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Three Isomers of (Triphenylstannyl)-*nido*-pentaborane(9): Isolation and Structural Characterization of 2,3-μ-($SnPh_3$)B_5H_8, 1-($SnPh_3$)B_5H_8, and 1-($SnClPh_2$)B_5H_8

Dileep K. Srivastava, Nigam P. Rath, and Lawrence Barton*

Department of Chemistry, The University of Missouri—St. Louis, St. Louis, Missouri 63121

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The reaction between K[B_5H_8] and $SnClPh_3$, in tetrahydrofuran for extended periods at room temperature, affords exclusively the 1-($SnPh_3$)B_5H_8 isomer (1). The 2,3-μ-isomer (2) is the exclusive product if the same reaction is carried out in CH_2Cl_2. Attempts to isolate the 2-isomer (3) always result in the presence of traces of 1, which is presumed to be the thermodynamically stable product. Isomerization of the bridging-isomer (2) does not afford an equilibrium mixture of the 1- and 2-isomers as in other group 14 derivatives of B_5H_9. Similarly 1-($SnClPh_2$)B_5H_8 (4) is the exclusive product if K[B_5H_8] and $SnCl_2Ph_2$ are stirred for 16 h at 25 °C in THF. The species are characterized by ^1H, ^{11}B, and ^{119}Sn NMR spectra. We report the first observation of ^{11}B–^{119}Sn coupling in a pyramidal borane from both ^{11}B and ^{119}Sn spectra for both 1 and 4 and identify the bridging moiety in 2, 2,3-μ-($SnPh_3$)B_5H_8, from its ^{119}Sn spectra. The crystal structures of 2 and 4 are reported. 2 crystallizes in the monoclinic space group $P2_1/n$, with a = 14.132 (3) Å, b = 9.733 (2) Å, c = 14.539 (2) Å, β = 96.90 (2)°, and Z = 4, and 4 crystallizes in the orhorhombic space group $Pmc2_1$ with a = 16.358 (2) Å, b = 6.427 (2) Å, c = 16.014 (2) Å, and Z = 4. For 2, the $SnPh_3$ group occupies a bridging position with an angle between the basal BBBB plane and the BBSn plane of 53°. 1 and 4 are the first examples of a bulky group of substituents occupying an apical position in *nido*-B_5H_9, and the structure determination for 4 is the first for a nido-pyramidal borane apically substituted with a non-halogen atom.

Introduction

It is well established that nido-pyramidal boranes 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 in these boranes may be replaced with Lewis acids.[2] The lewis acids range from simple species such as the proton[3] and borane(3)[4] through more complex main-group[2a,5] species and transition-metal moieties.[6] The main-group species thus introduced into the cluster include elements from groups 2,[7] 13,[8] 14,[9] and 15.[10] There are several examples of group 14 derivatives of pentaborane(9) and they include species with the MR_3 moiety (M = Si, R_3 = H_3,[9b,c] H_2Cl,[9e] Me_3,[9a,bc] Et_3,[9b] F_3;[9f] M = Ge, R_3 = H_3, Me_3, Et_3; M = Sn or Pb, R_3 = Me_3[9b]) replacing a bridging proton. Some of these systems rearrange in the presence of base to form the 2-isomer, and at elevated temperatures or in the presence of strong base, conversion to the 1-isomer occurs, without cleavage of the substituent–boron bond.[11] The rearrangements observed thus far, that is those for the SiR_3 and GeR_3 species, afford mixtures which favor the 1-isomer, but the thermodynamically favored product mixture always contains appreciable concentrations of the 2-isomer in the product mixture.[12]

Herein we report the synthesis and characterization of the 1-, 2-, and 2,3-μ-triphenylstannyl derivatives of B_5H_9, and also 1-($SnClPh_2$)B_5H_8. We also report some ^{119}Sn and other NMR data for these systems and results of studies of the interconversion of the isomers of $SnPh_3B_5H_8$. A preliminary report described the synthesis and NMR spectra of 1-($SnPh_3$)B_5H_8 (1).[13]

