leq 22$, $-24 \leq l \leq 26$, 32656 measured reflections, 18048 of which are independent and 11502 observed ($F > 4\sigma(F)$), semiempirical absorption correction with SADABS (max/min transmission 1.000/0.928), $R_1 = 0.0618$, $wR_2 = 0.1185$ ($F > 4\sigma(F)$), GOF(F^2) = 1.042; maximum residual electron density 1.287 e Å^{-3}. The weighting factor is $w^{-1} = \sigma^2 F_o^2 + (P)^2 + P$ with $P = (F_o^2 + 2F_c^2)/3$. The structure was solved by direct methods (SHELXL; G. M. Sheldrick **1997**). All non-hydrogen atoms of the prismane were refined anisotropically. The hydrogen atoms were introduced in calculated positions and included in the refinement with a riding model and fixed isotropic U_i values. The unit cell contains in addition to the nondisordered molecules $(t\mathrm{Bu}_3\mathrm{Si})_6\mathrm{Sn}_6$ strongly disordered molecules $(t\mathrm{Bu}_3\mathrm{Si})_2$ with an occupancy factor of 0.8 and four molecules of *tert*-butyl methyl ether. The disorder could only be approximately resolved. The *t*Bu groups of the disilane and the atoms of the ether molecules were refined with isotropic thermal parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-113897. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[16] In fact thermolysis of the tristannacyclopropene $(t\mathrm{Bu}_3\mathrm{Si})_4\mathrm{Sn}_3$ did not give $(t\mathrm{Bu}_3\mathrm{Si})_8\mathrm{Sn}_8$ but rather the supersilyl-poorer $(t\mathrm{Bu}_3\mathrm{Si})_6\mathrm{Sn}_8$ with an Sn_8 cubane framework.[9] N. Wiberg, H.-W. Lerner, S. Wagner, H. Nöth, T. Seifert, unpublished results.

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Syntheses and Ligating Properties of Molybdocene Alkoxides—The First Heterodimetallic Alkoxide Containing Molybdenum and Bismuth**

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The unique property of $[Bi_2MoO_6]$ to act as a heterogeneous catalyst for the technical propene oxidation[1a] remains a subject of intense discussion.[1b] According to recent investigations, the oxygenation occurs at Bi-μ-O-Mo moieties,[1c] which encourages research aimed at preparing molecular species containing both Mo and Bi in oxo environments. In this context bismuth–molybdenum heterometallic alkoxides are of particular interest, as studies on metal alkoxides have clearly shown their potential to simulate the properties and structures of metal oxides.[2] There is, however, a dearth of information about even the homometallic alkoxides of bismuth.[3] While several groups have claimed the existence of a bismuth/transition metal precursor in their sol–gel processes,[4] only two heterometallic alkoxide complexes containing Bi and a transition metal (V[3] and Ti[5]) have been isolated and structurally characterized. This is particulary surprising as an increasing number of advanced oxide materials based on bismuth appear to display attractive properties,[5] and mixed-metal alkoxides could act as single-source precursors for such oxides. In an extension of our studies on the synthesis and formation of novel molybdenum alkoxides[6] we present here the first mixed Bi/Mo alkoxide, which to our knowledge is also the first structurally characterized example of a molecular compound with a discrete oxo linkage of any type between Bi and Mo.

All initial attempts to prepare the aforementioned type of species by methods established for the synthesis of other heterometallic alkoxides[7] such as Lewis acid–base reactions of certain alkoxides, or by applying the principles of the nonhydrolytic gel formation process,[8] yielded—in agreement with observations described in the literature[4]—insoluble, intractable solids. Since this is almost certainly a result of high aggregation levels, we decided to employ organomolybdenum compounds in which a part of the coordination sphere at the Mo center is protected by tightly bound organic ligands. For several reasons $[Cp_2Mo(OR)_2]$ compounds seemed to be ideally suited for our purpose, but—despite the vast literature on species bearing the Cp_2Mo fragment[9]—these alkoxides have not been described yet. This is probably due to the electron richness of the Cp_2Mo unit, which accordingly does not accept any strong π-donor ligands (note that the corresponding thiolates[9] are readily made!). Consequently $[Cp_2Mo{=}O]$ was chosen as an alternative reagent to treat bismuth alkoxides, since its oxo functionality possesses

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