Syntheses of Hetero-sila-*closo*-boranes

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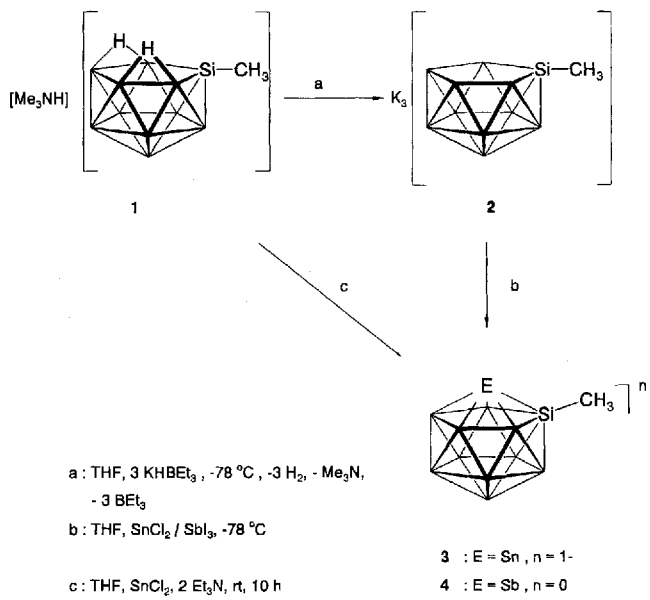
Addition of 3 equivalents of KH · BEt_3 to $[Me_3NH][MeSiB_{10}H_{12}]$ followed by addition of one equivalent of $SnCl_2$ or SbI_3 affords the stanna-sila-*closo*-borate(1−) **3** and stiba-sila-*closo*-borane **4**, respectively. $[MePh_3P]$ · **3** crystallizes in the orthorhombic space group $P2_12_12_1$.

Recently, we reported on the nucleophilic degradation of *o*-silaborane[1]. The pentagonal open face of the resulting *nido*-silaborate comprises a silicon atom and two B−B edges bridged by hyrogen atoms. This compound is a promising reagent for the syntheses of heterosilaboranes. The incorporation of group-14 and -15 elements into the skeleton of carboranes and boranes was reported for $C_2B_9H_{13}$[2], $B_{11}H_{14}^-$[3], $C_2B_4H_8$[4] and $CB_{10}H_{13}^-$[5,6,7] leading to the expected *closo*-clusters. In this paper we describe the preparation of $EMeSiB_{10}H_{10}$ hetero-sila-*closo*-borane clusters by using the $MeSiB_{10}H_{12}$ anion.

The reaction of $[Me_3NH][MeSiB_{10}H_{12}]$ (**1**) with 3 equivalents of KH · BEt_3 followed by the addition of one equivalent of $SnCl_2$ or SbI_3 yielded the hetero-sila-*closo*-boranes **3**, **4**.



The silaborane **1** is easily deprotonated either by treatment with a 1 M solution of superhydride (KH · BEt_3) in THF or with $NaK_{2.8}$ alloy in THF as solvent. Because of the low solubility of the K_3 · **2** salt, which is a known phenomenon for $CB_{10}H_{11}^{3-}$[8] and $B_{11}H_{11}^{4-}$[3], we are not able to present any NMR-spectroscopic characterization of this pyrophoric solid. The deprotonated silaborane **2** can be transformed to the first examples of hetero-sila-boranes in 65% yield for E = Sn and in 32% yield for E = Sb. **1** was also converted to the stanna-sila-borate **3** by using $SnCl_2$ and 2 equivalents of Et_3N in order to abstract HCl. This procedure afforded quantitatively the *closo*-cluster **3** as determined by ^{11}B-NMR spectroscopy, but the separation of the trimethylammonium chloride was unsatisfactory. Thus, in order to obtain pure $[MePh_3P]$ · **3** the deprotonation route was chosen (see Experimental). The stanna-sila-*closo*-borate **3** is an orange, water-stable anion which was crystallized as the $MePh_3P$ salt from CH_2Cl_2/Et_2O as orange rods. The stiba-sila-*closo*-borane **4** is a yellow sublimable (110°C, high vacuum) compound. The ^{11}B-NMR spectra of **3** and **4** are complex and can only be interpreted on the basis of 2D-^{11}B-^{11}B-NMR experiments. The clusters **3** and **4** have C_s symmetry with the mirror plane through E, Si, B9, and B12. Therefore six groups of signals with an intensity ratio of 1:1:2:2:2:2 are expected to appear in the ^{11}B-NMR spectra. In the case of E = Sn only four signals (2:3:4:1) are observed, indicating that some resonances are accidentally isochronic. However, for E = Sb six signals (2:2:1:2:2:1) are visible. Both ^{11}B-NMR spectra had to be analyzed on the assumption that the hetero atom E (E = Sn, Sb) is responsible for a stronger antipodal shift in the ^{11}B-NMR spectrum than the Si vertex. A convincing proof for this assumption is based on the ^{11}B-NMR values for B12 in $MeSiB_{11}H_{11}^-$ δ = −14.5[9], $MeSnB_{11}H_{11}^-$ δ = −10.9[3] and $SbB_{11}H_{11}^-$ δ = 9.4[10] in comparison with $B_{12}H_{12}^{2-}$ δ = −15.3[11]. The stronger antipodal effect for Sb and Sn in comparison with Si leads to the following ^{11}B-NMR shifts (B9 is opposite to Si and B12 is opposite to E): E = Sn, B12 δ = −2.3, B9 δ = −9.9; E = Sb, B12 δ = 7.9, B9 δ = −6.3. The resonance for the boron atom antipodal to E