Experimental Section

Materials. B_5H_9 was obtained from laboratory stock, and distilled before use. $SnClPh_3$ and $SnClMe_3$ were obtanied from Aldrich and used without further purification. $SnCl_2Ph_2$ was prepared as reported in the literature.[14] KH, obtained as a mineral oil suspension from Research Organic/Inorganic Chemical

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Table I. NMR Data for Organotin-Substituted Pentaboranes(9)[a]

compd	^{11}B data[b]	^{1}H data[c]	^{13}C{^{1}H} data[d]	^{119}Sn{^{1}H} data[e]
1-$(SnPh_3)B_5H_8$[f] (1)	−10.5 [d, 4 B, B(2–5), $^{1}J(^{11}B–^{1}H)$ = 164 Hz], −54.6 [s, 1 B, B(1), $^{1}J(^{11}B–^{119}Sn)$ = 1123 Hz]	−2.30 [s, br, 4 H, Hμ], 2.61 [q, 4 H, basal Ht, $^{1}J(^{1}H–^{11}B)$ = 160 Hz], 7.24 [m, 9 H, *m*-, *p*-C_6H_5], 7.48 [m, 6 H, *o*-C_6H_5, $^{3}J(^{119}Sn–^{1}H)$ = 46.5 Hz]	141.2 [q, i-C_6H_5, $^{2}J(^{13}C–^{11}B)$ = 8.2 Hz], 137.1 [s, br, *o*-C_6H_5, $^{2}J(^{119}Sn–^{13}C)$ = 33.8 Hz], 128.2 [s, br, *m*-C_6H_5, $^{3}J(^{119}Sn–^{13}C)$ = 62 Hz], 128.2 [s, br, *p*-C_6H_5]	−89.2 [q, $^{1}J(^{119}Sn–^{11}B)$ = 1117 Hz, $^{1}J(^{119}Sn–^{10}B)$ = 391 Hz]
2,3-μ-$(SnPh_3)B_5H_8$ (2)	−8.3 [d, 2 B, B(2,3), $^{1}J(^{11}B–^{1}H)$ = 153 Hz], −12.2 [d, 2 B, B(4,5), $^{1}J(^{11}B–^{1}H)$ = 160 Hz], −47.9 [d, 1 B, B(1), $^{1}J(^{11}B–^{1}H)$ = 178 Hz]	−2.75 [s, br, 2 H, Hμ(3,4), Hμ(2,5)], −2.17 [s, br, 1 H, Hμ(4,5)], 0.67 [q, br, 1 H, H(1), $J(^{11}B–^{1}H)$ = 175 Hz], 1.4–3.7 [q, br, 4 H, H(2–5), *J* unres], 7.24 [m, unres, 9 H, *m*-, *p*-C_6H_5], 7.39 [m, 6 H, *o*-C_6H_5, $^{3}J(^{119}Sn–^{1}H)$ = 59 Hz]	138.5 [s, i-C_6H_5], 136.3 [s, *o*-C_6H_5, $^{2}J(^{119}Sn–^{13}C)$ = 23 Hz], 129.1 [s, *m*-C_6H_5, $^{3}J(^{119}Sn–^{13}C)$ = 57 Hz], 129.6 [s, *p*-C_6H_5, *J* unres]	−98.3 [s, br]
2-$(SnPh_3)B_5H_8$ (3)	−8.4 [s, 1 B, B(2)], −10.1 [d, 2 B, B(3,5), $^{1}J(^{11}B–^{1}H)$ = 178 Hz], −12.1 [d, 1 B, B(4), $^{1}J(^{11}B–^{1}H)$ = 165 Hz], −47.9 [d, 1 B, B(1), $^{1}J(^{11}B–^{1}H)$ = 169 Hz]			−87.5 [q, $^{1}J(^{119}Sn–^{11}B)$ = 1061 Hz]
1-$(SnClPh_2)B_5H_8$ (4)	−9.84 [d, 4 B, B(2–5), $^{1}J(^{11}B–^{1}H)$ = 164 Hz], −50.8 [s, 1 B, B(1), $^{1}J(^{11}B–^{119}Sn)$ = 1270 Hz]	−1.88 [s, br, 4 H, Hμ], 2.78 [q, 4 H, basal Ht, $^{1}J(^{1}H–^{11}B)$ = 170 Hz], 7.3–7.55 [m, 10 H, C_6H_5, $^{3}J(^{119}Sn–^{13}C)$ = 26.8 Hz]	141.8 [q, i-C_6H_5, $^{2}J(^{13}C–^{11}B)$ = 13 Hz], 135.7 [s, *o*-C_6H_5, $^{2}J(^{119}Sn–^{13}C)$ = 24.5 Hz], 128.5 [s, *m*-C_6H_5], 129.4 [s, *p*-C_6H_5, *J* unres]	72.1 [q, $^{1}J(^{119}Sn–^{11}B)$ = 1272 Hz, $^{1}J(^{119}Sn–^{10}B)$ = 439 Hz]
2,3-μ-$(SnMe_3)B_5H_8$[g] (5)	−9.98 [d, 2 B, B(2,3), $^{1}J(^{11}B–^{1}H)$ = 158 Hz], −12.4 [d, 2 B, B(4,5), $^{1}J(^{11}B–^{1}H)$ = 163 Hz], −48.9 [d, 1 B, B(1), $^{1}J(^{11}B–^{1}H)$ = 175 Hz]	−3.18 [s, br, 2 H, Hμ(3,4), Hμ(2,5)], −2.29 [s, br, 1 H, Hμ(4,5)], 0.458 [s, 9 H, Sn–CH_3, $^{2}J(^{119}Sn–^{1}H)$ = 53 Hz], 0.53 [q, br, 1 H, H(1), *J* = 178 Hz], 2.38 [q, br, 4 H, H(2–5), *J* = 166 Hz]	−2.51 [s, Sn–CH_3], 15.3 [s, br, $^{1}J(^{13}C–^{119}Sn)$ = 343 Hz]	

