Organotin Derivatives of Hexaborane(10)

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*Summary: Derivatives of B_6H_{10}, in which a R_3M group {M = Sn, R = Ph (**I**), Me (**II**)} replaces a bridging hydrogen atom, have been prepared and characterized by NMR spectroscopy. The bridging H atoms, in the 2,3-μ-(R_3M)-B_6H_9 species, are fluxional on both the boron-11 and proton NMR time scale, but the motion appears to be partially quenched as observed for other 2,3-μ-metalla derivatives of hexaboranes. At temperatures above about -10 °C some simple motion of the cage relative to the R_3Sn group is invoked to account for the spectra of **I**. 2,3-μ-(Me_3Sn)B_6H_9 is unstable and could not be isolated or handled at temperatures above ca. -20 °C.*

Introduction

nido-pyramidal boranes such as B_5H_9 and B_6H_{10} contain bridging hydrogen atoms which are acidic and may be removed with strong bases.[1] The resulting anions are susceptible to electrophilic attack and thus the hydrogen atoms may be replaced with Lewis acids.[2] For B_5H_9, the Lewis acids used range from simple species such as a proton[1b,c] and borane(3)[3] to more complex main group[2a,4] species and transition metal moieties.[5] The main group units thus introduced into the cluster contain elements from p-block Groups II,[6] III,[7] IV,[8] and V.[9] For B_6H_{10}, there are fewer examples and they also include the proton,[10] through main group IIa,[11] IIb,[12] and III,[13] and Cu,[14] and some more complex examples incorporating two metals and two cages and involving either Pt[15] or Ti.[14b] There are several examples of group IV derivatives of pentaborane(9) in which the group IV atom replaces a proton, and they include species with the R_3M moiety (M = Si, $R_3 = H_3$,[8b] H_2Cl,[8d] Me_3,[8a,b] Et_3,[8b] F_3,[8e] M = Ge, $R_3 = H_3$, Me_3, Et_3; M = Sn, $R_3 = Me_3$,[8b] Ph_3;[8f,g] M = Pb, $R_3 = Me_3$[8b]) replacing a bridging proton. There are no known examples of similar derivatives of hexaborane(10). The only group IV derivatives of B_6H_{10} are the species 1-(Me_3M)B_6H_9[16a] (M = Si, Ge), which are formed in the reaction between salts of either $[2\text{-}(Me_3M)B_5H_7]^-$ or $[1\text{-}(Me_3M)B_5H_7]^-$ and H_2BCl. The related 2-(Me_3Si)-μ-(Me_2B)B_5H_7[16b] is also known but this latter formal hexaboranyl–group IV system is really a B_5H_9 derivative. Herein we report the synthesis and characterization of some organotin derivatives of B_6H_{10} in which the tin atom occupies a basal bridging site. We also exploit our recent discovery that ^{119}Sn NMR spectroscopy[8f,g] is a convenient way to characterize stannylborane clusters.

Experimental Section

Materials. Hexaborane(10)[17] was synthesized using standard literature procedures, and B_5H_9 was obtained from laboratory stock and distilled before use. *B_5H_9 is a hazardous material and must be handled with care. It is pyrophoric in air, and this property is somewhat unpredictable.* Ph_3SnCl and Me_3SnCl were used as obtained from Aldrich. KH, obtained as a mineral oil suspension from Research Organic/Inorganic Chemical Corp., was washed repeatedly with anhydrous pentane on the vacuum line before use until it was a free-flowing white powder. The activity of the powder in reactions with methanol was 85–95%. THF and diethyl ether were dried over $LiAlH_4$ followed by Na/benzophenone ketyl and stored over molecular sieves. CH_2Cl_2 was dried and distilled over P_2O_5. Pentane was dried over CaH_2 followed by Na/benzophenone and stored over molecular sieves. All solvents were reagent grade, were dried and distilled prior to use, and were stored in Pyrex vessels with Teflon stopcocks.