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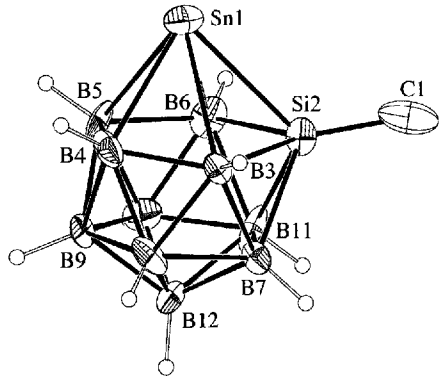
appears more downfield than the one antipodal to the Si atom.

Figure 1. Selected interatomic distances [Å]: Sn1–Si2 2.608(4), Sn1–B3 2.57(2), Sn1–B4 2.36(2), Sn1–B5 2.40(2), Sn1–B6 2.50(2), Si2–B3 2.11(2), Si2–B6 2.10(2), Si2–B7 2.03(2), Si2–B11 2.04(2), B3–B4 1.81(3), B4–B5 1.81(3), B5–B6 1.87(2)



The constitution of the anion **3** in solution determined on the basis of the spectroscopic data is consistent with the results of the crystal structure analysis (Figure 1). In the $SnSiB_{10}$ icosahedron, the B–B distances are in the range from 1.87(3) to 1.73(3) Å with the larger distances for the B–B edges bridged by the hetero atoms Si and Sn. The distances between the boron atoms and the hetero atoms Si–B: [2.11(2), 2.10(2), 2.03(2), 2.04(2) Å], Sn–B: [2.57(2), 2.36(2), 2.40(2), 2.50(2) Å] can be compared with data from other silaboranes[1,9] and the $[MeSnB_{11}H_{11}]^-$ stannaborate[3]. Considering the interatomic distances between the Si vertex and the boron framework, the silaborane skeleton shows only slight changes on cluster closure by the tin vertex. The remarkable Sn–Si connection [2.608(4) Å] in the icosahedron corresponds to other Sn–Si distances: $[(Me_3Si)_3Si]_2Sn(\mu\text{-}Cl)Li(THF)_3$ 2.666(11), 2.681(12)[12]; $Ph_3SnSiPh_2SnPh_3$ 2.579(5), 2.572(4) Å[13].

Both cell dimensions and space group as well as the orientation of our new *closo*-stanna-sila-borate **3** are closely related to the 7-sila-*nido*-undecaborate **1**[1].

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Experimental

Methyltriphenylphosphonium [2-Methyl-1-stanna-2-sila-closo-dodecaborate(1–)] ($MePh_3P \cdot$ **3**): A solution 0.250 g (1.12 mmol) of **1**[1] in THF was treated at −78 °C with 3.36 ml of a 1 M KH · BEt_3 THF solution. The cooling bath was removed, and the reaction mixture was stirred for 3 h at room temp. during which time a white precipitate formed. The solvent and the liberated BEt_3 were removed in vacuo, and the remaining white solid was suspended in 20 ml of THF. At −78 °C one equivalent (0.212 g, 1.12 mmol) of anhydrous $SnCl_2$ was added to the suspension, and the mixture was stirred overnight. The volatile components were removed in vacuo, and the orange solid was dissolved in 10 ml of water. After filtration of the solution, the borate **3** was precipitated with $[MePh_3P]Br$ (0.600 g, 1.68 mmol), dried in vacuo and recrystallized from 10 ml of CH_2Cl_2 covered with 20 ml of Et_2O; yield 0.406 g (0.728 mmol, 65.0%). – NMR, Varian 500, reference TMS (^1H, ^{13}C, ^{29}Si), $Et_2O \cdot BF_3$ (^{11}B), Me_4Sn (^{119}Sn), spectra at 25 °C in [D6]acetone: $^1H\{^{11}B\}$ NMR: δ = 0.62 (s, 3H, MeSi), 1.41 (s, 2H), 1.59 (s, 2H), (B3/6, B4/5), 2.25 (s, 2H, B8/10), 2.33 (s, 1H, B9), 2.39 (s, 2H, B7/11), 3.96 (s, 1H, B12). – ^{11}B NMR: δ = −11.5 (2 B, d, J = 140 Hz, B7/11), −9.9 (3 B, d, J = 140 Hz, B9, B8/10), −8.4 (4 B, d, J = 134 Hz, B3/6, B4/5), −2.3 (1 B, d, J = 134 Hz, B12). – $^{13}C\{^1H\}$ NMR: δ = −8.05 (MeSi). – ^{119}Sn NMR: δ = −610 (s, br). – ^{29}Si NMR: δ = −5.6 (s). – $C_{20}H_{31}B_{10}PSiSn$ (557.3): calcd. C 43.09, H 5.57; found C 42.30, H 5.39.

