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Synthesis of New Stanna- and Germaundecaboranes

Joel A. Dopke, Douglas R. Powell, Randy K. Hayashi, and Donald F. Gaines*

Department of Chemistry, University of Wisconsin at Madison, Madison, Wisconsin 53706

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While carboranes are well-known and well-studied,[1] the analogous heteroboranes containing tin and germanium moieties have received comparably less attention.[2,3] Previously reported stanna- and germaboranes include the pseudoicosahedral *closo*-$EB_{11}H_{11}^{2-}$ (E = Ge, Sn, Pb) species and methylated derivatives;[3f] neutral $R_2EB_{10}H_{12}$ (R = alkyl, Cl; E = Si, Ge, Sn), in which two terminal substituents prevent full insertion of the heteroatom;[3b−e] and the unusual stannaundecaborane, $Me_2Cl_2SnB_{10}H_{12}$.[3d] In the process of studying the chemistry of the reactive *nido*-decaborane dianion $B_{10}H_{12}^{2-}$, we recently reported the insertion of −BR,[4] −CH,[5] and −SiR[6] units to generate undecaboranes isoelectronic with the nido-$B_{11}H_{14}^-$ anion. Herein we report the synthesis of a related but new class of *nido* stanna- and germaundecaboranes by reaction of Sn(II) and Ge(II) halides with $Na_2B_{10}H_{12}$.

The reaction of $SnBr_2$ with a THF solution of $Na_2B_{10}H_{12}$ generates the air- and moisture-sensitive stannaborane salt, Na[7-Br-7-$SnB_{10}H_{12}$], in which the bromine occupies the terminal position on the tin heteroatom.[8] A typical yield, by ^{11}B NMR, is 90%. Metathesis with [Ph_3PMe]Br in THF affords the phosphonium salt, Ph_3PMe[7-Br-7-$SnB_{10}H_{12}$], red crystals of which were used for X-ray structural analysis. Representative bond distances are listed in Table 1.

Treatment of 7-Br-7-$B_{10}H_{12}^-$ with 1 equiv of MeLi in THF at −78 °C forms the linked species 7,7′-$(SnB_{10}H_{12})_2^{2-}$, in which the clusters are joined via an Sn−Sn bond.[9] It is postulated that this linkage is forged after elimination of LiBr, formation of the intermediate 7-Me-7-$SnB_{10}H_{12}^-$, and oxidative elimination of C_2H_6. Air- and moisture-sensitive red crystalline plates of $[Bu_4N]_2$[7,7′-$(SnB_{10}H_{12})_2$] were used to establish the X-ray crystallographically determined structure shown in Figure 1. Representative bond distances are listed in Table 1.

Table 1. Selected Bond Distances (Å) for Ph_3PMe[7-Br$SnB_{10}H_{12}$], $[Bu_4N]_2$[7,7′-$(SnB_{10}H_{12})$)], and Ph_3PMe[7-I$GeB_{10}H_{12}$]

	7-Br$SnB_{10}H_{12}^-$	7,7′-$(SnB_{10}H_{12})_2^{2-}$	7-I$GeB_{10}H_{12}^-$
E−B(8)[a]	2.521(5)	2.478(6)	2.203(7)
E−B(11)	2.546(5)	2.489(7)	2.218(7)
E−B(2)	2.495(5)	2.484(7)	2.216(6)
E−B(3)	2.487(4)	2.483(9)	2.218(7)
E−X[b]	2.5868(5)	2.8886(6)	2.5901(8)
B(8−9)	1.806(7)	1.877(8)	1.855(10)
B(9−10)	2.028(7)	1.944(9)	1.925(10)
B(10−11)	1.801(7)	1.856(9)	1.857(10)
av B−B	1.787	1.813	1.801

[a] E = Sn or Ge. [b] X = Br, Sn, or I.

Similarly, the air- and moisture-sensitive iodogermaborane, 7-I-7-$GeB_{10}H_{12}^-$, is formed by the reaction of $Na_2B_{10}H_{12}$ with GeI_2 in THF. A typical yield, by ^{11}B NMR, is 75% with $B_{10}H_{14}$ as the primary contaminant. Metathesis with [Ph_3PMe]Br in THF affords the yellow phosphonium salt which may be acquired, decaborane free, by washing with ether.[8] The X-ray crystallographically determined structure of Ph_3PMe[7-I-7-$GeB_{10}H_{12}$] is shown in Figure 2. Representative bond distances are listed in Table 1.