Apparatus. Standard high-vacuum line and drybox techniques were employed in this work.[18] NMR spectra were obtained on a Varian XL-300 high-resolution spectrometer operating at 300.1, 96.3, 76.6, and 111.7 MHz to observe ^1H, ^{11}B, ^{13}C, and ^{119}Sn resonances, respectively. ^{11}B chemical shifts are reported in ppm,

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Table I. NMR Data for 2,3-μ-(Triorganylstannyl)hexaboranes(9)

species (conditions)	^{11}B data δ in ppm	^{1}H data δ in ppm
2,3-μ-(Ph_3Sn)B_6H_9 (I) ($CDCl_3/CHClF_2$, −78 °C)	−45.1 (s, unres, 1B, *B*(*1*)), 6.9 (br, unres, 3B, *B*(*4–6*)), 39.2 (br, unres, 2B, *B*(*2,3*))	(−100 °C) −1.02 (s, br, 2H, H_μ), −0.08 (s, br, 1H, H_μ), obscured res (*H*(*1*)), 3.52 (s, br, 3H, *H*(*4–6*)), 5.55 (s, br, *H*(*2,3*)), 6.9–7.9 (m, *Ph*)
2,3-μ-(Ph_3Sn)B_6H_9 ($CDCl_3/CHClF_2$, −40 °C)	−44.9 (d, br, *B*(*1*)), 7.1 (br, unres, 3B, *B*(*4–6*)), 38.9 (br, unres, 2B, *B*(*2,3*))	
2,3-μ-(Ph_3Sn)B_6H_9 ($CDCl_3/CHClF_2$, 0 °C)	−44.5 (d, 1B, *B*(*1*), *J* = 152 Hz), 6.9 (br, unres, with br sh, 3B, *B*(*4–6*)), 38.8 (br, unres, 2B, *B*(*2,3*))	(0 °C) −1.13 (s, br, 2H, H_μ), −0.05 (s, br, 1H, H_μ), −1.08 (q, w, 1H, *H*(*1*), *J* = 155 Hz), 3.2–5.4 (v br, 5H, *H*(*2–6*))
2,3-μ-(Me_3Sn)B_6H_9 (II) (CD_2Cl_2, −35 °C)	−48.2 (d, 1B, *B*(*1*), *J* = 149 Hz), 29.8 (d, poor resol, 2B, *B*(*2,3*)), 4.18 (d, poor resol, *B*(*4–6*))	2.8–5.8 (v br, 5B, *H*(*2–6*)), −1.68 (s, br, 3H, H_μ), −1.26 (q, 1H, *H*(*1*), *J* = 143 Hz), 0.45 (s, br, 9H, CH_3)

Table II. Variable Temperature $^{1}H\{^{11}B\}$ NMR Data for 2,3-μ-(Triphenylstannyl)-*nido*-hexaborane(10) in CD_2Cl_2/THF-d_8

	proton chemical shift in ppm						
assgnt	+15 °C	−5 °C	−25 °C	−45 °C	−65 °C	−85 °C	−105 °C
H(2,3)			5.6	5.65	5.62	5.56	5.52
H_t(all)	4.3	very broad					
H(4,6)						3.47	3.45
H(4–6)			3.6	3.59	3.61		
H(5)						3.56	3.54
H(1)	−0.80	−0.77	−0.84	−0.88	−0.85	−0.92	−0.89
$H_{\mu 5,6}$	−0.03	−0.01	−0.05	−0.07	−0.03	−0.09	−0.04
$H_{\mu 2,6}$ $H_{\mu 3,4}$	−0.96	−0.92	−0.98	−1.01	−0.97	−1.03	−1.05

positive signs denoting a shift at a lower field with respect to $Et_2O{\cdot}BF_3$ (0.0 ppm). ^{1}H, ^{13}C, and ^{119}Sn chemical shifts were measured relative to Me_4Si, $CDCl_3$, and Me_4Sn, respectively, the last as external standard (δ = 0.0 ppm). The $^{1}H\{^{11}B\}$ spectra were obtained using a Bruker AM 250 spectrometer operating at 250.14 MHz,[19] and the mass spectra were obtained on solid samples at 70 eV on a Varian/Mat 311A spectrometer equipped with a Technivent data system. IR spectra, KBr pellets or Nujol mulls prepared in the drybox, were measured on a Perkin-Elmer 1604 FT-IR spectrometer. Analyses were performed by Schwarzkopf Microanalytical Laboratories.