[a] All spectra were recorded at 298 K in $CDCl_3$. [b] Chemical shifts are relative to $BF_3{\cdot}OEt_2$ (δ 0.0 ppm) determined by assignment relative to BCl_3 (δ 46.8) as an external standard. Uncertainties: δ, ±0.2 ppm; *J*, ±5 Hz. [c] Relative to TMS (0.0 ppm). [d] Relative to $CDCl_3$ (77.0 ppm). [e] Relative to external Me_4Sn (0.0 ppm). Abbreviations: s = singlet, d = doublet, q = quartet, m = multiplet, unres = unresolved coupling, o = ortho, m = meta, p = para, i = ipso, br = broad, Hμ = bridging hydrogen, Ht = terminal hydrogen. [f] Reference 13. [g] ^{1}H and ^{11}B NMR data have been reported earlier.

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, distillled from Na/benzophenone, and stored over molecular sieves. All solvents were reagent grade and were dried and distilled prior to use and stored in Pyrex vessels with Teflon stopcocks.

Apparatus. Standard high-vacuum-line and drybox techniques were employed in this work.[15] NMR spectra were obtained on a Varian XL-300 spectrometer operating at 300.1, 96.3, 76.6, and 111.7 MHz to observe ^{1}H, ^{11}B, ^{13}C, and ^{119}Sn resonances respectively. ^{11}B chemical shifts are reported in ppm, positive signs denoting a shift at a lower field with respect to $(C_2H_5)_2O{\cdot}BF_3$ reference (0.0 ppm). ^{1}H and ^{13}C chemical shifts were measured relative to $Si(CH_3)_4$ and $CDCl_3$, respectively. ^{119}Sn chemical shifts were obtained with respect to Me_4Sn (0.0 ppm) as an external reference. Mass spectra were run as solids at 70 eV on a Varian/Mat 311A spectrometer equipped with a Technivent data system. IR spectra were run as Nujol mulls prepared in the drybox or as KBr pellets on a Perkin-Elmer 1604 FT-IR spectrometer. Elemental analyses were performed by Atlantic Microlabs Inc.

Reaction between $K[B_5H_8]$ and $SnClPh_3$. In a typical reaction, 2 mmol of $SnClPh_3$ was added to 2 mmol of $K[B_5H_8]$ in 10 mL of THF at −78 °C. The reaction mixture was allowed to warm to 0 °C over a period of 2 h and stirred at that temperature for 3–4 h. After workup of the reaction mixture, the product was characterized by ^{11}B and ^{119}Sn NMR spectroscopy, which indicated the presence of a mixture of all three possible isomers, 2,3-μ-$(SnPh_3)B_5H_8$, 2-$(SnPh_3)B_5H_8$, and 1-$(SnPh_3)B_5H_8$ (see text).