The ^{11}B NMR spectra of these stanna- and germaboranes show six doublet resonances of relative intensity 2:2:2:2:1:1, consistent with species possessing C_s symmetry. For reasons not yet understood, the stannaborane resonances tend to be broadened. The ^{11}B NMR spectra for 7-Br-7-$SnB_{10}H_{12}^-$ and 7-I-7-$GeB_{10}H_{12}^-$ have been assigned unambiguously on the basis of their $^{11}B-^{11}B$ COSY spectra. All expected connectivities are observed. Two-dimensional NMR experiments for 7,7′-$(SnB_{10}H_{12})_2^{2-}$ have allowed partial assignment and derivation of an internally consistent set of connectivities. ^{11}B NMR data, coupling constants, and assignments have been included in the Supporting Information.

Structurally, these new heteroborane anions possess characteristics of both classical borane structures and EX_3^- (E = Ge, Sn; X = halide) species. The heteroatom resides in a roughly pyramidal environment, similar to the EX_3^- anions, consistent with tin and germanium atoms in the +2 oxidation state.[10] The

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(1) For examples, please see: *Gmelin Handbook of Inorganic Chemistry, Boron*, 8th ed.; Springer-Verlag: New York, 1988; 3rd Suppl., Vol 4.

(2) Rudolph, R. W.; Voorhees, R. L.; Cochoy, R. E. *J. Am. Chem. Soc.* **1970**, *92*, 3351. Wong, K.-S.; Grimes, R. N. *Inorg. Chem.* **1977**, *16*, 2053. Hosmane, N. S.; Sirmokadam, N. N.; Herber, R. H. *Organometallics* **1984**, *3*, 1665. Hosmane, N. S.; de Meester, P.; Maldar, N. N.; Potts, S. B.; Chu, S. S. C.; Herber, R. H. *Organometallics* **1986**, *5*, 772. Islam, M. S.; Siriwardane, U.; Hosmane, N. S.; Maguire, J. A.; de Meester, P.; Chu, S. S. C. *Organometallics* **1987**, *6*, 1936.

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(4) Bridges, A. N.; Hayashi, R. K.; Gaines, D. F. *Inorg. Chem.* **1994**, *33*, 1243.

(5) Bridges, A. N.; Gaines, D. F. *Inorg. Chem.* **1995**, *34*, 4523.

(6) Dopke, J. A.; Bridges, A. N.; Schmidt, M. R.; Gaines, D. F. *Inorg. Chem.* **1996**, *35*, 7186.

(7) In accordance with Wade's rules: Wade, K. *Electron Deficient Compounds*; Meredith Corporation: New York, 1971.

(8) Since preparations of 7-I-7-$GeB_{10}H_{12}^-$ and 7-Br-7-$SnB_{10}H_{12}^-$ are very similar, only a description of the synthesis of the stannaborane is provided here: A solution of $Na_2B_{10}H_{12}$ (prepared from 4.19 mmol of $B_{10}H_{14}$ and excess NaH)[5] in 60 mL of THF was added to a 200 mL Schlenk flask containing a magnetic stir bar and a slurry of $SnBr_2$ (1.31 g, 4.67 mmol) in 20 mL of THF. The solution immediately turned an opaque red-orange, and gray-black material (probably metallic tin) deposited upon stirring for 2 h. Anhydrous [Ph_3PMe]Br (1.43 g, 4.03 mmol) was added to the solution under nitrogen, and the flask contents were stirred overnight. The flask contents were filtered and the volatiles removed from the filtrate in vacuo. The residue was dissolved in THF (15 mL), and then Et_2O (75 mL) was added to precipitate the free-flowing, red-orange powder.