Synthesis of 2,3-μ-(Ph_3Sn)B_6H_9 (I). In a typical reaction, a reaction vessel attached to an extractor was charged with an excess of KH (0.08 g, 2 mmol) in the drybox. After evacuation on the vacuum line, 0.15 mL of B_6H_{10} (1.5 mmol) and 10 mL of Me_2O were condensed in at −196 °C. Deprotonation, under continual stirring, was carried out at −78 °C (2 h). When H_2 evolution ceased, 1.5 mmol of H_2 was recovered on a Toepler pump. The solution was filtered at −78 °C into a two-necked flask to afford a clear colorless solution.[13] The flask was cooled to −196 °C and, under positive nitrogen flow, the vessel was sealed with a tipper tube containing 0.58 g (1.5 mmol) of Ph_3SnCl. An additional 5 mL of CH_2Cl_2 was distilled into the solution. The solution was stirred at −78 °C, and the Ph_3SnCl was added as stirring continued at −78 °C. The resulting mixture was stirred for 12 h and then warmed to −35 °C and stirred for an additional 7–8 h. Removal of volatiles at −35 °C afforded a white foamy residue. CH_2Cl_2 (20 mL) was condensed in, and the contents of the flask were filtered at −78 °C in a vacuum extractor to remove KCl. The volatiles were removed from the colorless filtrate, and the viscous residue was dried under vacuum, first at −35 °C and later at room temperature for several days. A white solid, mp 140–142 °C dec, was obtained in 48% yield. Anal. Calcd for $C_{18}H_{24}B_6Sn$: C, 51.0; H, 5.66; B, 15.55. Found: C, 51.76; H, 5.31; B, 15.13. ^{11}B and ^{1}H NMR data are given in Table I, and $^{1}H\{^{11}B\}$ data in CD_2Cl_2/THF-d_8 are given in Table II. $^{13}C\{^{1}H\}$ NMR (δ in ppm, $CD_2Cl_2/CHClF_2$, −40 °C): 139.28 (s, 3C, *i*-C), 136.9 (s, 6C, *o*-C), 130.0 (s, 3C, *p*-C), 129.3 (s, 6C, *m*-C). Mass spectrum: parent cluster at *m*/*z* (max) = 424, with a cutoff at *m*/*z* = 430 corresponding to $[^{11}B_6{}^{1}H_{24}{}^{12}C_{18}{}^{124}Sn]^+$, and also envelopes due to Ph_3Sn^+ (*m*/*z* = 351), Ph_2Sn^+ (*m*/*z* = 274), $PhSn^+$ (*m*/*z* = 197), Sn^+ (*m*/*z* = 120), and $B_6H_x^+$ (*m*/*z* = 76–66). The observed data for the molecular ion envelope are *m*/*z* (int) 416 (0.0), 417 (3.3), 418 (5.1), 419 (11.9), 420 (32.2), 421 (61.5), 422 (80.2), 423 (92.5), 424 (100.0), 425 (91.02), 426 (69.2), 427 (28.4), 428 (20.9), 429 (18.8), 430 (14.8), and 431 (3.5). The calculated values[20] are *m*/*z* (int) 416 (1.3), 417 (2.5), 418 (3.8), 419 (8.8), 420 (24.8), 421 (51.0), 422 (75.4), 423 (90.7), 424 (100.0), 425 (90.4), 426 (61.8), 427 (21.4), 428 (15.2), 429 (13.0), 430 (9.2), and 431 (1.6). The molecular ion profile and the calculated one are given in the supplementary material. IR (KBr pellet) (cm^{-1}): 3062 (m), 2965 (m), 2578 (m), 2571 (m, sh), 2553 (m), 2500 (w), 2488 (m), 1430 (m), 1261 (s), 1098 (s), 1071 (m, sh), 1022 (s), 850 (w), 803 (s), 734 (m), 728 (m), 694 (m).

Reaction of 2,3-μ-(Ph_3Sn)B_6H_9 with HCl. An NMR tube sealed to a standard taper joint was loaded with 2,3-μ-(Ph_3Sn)B_6H_9 (ca. 0.02 g, 0.05 mmol) in the drybox. After evacuation, 0.5 mL of Et_2O and an excess of anhydrous HCl (ca. 0.2 mmol) was condensed in at −196 °C. The tube was sealed and allowed to stand, with occasional shaking, for 6 h at −35 °C. A ^{11}B NMR spectrum of the mixture at −35 °C indicated the presence of B_6H_{10} as the only boron-containing species.