Preparation of 1-$(SnPh_3)B_5H_8$ (1). A reaction vessel attached to an extractor was charged with an excess of KH inside the drybox. After evacuation on the vacuum line, 0.28 mL of B_5H_9 (2.7 mmol) and 10 mL of THF were condensed in at −196 °C. Deprotonation, under continual stirring, was carried out at −78 °C (2 h). When H_2 evolution ceased, 2.7 mmol of H_2 was recovered on a Toepler pump. The solution was filtered at −78 °C into a two-necked flask. A clear colorless solution was obtained.[16] The flask was cooled to −196 °C, and under positive nitrogen flow, the vessel was sealed with a tipper tube containing $SnClPh_3$. After evacuation, the solution was stirred at −78 °C and 2.7 mmol of $SnClPh_3$ (1.04 g) was added. The mixture was warmed to room temperature over a period of 3–4 h and stirred at that temperature for 12 h. The volatiles were removed in vacuo to give an off-white residue. The residue was extracted with 10 mL of CH_2Cl_2, the solution was concentrated, and addition of pentane provided 1 as a yellowish white solid, which was dried in vacuo. The solid melts at 94–96 °C with decomposition and is obtained in 61% yield. It is soluble in CH_2Cl_2, $CHCl_3$, Me_2O, THF, and benzene and insoluble in pentane and hexane. NMR spectra are tabulated in Table I. The compound appears to be air and light sensitive. In turns deeper yellow and eventually orange when warmed above 0 °C or exposed to light, and the NMR spectrum of this material indicates substantial decomposition. Elemental analysis gave unsatisfactory results, presumably due to the instability of the material, but as indicated below, mass spectra were supportive of the formulation. The IR spectrum, run as a KBr pellet, showed the following absorbances (cm^{-1}): 3058 (m), 3000 (m), 2967 (w), 2595 (s), 1950 (w), 1879 (w), 1847 (m), 1478 (m), 1456 (w), 1427 (s), 1400 (m), 1328 (w), 1294 (w), 1260 (m), 1189 (w), 1156 (w), 1100 (m, br), 1072 (m, sh), 1021 (m), 996 (m), 904 (s), 872 (w), 857 (m), 806 (m), 728 (s), 699 (s), 683 (s, sh), 650 (m, sh), 600 (w), 450 (s), 450 (s), 441 (s). NMR data are given in Table I. The mass spectrum exhibits the expected B_5Sn envelope with a cutoff at *m/z* 418 attributed to $[^{11}B_5{}^{124}Sn^{12}C_{18}{}^{1}H_{23}]^+$. The observed *m/z* values (relative intensity) for the $SnPh_3B_5H_8$ molecular ion cluster were 418 (35.19), 417 (33.63), 416 (37.43), 415 (37.43), 414 (94.97), 413 (94.97), 412 (96.08), 411 (100), 410 (79.33), 409 (60.43), 408 (37.43), 407 (30.17), and 406 (29.05). The calculated *m/z* data were 418 (1.96), 417 (10.91), 416 (13.36), 415 (15.51), 414 (22.60), 413 (70.65), 412 (94.13), 411 (100), 410 (87.08), 409 (71.43), 408 (45.30), 407 (19.32), and 406 (6.02). The fit is not so good, and this may be ascribed to the low intensity of the molecular ion cluster which is affected by baseline noise. The [M − Ph]$^+$ cluster, has a base peak at *m/z* 335, and a cutoff at *m/z* 341 corresponding

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(16) We find that the use of excess KH, followed by filtration of the solution is more convenient than the use of a stoichiometric amount of KH, and it provides a purer product free from unreacted KH and any traces of KOH.

