Silicon Insertion into Boranes: A Rational Synthetic Route to Silicon-Containing Heteroboranes

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While carboranes are well-known and well-studied,[1] the analogous silicon compounds have only recently been prepared.[2−6] Recent investigations of heteroatom insertion into decaborane using the reactive dianion *nido*-$B_{10}H_{12}^{2-}$ in our laboratories have led to the insertion of a −CH cluster fragment from X_2CH_2 (X = halogen)[7] to produce the monocarborane, 7-H-7-$CB_{10}H_{12}^-$. We now report the analogous monosilaborane anions, 7-R-7-$SiB_{10}H_{12}^-$ (R = H, Me, Ph) by insertion of an -SiR unit from $HRSiCl_2$ into the *nido*-$B_{10}H_{12}^{2-}$ framework.

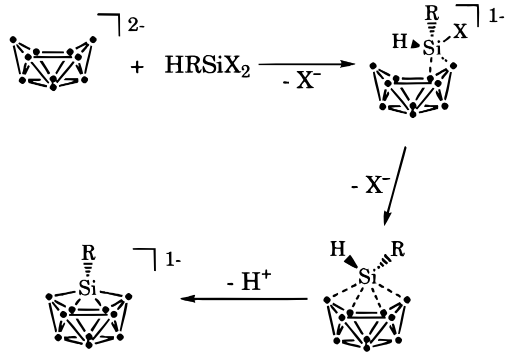
The silaboranes, 7-R-7-$SiB_{10}H_{12}^-$, are consistently formed in a 2:1 ratio with decaborane(14), regardless of the R substituent, according to eq 1. Subsequent washing with *i*-Pr_2O

$$3Na_2[B_{10}H_{12}] + 2HRSiCl_2 \rightarrow 2Na[RSiB_{10}H_{12}] + B_{10}H_{14} + 4NaCl \qquad R = H, Me, Ph \qquad (1)$$

to remove decaborane and filtration to remove NaCl result in a near-quantitative yield of 7-R-7-$SiB_{10}H_{12}^-$ based on the observed stoichiometry. The silaboranes are isolated as free-flowing, air and moisture sensitive, off-white solids that slowly decompose to decaborane and the arachno anion, $B_{10}H_{15}^-$ (based on ^{11}B NMR).[8] Dissolution of the silaborane salts in THF, polyethers, acetonitrile, or diethyl ether (in which they are moderately soluble) produces yellow to orange solutions. Not surprisingly, sodium salts of 7-R-7-$SiB_{10}H_{12}^-$ exhibit enhanced solubility when R = Me or Ph.

Although no intermediates in the synthesis of the silaborane anions have been observed, the mechanism of insertion may be envisaged to proceed via successive loss of chloride by the halosilane, formation of three-center, two-electron bonds between silicon and facial $B_{10}H_{12}^{2-}$ borons, and deprotonation of the silyl fragment (Scheme 1). Following loss of chloride, the halosilane fragment is postulated to initially occupy a bridging position to form a μ-HRSiCl-$B_{10}H_{12}^-$ species. Subsequent loss of the remaining chloride allows the formation of a second intermediate, μ_2-HRSi-$B_{10}H_{12}$, perhaps similar in structure to those group IV heteroboranes described by Norman and coworkers.[2] Proton abstraction by $B_{10}H_{12}^{2-}$ or $B_{10}H_{13}^-$ leads to full insertion of the silicon atom.[9] Deprotonation of μ_2-HRSi-$B_{10}H_{12}$ by $B_{10}H_{13}^-$ and $B_{10}H_{12}^{2-}$ is implied by the presence and statistical quantity of decaborane in the product mixture, and is indicative of the high acidity of the silyl proton.

Scheme 1



The ^{11}B NMR spectrum of 7-H-7-$SiB_{10}H_{12}^-$ consists of six doublets of relative intensity 1:2:2:2:2:1. All signals collapse to singlets upon proton decoupling, in good agreement with that expected for an 11-vertex, 10-boron structure possessing C_s symmetry (Figure 1). Boron chemical shift data for the species 7-R-7-$SiB_{10}H_{12}^-$ (R = H, Me, Ph) and the monocarborane, 7-H-7-$CB_{10}H_{12}^-$, are summarized in Table 1. All expected couplings are present in the two-dimensional ^{11}B-^{11}B COSY NMR spectrum of 7-H-7-$SiB_{10}H_{12}^-$, allowing cluster connectivities and assignments to be made. No conclusive evidence for a B8(B11)−B9(B10) coupling is observed, consistent with the proposed presence of bridging hydrogens spanning these connectivities[9] (the anion, 7-Me-7-$SiB_{10}H_{12}^-$, has been crystallographically characterized by Wesemann et al.[3]).