Synthesis of 2,3-μ-(Me_3Sn)B_6H_9 (II). The method used was very similar to that used for I, that is the reaction between $K[B_6H_9]$ with Me_3SnCl in Me_2O/CH_2Cl_2. The reagents are mixed at −78 °C and stirred at −35 °C for 5 h. Removal of KCl by filtration and removal of solvent under vacuum afford a yellow residue which is dried in vacuo for several days. The product is solid at −78 °C, viscous at −35 °C, and liquid at 0 °C. It is unstable at room temperature. The compound obtained at −78 °C was stored at −78 °C, and an NMR sample was prepared on the vacuum line at −78 °C in CD_2Cl_2 and stored at that temperature. Boron-11 and proton NMR data are given in Table I. $^{13}C\{^{1}H\}$ NMR (δ in ppm, CD_2Cl_2, −80 °C): −2.68 (s, br, $J_{^{13}C-^{119}Sn}$ = 174 Hz). The $^{119}Sn\{^{1}H\}$ spectrum, under the same conditions, affords a single broad resonance at δ = −20.33. Quartets were not observed in the range +500 to −500 ppm. Mass spectra obtained from a sample stored at −35 °C and run by vaporizing the species into the spectrometer due to our inability to handle samples of the species at room temperature, exhibited an intense cluster identical with that for B_6H_{10} and no indication of the peaks due to 2,3-μ-(Me_3Sn)B_6H_9 could be observed. Also seen in the spectrum were ion clusters due to Me_3Sn^+, Me_2Sn^+, and $MeSn^+$, and Sn^+.

Results and Discussion

Preparation and Properties. Two organotin derivatives of B_6H_{10} were prepared according to Scheme I. The Ph_3Sn derivative, I, was isolated in 48% yield as a white solid which melts with decomposition at 140–142 °C. It is soluble in CH_2Cl_2, $CHCl_3$, Me_2O, THF, pentane, and

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[19] We acknowledge Mr. Robert Godfroid for obtaining these spectra for us at The Ohio State University.

[20] Program for the calculation of isotopic distributions from molecular formula: Stolz, W.; Korzenioski, R. W. In *Introduction to Organic Spectroscopy*; Lambert, J. B., Shurvell, H. F., Lightner, D. A., Cooks, R. G., Eds.; Macmillan: New York, 1987; pp 401–406.

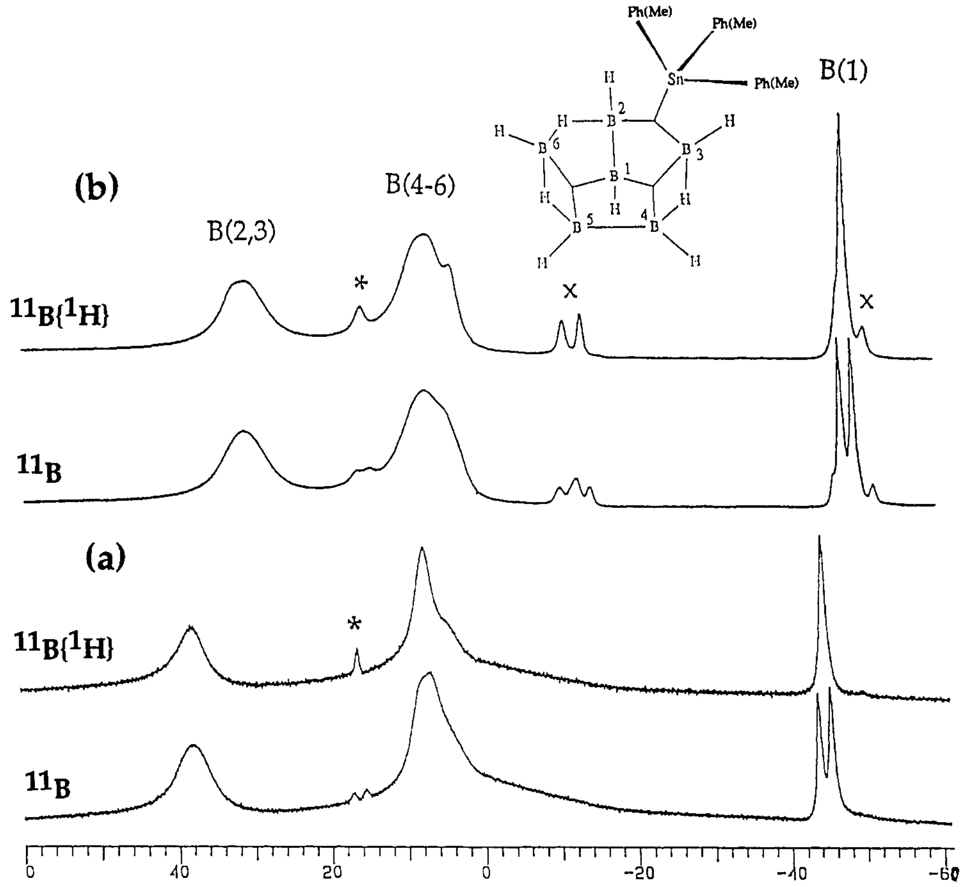
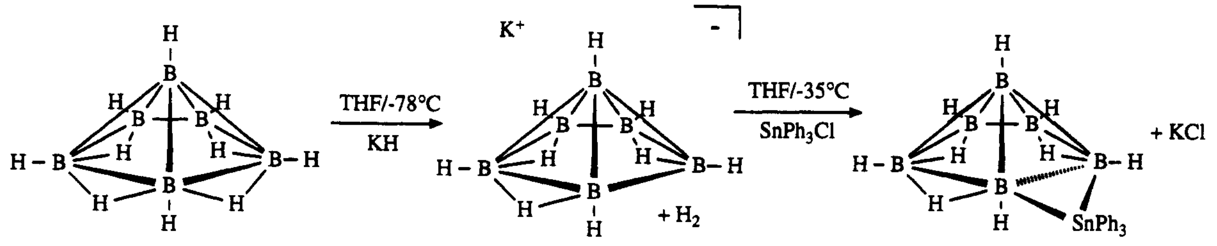