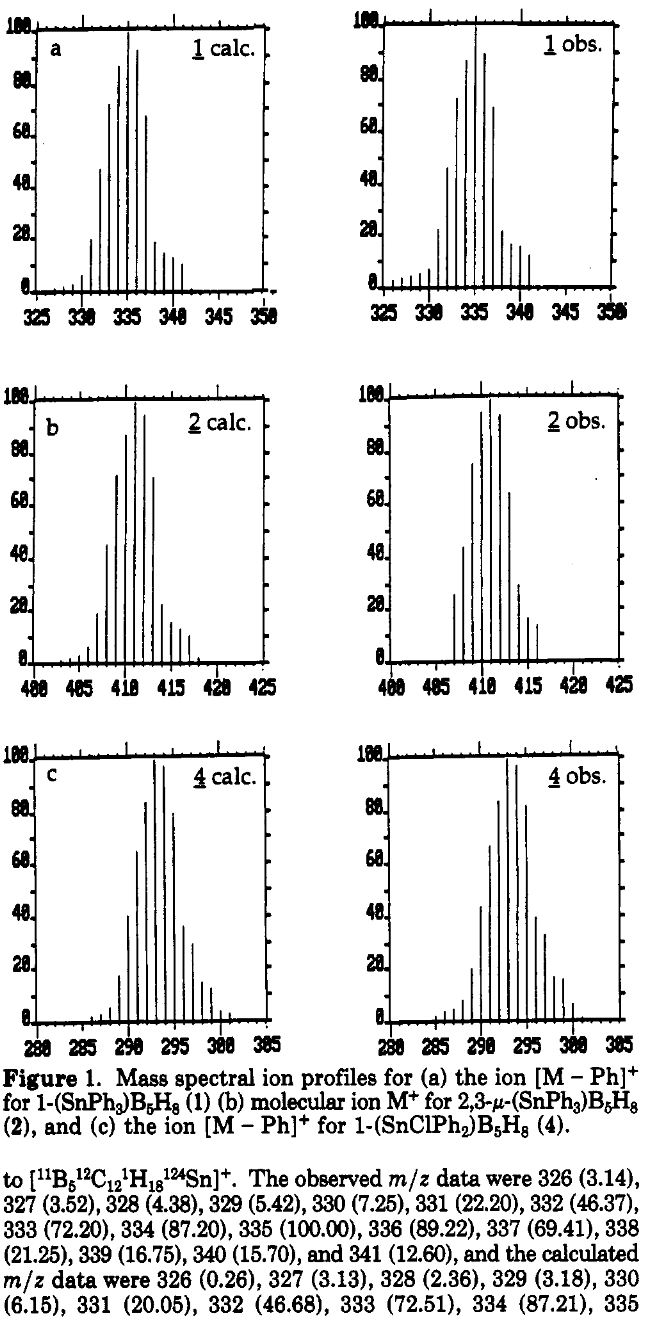

Figure 1. Mass spectral ion profiles for (a) the ion $[M - Ph]^+$ for 1-$(SnPh_3)B_5H_8$ (1) (b) molecular ion M^+ for 2,3-μ-$(SnPh_3)B_5H_8$ (2), and (c) the ion $[M - Ph]^+$ for 1-$(SnClPh_2)B_5H_8$ (4).

to $[^{11}B_5{}^{12}C_{12}{}^{1}H_{18}{}^{124}Sn]^+$. The observed *m/z* data were 326 (3.14), 327 (3.52), 328 (4.38), 329 (5.42), 330 (7.25), 331 (22.20), 332 (46.37), 333 (72.20), 334 (87.20), 335 (100.00), 336 (89.22), 337 (69.41), 338 (21.25), 339 (16.75), 340 (15.70), and 341 (12.60), and the calculated *m/z* data were 326 (0.26), 327 (3.13), 328 (2.36), 329 (3.18), 330 (6.15), 331 (20.05), 332 (46.68), 333 (72.51), 334 (87.21), 335 (100.00), 336 (92.70), 337 (68.45), 338 (19.12), 339 (14.95), 340 (13.11), and 341 (10.63). The fit is excellent, and it is shown in Figure 1 along with the calculated data for comparison.