(9) A sample of Et_4N[7-Br-7-$SnB_{10}H_{12}$] (from 0.51 g, 4.20 mmol $B_{10}H_{14}$), dissolved in THF (40 mL) in a 200 mL Schlenk flask containing a magnetic stir bar, was cooled to −78 °C, and MeLi (1.5 M in Et_2O, 2.2 mL, 3.3 mmol) was added dropwise. A light-colored precipitate formed immediately. After 30 min at −78 °C, the flask was warmed to room temperature over 1 h. Diethyl ether (100 mL) was added to the reaction mixture, and the flask contents were allowed to stand overnight. The flask contents were filtered, leaving a red solid product, $[Et_4N]_2$[7,7′-$(SnB_{10}H_{12})_2$], which was washed through the frit with two 15 mL portions of methylene chloride. Diethyl ether (100 mL) was added to the filtrate, causing the red product to precipitate.

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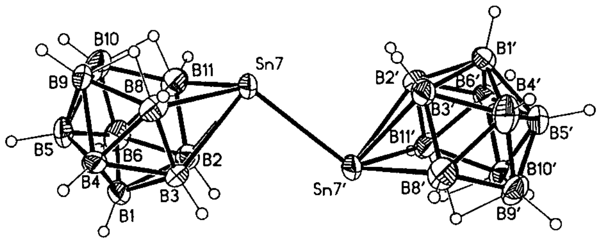

Figure 1. Crystallographically determined structure of $[Bu_4N]_2[7,7'-(SnB_{10}H_{12})_2]$ with thermal ellipsoids drawn at the 50% probability level.

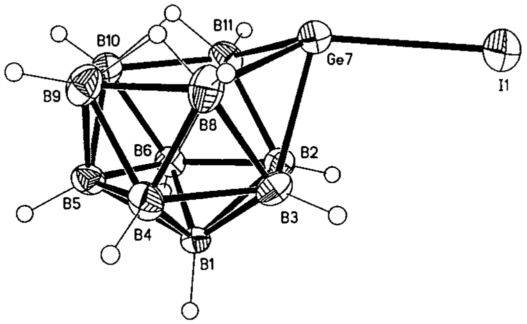

Figure 2. Crystalographically determined structure of $Ph_3PMe[7\text{-}I\text{-}7\text{-}GeB_{10}H_{12}]$ with thermal ellipsoids drawn at the 50% probability level.

terminal moiety on the heteroatom lies below the plane of the open cluster face, while terminal hydrogens on B(8)−B(11) lie above the plane. The observed ^{119}Sn chemical shifts for the bromostannaborane ($\delta = -268$ ppm relative to $SnMe_4$) and the linked stannaborane clusters ($\delta = -336$ ppm) are consistent with observed values for other tin(II)-containing boranes.[2,3f]

Despite the difference in heteroatom oxidation state, the NMR data is consistent with species analogous to the silaboranes 7-R-7-$SiB_{10}H_{12}^-$, suggesting the heteroatom to be inserted in a similar fashion.[6,11] Todd et al. synthesized dianionic closo stanna- and germaboranes in which the heteroatom is bare.[3f] In these instances, the +2 heteroatom contributes two electrons toward cluster bonding much like a BH unit.[7] Methylation of the group IV heteroatom with MeI converts it to a three-electron donor. The cluster bonding appears to be analogous to that proposed for the heteroboranes described here. The E−X moiety (X = Br^-, I^-, 7-$SnB_{10}H_{12}^-$) must donate three electrons to cluster bonding for these stanna- and germaboranes to be isoelectronic with the nido silaborane anions and $B_{11}H_{14}^-$.[7] Further studies of these new group IV heteroundecaboranes are underway.

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Supporting Information Available: Figures showing NMR data for 7-Br-7-$SnB_{10}H_{12}^-$ (^{11}B, ^{11}B{^{1}H}, ^{119}Sn, ^{11}B−^{11}B COSY), 7,7′-$(SnB_{10}H_{12})_2^{2-}$ (^{11}B, ^{11}B{^{1}H}, ^{119}Sn), and 7-I-7-$GeB_{10}H_{12}^-$ (^{11}B, ^{11}B{^{1}H}, ^{11}B−^{11}B COSY) and structure tables for 7-Br-7-$SnB_{10}H_{12}^-$, 7,7′-$(SnB_{10}H_{12})_2^{2-}$, and 7-I-7-$GeB_{10}H_{12}^-$ (78 pages). Ordering information is given on any current masthead page.

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