Figure 1. 96.3-MHz ^{11}B NMR spectra of (a) 2,3-μ-$(Ph_3Sn)B_6H_9$ (**I**) in $CDCl_3/CHClF_2$ at 0 °C and (b) 2,3-μ-$(Me_3Sn)B_6H_9$ (**II**) in CD_2Cl_2 at -35 °C. x = 2,3-μ-$(Me_3Sn)B_5H_8$, * = B_6H_{10}.

Scheme I



hexane, but solutions decompose slowly above -25 °C and rapidly at room temperature. All NMR spectra run above -35 °C contain traces of B_6H_{10}. The solid is unstable in air but may be stored at 0 °C under N_2 for 2 weeks, after which a color change from white to yellow occurs and NMR spectra indicate decomposition. Attempts to grow crystals suitable for X-ray structural determination in CH_2Cl_2/pentane or CH_2Cl_2/Et_2O at low temperatures resulted in the formation of a yellow/brown precipitate. Satisfactory elemental analytical data and mass spectra were obtained for the species. Formation of B_6H_{10} on reaction with anhydrous HCl at temperatures below -35 °C indicates that protonation of the species has occurred and further supports our contention that the Ph_3Sn moiety resides on a bridging position in the B_6 cluster. Such would not be expected if the Sn moeity were in either the 1- or 2-positions. It is known that *nido*-metallaboranes, with the metal-containing moiety in a bridgion position, are readily protonated to afford the parent borane.[21] The situation is not quite so simple for B_6H_{10} derivatives since these species contain a B–B bond which is also susceptible to protonation,[22] so the criterion is not conclusive.

NMR data for **I** are given in Tables I and II and displayed in Figures 1a and 2. The ^{11}B NMR spectrum of **I** at 0 °C clearly indicates a pyramidal structure in which there are four environments for the B atoms. A broad resonance at δ = 38.8 ppm of area 2 is assigned to borons 2 and 3. The broad resonance at approximately δ = 6.9 ppm has a shoulder at a higher field, ca. δ = 5.0 ppm. These may be assigned to borons 4–6, with the shoulder arising from boron 5. The apical boron signal is seen as a much sharper resonance (δ = -44.5 ppm) as a doublet (J = 152 Hz). These data are consistent with the boron skeleton shown in Figure 1. The broad resonance in the ^{119}Sn NMR spectrum of **I**, at δ = -93.8 ppm with fwhm = 124.1 Hz, is expected for a species with the Sn atom in a bridging position. We previously demonstrated that ^{119}Sn NMR spectra are very useful in identifying the isomers of tin-substituted pentaboranes(9).[8f,g] The related 2,3-μ-(Ph$_3$-

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[21] (a) Brice, V. T.; Shore, S. G. *J. Chem. Soc., Dalton Trans.* **1975**, 334. (b) Greenwood, N. N.; Staves, J. *J. Chem. Soc., Dalton Trans.* **1977**, 1786.