Preparation of 2,3-μ-$(SnPh_3)B_5H_8$ (2). A reaction vessel attached to an extractor was charged with an excess of KH in the drybox. After evacuation of the vessel on the vacuum line, 0.17 mL of B_5H_9 (1.6 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, 1.6 mmol of H_2 was recovered on a Toepler pump. The solution was filtered at −78 °C into a two-necked flask. A clear colorless solution was obtained. Volatiles were removed from the filtrate at −78 °C, and the white residue thus obtained was dried at −78 °C in vacuo for 12 h. The flask was cooled to −196 °C, and under positive nitrogen flow, the vessel was sealed with a tipper tube containing $SnClPh_3$. After evacuation, 10 mL of CH_2Cl_2 was distilled into the reaction vessel. The resulting suspension was stirred at −78 °C, and 1.6 mmol of $SnClPh_3$ (0.61 g) was added. The mixture was warmed to 0 °C over a period of 2 h and stirred at that temperature for 3 h. A white turbid solution was obtained. The contents of the flask were filtered at 0 °C in a vacuum extractor to remove KCl. After the volume of the colorless filtrate was reduced, 8 mL of pentane was added. On standing at −78 °C, 2 precipitated and it was isolated in 53% yield as a white solid on drying in vacuo at room temperature for several hours. It is soluble in CH_2Cl_2, $CHCl_3$, Me_2O, THF, and C_6H_6 and insoluble in pentane and hexane and melts with decomposition at 139–141 °C. The compound appears to be air stable for extended periods. Anal. Calcd for $C_{18}H_{23}B_5Sn$: C, 52.43; H, 5.57. Found: C, 52.35; H, 5.69. The IR spectrum, run as a KBr pellet, showed the following absorbances (cm^{-1}): 3061 (m), 2969 (w), 2591 (s), 2546 (m), 1961 (w, br), 1884 (w, br), 1815 (w), 1480 (s), 1428 (s), 1331 (w), 1330 (w), 1261 (w), 1146 (w), 1100 (m), 1073 (m), 1015 (m), 997 (s), 938 (m), 884 (m), 800 (s), 708 (s), 696 (s), 654 (m), 615 (s), 444 (s). NMR data are given in Table I. The mass spectrum exhibits a molecular ion cluster at *m/z* (maximum) 418 attributed to $[^{11}B_5{}^{124}Sn{}^{12}C_{18}{}^{1}H_{23}]^+$ although it was of very low intensity and thus not picked up in the data given in Figure 1. Also observed were ion clusters due to $M - Ph^+$ (*m/z* 341), $SnPh_3^+$ (*m/z* 351), $SnPh_2^+$ (*m/z* 197) and $B_5H_x^+$. The $SnPh_n^+$ (n = 1–3) ions were seen to grow in the spectrum as time elapsed during the running of spectra and the intensity of the molecular ion cluster diminished in intensity, presumably as the sample decomposed thermally. The observed *m/z* (intensity) values were 416 (13.94), 415 (16.36), 414 (29.65), 413 (63.80), 412 (93.54), 411 (100), 410 (94.32), 409 (74.95), 408 (43.54), and 407 (26.13). The calculated *m/z* (intensity) values were 418 (1.96), 417 (10.91), 416 (13.36), 415 (15.51), 414 (22.60), 413 (70.65), 412 (94.13), 411 (100), 410 (87.08), 409 (71.43), and 408 (45.30). Details of the molecular ion envelope, along with the calculated one, are displayed in Figure 1.

Attempted Preparation of 2-$(SnPh_3)B_5H_8$ (3). A series of reactions were carried out in efforts to isolate pure 2-$(SnPh_3)B_5H_8$; however all attempts resulted in the isolation of material containing either 2,3-μ-$(SnPh_3)B_5H_8$, 1-$(SnPh_3)B_5H_8$, or both isomers as an impurity. Details of some of these attempts are given below.

(a) The reaction of $K[B_5H_8]$ with $SnClPh_3$ in THF at 0 °C for 90 min afforded a mixture of the μ- and 2-isomers along with traces of the 1-isomer. If the mixture was stirred at −35 °C for 12 h, a mixture of the 2- and 2,3-μ-isomer was found, but when shorter reaction times were used at −35 °C, reaction was incomplete and unreacted $K[B_5H_8]$ was recovered in the product mixture.