The ^{29}Si NMR spectrum of 7-H-7-$SiB_{10}H_{12}^-$ shows a broad doublet centered at −41.7 ppm (J_{Si-H} = 242 Hz). This compares favorably with the reported ^{29}Si resonance of −36.4 ppm reported[3] for 7-Me-7-$SiB_{10}H_{12}^-$. The signal collapses to a broad singlet ($\Delta w_{1/2}$ = 142 Hz) upon proton decoupling and exhibits no resolvable coupling to cage borons. The terminal Si−H proton is not observed in the ^1H NMR spectrum but emerges as a broad singlet (δ = 2.46 ppm relative to TMS) when ^{11}B decoupling is applied. The two bridging hydrogens spanning B8(B11)−B9(B10) are observed as a broad singlet at −5.55 ppm while terminal hydrogens on boron occupy a region between 0.96 and 1.95 ppm. Electrospray ionization (ESI) mass spectra of 7-H-7-$SiB_{10}H_{12}^-$ in acetonitrile, in the negative ion mode, exhibit a parent mass envelope centered at *m/z* 149.2, and an isotope pattern in good agreement with the calculated parent (7-H-7-$SiB_{10}H_{12}^-$: *m/z* 149.172).

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

(2) Loffredo, R. E.; Norman, A. D. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 599. Loffredo, R. E.; Norman, A. D. *J. Am. Chem. Soc.* **1971**, *93*, 5587.

(3) Wesemann, L.; Englert, U.; Seyferth, D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2236.

(4) Wesemann, L.; Englert, U. *Angew. Chem., Int. Ed. Engl.* **1995**, *35*, 527.

(5) Seyferth, D.; Büchner, K.; Rees, W. S.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 918.

(6) Wesemann, L.; Ganter, B. *Organometallics* **1996**, *15*, 2569.

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

(8) In a typical synthesis of 7-H-7-$SiB_{10}H_{12}^-$, a solution of $Na_2[B_{10}H_{12}]$ (6.34 mmol) in THF[7] is prepared and degassed in a 100 mL high-vacuum reactor with a magnetic stir bar. The THF is removed in vacuo and ~20 mL of dry diethyl ether is distilled into the vessel at −196 °C. Excess H_2SiCl_2 (purified by repeated fractional condensation at −126 °C to remove HCl) is then condensed into the vessel (14.3 mmol) at −196 °C. A −78 °C bath is then placed around the reactor, and the system is allowed to stir and warm to room temperature overnight. The volatiles are removed in vacuo and discarded. The crude product is washed with 3 × 15 mL portions of dry *i*-Pr_2O. The solid is then extracted with dry THF and the filtrate evaporated under vacuum to yield 1.19 g (4.44 mmol, 70% yield) of $Na[SiB_{10}H_{13}]$.

(9) As per Wade's rules: Wade, K. *Electron Deficient Compounds*; Meredith Corporation: New York, 1971.

(10) Gaines, D. F.; Edvenson, G. M.; Hill, T. G.; Adams, B. R. *Inorg. Chem.* **1987**, *26*, 1813.

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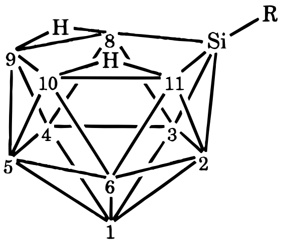

= B-H

R = H, Me, Ph

Figure 1.