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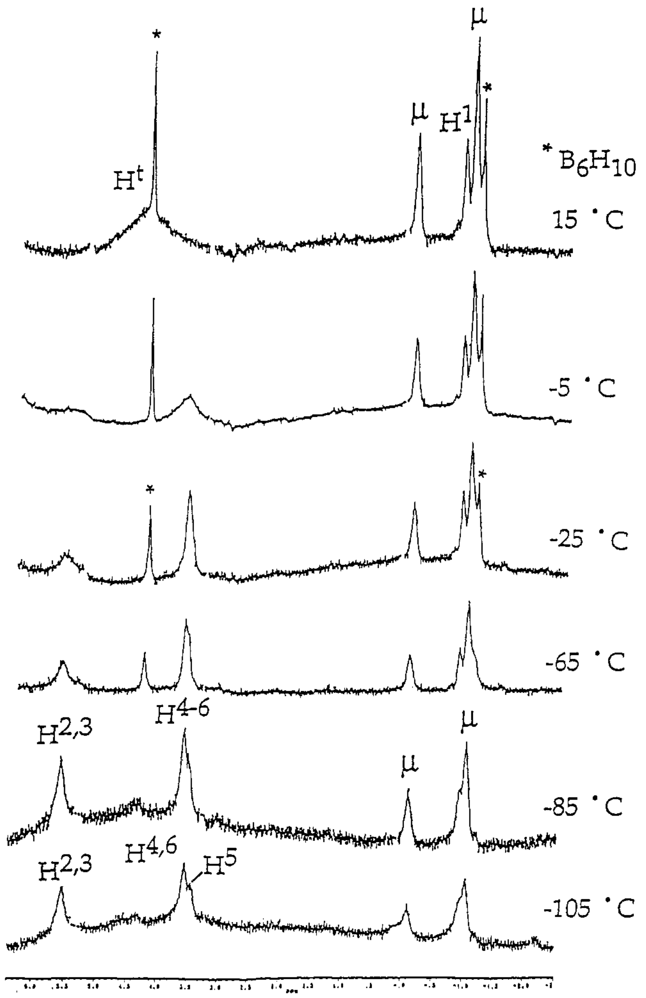

Figure 2. 250.1-MHz $^1H\{^{11}B\}$ NMR spectra of 2,3-μ-(Ph$_3$Sn)B$_6$H$_9$ (**I**) in CD$_2$Cl$_2$/THF-d_8 at various temperatures.

Sn)B$_5$H$_8$, for which a crystal structure determination confirms the structure, exhibits a broad resonance at δ = −93.3 Hz with fwhm = 108 Hz.[9g] The ^{1}H spectrum at −120 °C, is consistent with the ^{11}B spectrum. The terminal basal H atoms fall into groups of 2 and 3 at ca. δ = 5.55 and 3.52 ppm assigned to H(2,3) and H(4–6), respectively. The latter contains an upfield shoulder assigned to H(5). The upfield region of the spectrum exhibits resonances in a 1:2 area ratio at δ = −0.08 and −1.02 ppm, respectively. The apical boron atom signal is not seen in the coupled spectrum at low temperatures, and at higher temperatures the basal H atoms are seen as broad overlapping quartets which are not distinguished. Only at higher temperatures, ca. 0 °C, is the apical quartet seen, but decomposition is quite rapid at this temperature. The absence of quartets for the basal terminal hydrogen atoms at lower temperatures is ascribed to "thermal decoupling" due to quadrupolar relaxation of the boron nuclei.[23] The variable temperature boron-11 decoupled proton NMR spectrum, displayed in Figure 2 and listed in Table II, provides much more information. At high field and temperatures above −65 °C, the apical signal is observed clearly at ca. δ = 0.8 ppm, slightly overlapped with the upfield one of two resonances, of an area ratio of 1:2, assigned to bridging H atoms. Also observed in the spectrum is a B$_6$H$_{10}$ impurity which grows as the sample is warmed. This confirms that