(b) If 2 was stirred in CH_2Cl_2 at ambient temperature for 5 days, thermal rearrangement to 3 was not observed, and 2 was found unchanged. The μ-isomer was also unaffected when stirred in Et_2O for 3 days at ambient temperature or when a C_6D_6 solution was warmed to 80 °C in the NMR probe.

Reaction of 1 and 2 with 2,6-Lutidine. In an NMR tube, three drops of 2,6-lutidine were added to a solution of 1-$(SnPh_3)B_5H_8$ (0.02 g) in 0.5 mL $CDCl_3$. The NMR tube was stirred at 25 °C and monitored at regular intervals by ^{11}B NMR spectroscopy. After about 1 week, degradation was complete. The final reaction mixture contained lutidine·BH_3 and unidentified species (^{11}B NMR δ = 9.8 and −25 ppm). At no stage was any 2-$(SnPh_3)B_5H_8$ observed. Using the procedure described above, when 2,3-μ-$(SnPh_3)B_5H_8$ was reacted with 2,6-lutidine in ether, no indication of 2-$(SnPh_3)B_5H_8$ formation was observed. The reaction also resulted in degradation of the species.

Since we were able to isolate the pure 1- and 2,3-μ-isomers, we could extract NMR data for the 2-isomer, from the spectra of the mixture of the three isomers, and they are given in Table I.

Preparation of 1-$(SnClPh_2)B_5H_8$ (4). The procedure is similar to the one employed in the synthesis of 1. In a typical reaction, 0.18 mL (1.7 mmol) of B_5H_9 in 10 mL of THF was reacted with an excess quantity of KH to produce $K^+[B_5H_8]^-$ which was then allowed to react with $SnCl_2Ph_2$ (0.584 g, 1.7 mmol) at −78 °C. The reaction mixture was warmed to room temperature over a period of 3 h and stirred at that temperature for an additional 16 h. Following solvent removal, the residue was extracted with 10 mL of methylene chloride. The volume of the solution was reduced, and excess pentane was added. On standing at −78 °C, 4 was obtained as a white solid and it was dried in vacuo at ambient temperature. During vacuum drying, the color of the solid changed to light yellow and, after 24 h, a light orange solid was obtained. Boron-11 NMR data were independent of the color change. Compound 4, which melts at 87–90 °C, was obtained in 56% yield. It is soluble in CH_2Cl_2, $CHCl_3$, THF, and C_6H_6 and insoluble in pentane and hexane. The compound appears to be air sensitive, and it did not give satisfactory elemental analysis. The IR spectrum, run as a KBr pellet, showed the following absorbances (cm^{-1}); 3069 (m), 3046 (w), 2961 (m), 2592 (s), 1961 (w), 1885 (w), 1846 (m), 1800 (w), 1777 (w), 1476 (m), 1453 (w), 1431 (s), 1392 (m), 1262 (s), 1154 (m), 1100 (m), 1069 (s), 992 (m), 900 (w), 885 (m), 869 (s), 800 (s), 731 (s), 700 (vs), 508 (w, br), 454 (s), 435 (m). NMR data are given in Table I. The mass spectrum exhibits a B_5Sn envelope with a cutoff at m/z 301 corresponding to $[^{11}B_5{}^{124}Sn^{37}Cl^{12}C_6{}^1H_{13}]^+$ attributed to the loss of C_6H_5 from the molecular ion. The observed m/z (intensity) data for the $[M - Ph]^+$ ion cluster were 286 (3.95), 287 (4.90), 288 (8.22), 289 (20.25), 290 (43.74), 291 (66.54), 292 (83.37), 293 (100), 294 (97.06), 295 (81.60), 296 (39.82), 297 (32.78), 298 (16.78), 299 (15.85), 300 (6.23), and 301 (0.88). The calculated m/z (intensity values were 286 (2.03), 287 (2.89), 288 (5.74), 289 (17.71), 290 (40.61), 291 (64.97), 292 (83.37), 293 (100), 294 (96.67), 295 (79.45), 296 (36.30), 297 (29.06), 298 (14.48), 299 (12.21), 300 (3.89), and 301 (2.70). The $[M - Ph]^+$ ion profile is given in Figure 1, along with the calculated values.