X-ray Structure Analysis of **3** · $[MePh_3P]$: M = 557.33 g mol^{-1}, orthorhombic space group $P2_12_12_1$, (no. 19), a = 11.453(9), b = 15.324(7), c = 15.38(1) Å, V = 2699(3) Å^3, Z = 4, $d_{calcd.}$ = 1.372 g cm^{-3}, μ Mo-K_α) = 10.60 cm^{-1}, F(000) = 1120. Enraf-Nonius CAD4, ω scan, Mo-K_α radiation (0.71073 Å), graphite monochromator, 6011 reflections ($-h$, $-k$, $\pm l$) at 203 K, with $3 \leq \Theta \leq 27°$, crystal size 0.1 × 0.1 × 0.2 mm^3. Empirical absorption correction using DIFABS[14] (min. transmission 0.53, max. transmission 1.00, average transmission 0.86). Structure solution with Patterson methods. Refinement[15] with anisotropic displacement parameters for the atoms in the cluster and the P atom, isotropic thermal parameters for the other non-hydrogen atoms converged at R = 0.086, R_w = 0.064 for 203 parameters and 2536 independent observations with $I > 1.0\sigma(I)$. Hydrogen atoms were treated as riding atoms with idealized geometry (dist. C–H 0.98, B–H: 1.1 Å). A final difference Fourier syntheses showed a residual electron density of 1.3 eÅ^{-3}[16].

2-Methyl-1-stiba-2-sila-closo-dodecaborane(11) (**4**): A solution of 0.358 g (1.60 mmol) of **1**[1] in THF was treated at −78 °C with 4.8 ml of a 1 M KH · BEt_3 THF solution. The cooling bath was removed, and the reaction mixture was stirred for 3 h at room temp. during which time a white precipitate formed. The solvent and the BEt_3 were removed in vacuo, and the remaining white solid was suspended in 20 ml of THF. At −78 °C one equivalent (0.804 g, 1.60 mmol) of SbI_3 was added to the suspension, and the reaction mixture was stirred overnight at room temp. All volatile components were removed in vacuo, and the stiba-sila-borane was sublimed at 110 °C in vacuo; yield 0.144 g (0.51 mmol, 32%). – NMR, Varian 500, reference TMS (^1H, ^{13}C, ^{29}Si), $Et_2O \cdot BF_3$ (^{11}B), spectra at 25 °C in [D6]acetone: $^1H\{^{11}B\}$ NMR: δ = 1.26 (s, 3H, MeSi), 2.18 (s, 2H, H4/5), 2.38 (s, 2H, H3/6), 2.81 (s, 2H H8/10), 3.10 (s, 2H, H7/11), 3.14 (s, 1H, H9), 5.35 (s, 1H, H12). – ^{11}B NMR: δ = −9.4 (2 B, d, J = 147 Hz, B7/11), −8.5 (2 B, d, J = 147 Hz, B8/10), −6.3 (1 B, d, J = 134 Hz, B9), −5.7 (2 B, d, J = 134 Hz, B4,5), −4.9 (2 B, d, J = 140 Hz, B3/6), 7.9 (1 B, d, J = 134 Hz, B12). – $^{13}C\{^1H\}$ NMR: δ = −10.2 (MeSi). – ^{29}Si NMR: δ = 6.0 (s). – MS (MAT 95, Finnigan MAT): calcd for $^{12}C^1H_{13}{}^{11}B_{10}{}^{28}Si^{123}Sb$ 286.07586, found 286.07587.

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