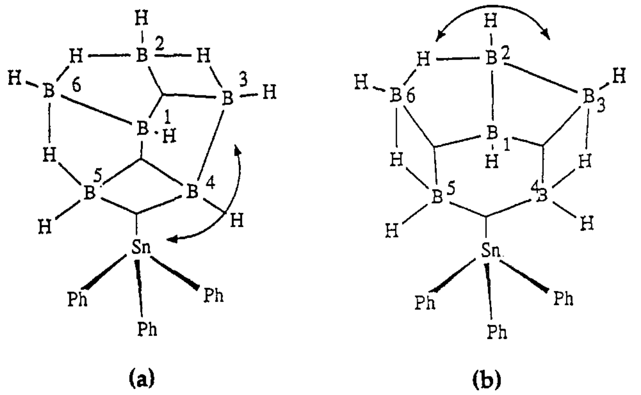

Figure 3. (a) Proposed motion of the B$_6$H$_9$ cage relative to the Sn moiety in **I**. (b) Proposed motion of H$_\mu$ atoms in **I**.

2,3-μ-(Ph$_3$Sn)B$_6$H$_9$ decomposes at higher temperatures. The region assigned to the basal terminal H atoms is also very informative. At 15 °C, only a broad, apparently single, resonance is observed at δ = 4.3 ppm, which splits in two as the temperature is lowered. At −5 °C, the broad peak already is splitting in two and, at −25 °C, two peaks at δ = 3.6 and 5.6 ppm, of an approximate area ratio of 2:3, respectively, are clearly observed. These are assigned to H(2,3) and H(4–6), respectively. As the temperature is further lowered, the shoulder, observed in the previously described spectra, appears at δ = 3.46 ppm. This is assigned to H(5). The weighted average of these resonances is δ = 4.3 ppm, the same as that for the single resonance observed at 15 °C.

It is well-known that the bridging H atoms in B$_6$H$_{10}$ and [B$_6$H$_9$]$^-$ species are fluxional on the NMR time scale at higher temperatures whereas the terminal H atoms are static.[24] In Mg(THF)$_2$(B$_6$H$_9$)$_2$, the only well-characterized metalla derivative of B$_6$H$_{10}$ which contains a basal B–B bond,[11,12] motion of both the bridging H atoms and the boron framework relative to the metal group is invoked to account for the observed spectra. In that system, the bridging hydrogen environment is exchange-averaged at higher temperatures and thus a single resonance is observed. At lower temperatures the motion slows such that two resonances in a 2:1 area ratio are seen. The authors suggest that the motion of the H atoms is partially quenched in that two H atoms are static and one moves between two available sites. In the case of 2,3-μ-(Ph$_3$Sn)B$_6$H$_9$ two resonances for the bridging hydrogens are seen in the temperature range −120 °C to room temperature. We are unable to distinguish between a process similar to that proposed for Mg(THF)$_2$(B$_6$H$_9$)$_2$ and one in which the three bridging H atoms move rapidly between the four available sites.[11] In the case of 2,3-μ-(Ph$_3$Sn)B$_6$H$_9$, we favor a process such as that shown in Figure 3b. That is, the H$_\mu$ atoms adjacent to the Sn atom are static on the NMR time scale but the third one moves between the two vacant sites between B(5) and B(6) and between B(4) and B(5). The Ph$_3$Sn group is quite large and stericaly significant, and perhaps this accounts for the difference between it and the Mg(THF)$_2$ moiety in (THF)$_2$Mg-

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$(B_6H_9)_2$.[11] The Ph_3Sn group might restrict the extent of bridge H atom motion. The observation of three environments for the basal H atoms at all temperatures below ca. −10 °C may be explained by assuming that motion of the cage relative to the Ph_3Sn group does not occur at these temperatures. The broad resonance at 15 °C, in the region where the basal terminal hydrogen signals are seen at lower temperatures, may be due to decomposition of the sample, although the fact that the observed chemical shift is the weighted average of those seen at lower temperatures suggests that it is an averaged resonance. At −5 °C a broad resonance is observed at $\delta = 4.3$ ppm, which is essentially the weighted average of the resonances at −25 °C, which are observed at $\delta = 3.6$ (area 3) and 5.6 (area 2), respectively. This suggests that at −5 °C the basal H atoms are equivalent due to some motion of the cage relative to the tin substituent and thus a single resonance is observed for the terminal H atoms. Such motion could possibly be effective 1,2-migration of the Ph_3Sn moiety, as shown in Figure 3a. This latter is actually less likely than an equivalent motion of the lighter borane cage relative to the Sn atom. Such dynamic behavior is consistent with the observation of two resonances for the bridging H atoms. Processes equivalent to that shown in Figure 3a would result in two resonances for the H_μ atoms, since one H_μ atom is always between two others irrespective of the extent of motion of the bridging H atoms. We have described a more complex exchange-averaged process system recently[28] in the analysis of the NMR spectra of a related species, the anion $[Fe(CO)_4B_6H_9]^-$. In the anion, more extensive 1,3-motion of the cage relative to the metal atoms was invoked to explain the NMR spectra. In the case of **I**, we would expect to observe a single ^{11}B resonance for the basal boron atoms at 15 °C if the borane cage is effectively spinning relative to the metal atom. The observation is complicated by the broadness of the peaks and the presence of B_6H_{10} from decomposition of the sample and is not clearly seen. Thus we presume that the spectra are due to the motion of H atoms and the Ph_3Sn group above −10 °C to generate a system with an effective plane of symmetry and that below this temperature the motion of the metal moiety is quenched but some motion of the bridging H atoms continues with retention of the plane of symmetry.