Table 1. ^{11}B Chemical Shifts and Couplings of the Silaboranes in THF, with All Shifts Referenced Externally to $BF_3 \cdot OEt_2$ in C_6D_6 and J_{B-H} (in Hz) Given Below the Appropriate Shift

species	B5	B2/B3	B8/B11	B9/10	B4/6	B1
7-H-7-$SiB_{10}H_{12}^-$	−7.1	−14.7	−19.4	−21.6	−24.4	−29.4
	134	138	141	139	141	139
7-Me-7-$SiB_{10}H_{12}^-$[a]	−12.5	−14.7	−22.1	−23.8	−25.2	−32.7
	132	139	141	149	137	141
7-Ph-7-$SiB_{10}H_{12}^-$	−11.5	−14.8	−22.0	−23.6	−25.7	−31.9
	134	139	146	144	141	136
7-H-7-$CB_{10}H_{12}^-$	−0.3	−11.6	−11.6	−22.7	−31.0	−26.1
	127	142	137	157	127	142

[a] ^{11}B chemical shifts in good agreement with published data.[3]

The 7-Me-7-$SiB_{10}H_{12}^-$ anion was identified by comparison of its ^{11}B and ^{29}Si NMR spectra to literature values[3] and its ESI mass spectrum (7-Me-7-$SiB_{10}H_{12}^-$: *m/z* 163.6). The silaborane 7-Ph-7-$SiB_{10}H_{12}^-$ has been characterized on the basis of its $^{11}B/^{11}B\{^1H\}$ NMR spectra, found to be characteristic of the silaborane anions.

There are small variations in the ^{11}B chemical shifts for cluster borons of the silaborane anions as the substituent group on the silicon changes. The chemical shifts of the methyl- and phenylsilaborane derivatives appear at higher field than those of 7-H-7-$SiB_{10}H_{12}^-$, likely due to the increased electron-donating ability of the R group compared to hydrogen. An antipodal effect due to the electropositive silicon atom and its substituent is most pronounced at the B1 and B5 positions. The parent silaborane, 7-H-7-$SiB_{10}H_{12}^-$, and the monocarborane, 7-H-7-$CB_{10}H_{12}^-$, exhibit large differences in their ^{11}B chemical shifts, likely a reflection of the difference between carbon and the more electropositive silicon (in reference to boron). Large upfield shifts of the B1 and B5 resonances accompany the change from carbon to silicon. Boron vertices adjacent to the heteroatom (B2, B3, B8, B11) exhibit significant deshielding in the monocarborane when compared to the silaborane, although this effect is less pronounced for B2 and B3. The B4(B6) resonance of 7-H-7-$SiB_{10}H_{12}^-$ appears downfield of that for 7-H-7-$CB_{10}H_{12}^-$, while the B9(B10) resonances remain comparable.

The electropositivity of silicon in relation to boron may lend credence to the instability of the cluster. It is logical to assume that the silicon vertex would adopt a positive charge relative to the rest of the cluster. Wesemann et al. initially prepared 7-Me-7-$SiB_{10}H_{12}^-$ by nucleophilic degradation of the *closo* disilaborane 1,2-Me_2-1,2-$Si_2B_{10}H_{10}$ with hydroxide indicating that even in a *closo* configuration, silicon vertices are attacked preferentially by nucleophiles.[3] The open-faced, 11-vertex structure of the silaborane anions may expose the heteroatom even further to nucleophilic attack. Samples of 7-H-7-$SiB_{10}H_{12}^-$ treated with ~1 equiv. of $NaHBEt_3$ in THF decomposed to give a mixture of $B_{10}H_{14}^{2-}$ and $B_{10}H_{10}^{2-}$. While the silicon-containing byproduct was not identified, the degradation products suggest nucleophilic attack by hydride at silicon. Coordinating solvents may stabilize the positive charge on silicon, suggested by the observed long lifetime of 7-H-7-$SiB_{10}H_{12}^-$ in acetonitrile.

Insertion of an −SiR unit to generate 7-R-7-$SiB_{10}H_{12}^-$ has several advantages over the previously published synthesis[3] of 7-Me-7-$SiB_{10}H_{12}^-$. The nature of the substituent, R, appears to be limited only by the synthetic availability of the appropriate dihalosilane whereas the previous method limits the R moiety to methyl. Precursors for the insertion pathway can be made and purified in high yield, and the insertion reaction also proceeds in high yield. Continued investigations of group IV heteroatom insertion reactions with boron hydride anions are in progress.

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Supporting Information Available: Figures showing NMR data (^{11}B, ^{29}Si, $^{29}Si\{^1H\}$, and two-dimensional ^{11}B-^{11}B COSY) and ESI mass spectra for 7-H-7-$SiB_{10}H_{12}^-$, and NMR data (^{11}B, $^{11}B\{^1H\}$) for 7-Ph-7-$SiB_{10}H_{12}^-$ are available (6 pages). Ordering information is given on any current masthead page.

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