Treatment of **I** with bases, followed by NMR spectral examination, reveals no evidence for rearrangement from the bridging to the 2- or 1-isomer. The only observation is degradation of the species. Observation is not easy since the species decomposes at temperatures at which the rearrangement is expected to occur. The analogous pentaboran(9)yl derivatives readily rearrange in the presence of base to afford the 2- and ultimately the 1-isomers.[8f,g,25,26] Although we were unable to grow crystals, we are confident, on the basis of the spectroscopic and analytical data described above, that we have identified only the second main group derivative of hexaborane(10) with the substituent, in this case, replacing a bridging hydrogen atom.

II, 2,3-μ-$(Me_3Sn)B_6H_9$, clearly is unstable at temperatures above −35 °C. It appears to melt just below −35 °C, and it decomposes just below ambient temperature perhaps due to reduction of the Sn moiety by the borane. Elemental analytical and spectroscopic data, on samples prepared and stored at −35 °C prior to measurement at ambient temperature, all suggest substantial decomposition. NMR spectra suggest that 2,3-μ-$(Me_3Sn)B_6H_9$ is stable at low temperatures. The ^{11}B spectrum at −35 °C, displayed in Figure 1b, contains resonances indicative of traces of B_6H_{10} and 2,3-μ-$(Me_3Sn)B_5H_8$. The region in which basal B atoms are expected to be observed shows two broad resonances in an area ratio of 2:3, with the larger resonance containing a shoulder, and a sharp doublet upfield of area 1. This suggests an arrangement of six boron atoms in a pentagonal pyramidal arrangement with a plane of symmetry. This would occur if the H_μ atoms were fluxional. The ^1H NMR spectrum, listed in Table I, is consistent with this conclusion. A single broad resonance of area 5 in the region where basal terminal H atoms are expected, presumably due to partially thermally decoupled signals which overlap, and a single broad resonance of area 3 in the bridging hydrogen region, along with a quartet arising from the apical H atom, are expected for a 2,3-μ-hexaboranyl derivative. The ^{119}Sn NMR spectrum consists of a single broad resonance at $\delta = -20.33$ ppm, as expected for a system containing a Sn moiety in a basal bridging position, analogous to **I** above and also to the species 2,3-μ-$(Ph_3Sn)B_5H_8$.

Perhaps the most important feature of the hexaboranyl derivatives, which distinguish them from their pentaboranyl congeners, is their fluxionality. This is a consequence of the basal B–B bond,[24,28] which may also be the reason for the decreased stability of the hexaboranes. There is clearly a remarkable difference in the stability of the main group borane derivatives 2,3-μ-$(R_3M)B_5H_8$ and 2,3-μ-$(R_3M)B_6H_9$. The former retain their integrity at room temperature and may be isomerized to the 2- and 1-isomers.[8f,g,25,26] On the other hand the hexaboranyl derivatives are much less stable than their pentaboranyl congeners and quite difficult to work with. Isomerization of such species has not been observed; rather, decomposition occurs in the presence of bases. Thus the latter are quite rare and present a challenge to chemists. We are attempting to extend the chemistry of hexaboranyl derivatives.

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Supplementary Material Available: Figures of the observed and calculated mass spectral parent profiles showing the isotopic distribution, the ^{119}Sn NMR spectrum at −40 °C, and the ^1H NMR spectrum of **I** at −120 °C (3 pages). Ordering information is given on any current masthead page.

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