Preparation of 2,3-μ-$(SnMe_3)B_5H_8$ (5). The procedure described in ref 9b was slightly modified. In a typical reaction, 0.25 mL of B_5H_9 in 10 mL of THF was reacted with excess KH at −78 °C. After H_2 evolution had ceased and the solution had been filtered, 2.5 mmol (0.5 g) of $SnClMe_3$ was added to the clear $K[B_5H_8]$ solution at −78 °C. A white gelatinous suspension formed, and the reaction mixture warmed slowly to 0 °C and stirred for 3 h. The volatiles were then removed at −35 °C in vacuo, and the residue was extracted with pentane. Following purification,[9b] a colorless liquid (5) was obtained in 60% yield. Characterization confirmed that the species was the same as that prepared by Gaines et al.[9b] NMR data are given in Table I.

Attempts To Isomerize 2,3-μ-$(SnMe_3)B_5H_8$ to the 2- and/or the 1-Isomers. (a) If the reaction of $K[B_5H_8]$ with $SnClMe_3$ was carried out at room temperature over a period of 21 h, the product obtained after workup of the reaction mixture was only 2,3-μ-$(SnMe_3)B_5H_8$. There was no indication of the presence of either 1-$(SnMe_3)B_5H_8$ or 2-$(SnMe_3)B_5H_8$.

(b) To a solution of 0.05 g of 2,3-μ-$(SnMe_3)B_5H_8$ in 0.5 mL $CDCl_3$ at ambient temperature in an NMR tube was added 0.3 mL of 2,6-lutidine. The color of the solution changed to pale yellow, and the solution became turbid. The contents of the NMR tube were monitored at regular intervals by ^{11}B NMR spectroscopy. After about 2 h the mixture contained only degradation products, similar to those resulting from the addition of 2,6-lutidine to 2.

(c) Using the procedure described above, when 2,3-μ-$(SnMe_3)B_5H_8$ in $CDCl_3$ was treated with hexamethylenetetramine in an NMR tube at ambient temperature, a turbid solution was obtained after agitating for 2 h. The ^{11}B NMR spectrum showed the presence of unreacted 2, and some unidentified peaks, presumably resulting from degradation.

X-ray Structure Determinations. Colorless crystals of appropriate dimensions suitable for X-ray diffraction analysis were grown from slow evaporation of CH_2Cl_2 solutions, by slowly warming solutions from −78 °C to room temperature on the vacuum line. Each was mounted on a glass fiber in a random orientation. Preliminary examination was carried out with Mo Kα radiation using a Siemens R3m/V automated diffractometer equipped with a graphite monochromator. Final cell parameters and orientation matrices were obtained by least squares refinement of 40 automatically centered reflections, (30° < 2θ < 40°) in each case. Axial photographs of the three axes were taken to confirm the cell lengths and lattice symmetry. An ω-scan of representative reflections indicated acceptable crystal quality.

Data were collected using the θ–2θ scan technique and the intensities of four standard reflections were measured every 50 reflections. No absorption correction was applied to the data in either of the two cases.

Table II. Summary of Crystallographic Data for 2 and 4

	2	4
empirical formula	$C_{18}H_{22}B_5Sn$	$C_{12}H_{18}B_5ClSn$
fw	412.1	370.5
cryst color and habit	colorless rectangular	colorless rectangular
cryst size, mm	0.5 × 0.5 × 0.2	0.5 × 0.4 × 0.2
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$	$Pmc2_1$
unit cell dimens		
a, Å	14.132 (3)	16.358 (2)
b, Å	9.733 (2)	6.427 (2)
c, Å	14.539 (2)	16.014 (2)
β, deg	96.90 (2)	
V, Å^3	1985.3 (5)	1683.6 (6)
Z, molecules/cell	4	4
D_{calcd}, mg m^{-3}	1.379	1.462
wavelength, Å	0.710 73	0.710 73
scan type	$2\theta-\theta$	$2\theta-\theta$
scan sp in ω (min–max), deg min^{-1}	3.97–19.53	3.97–19.53
2θ range, deg	3–60	3–60
T, K	298	298
abs coeff, mm^{-1}	1.282	1.656
abs structure	n/a	η = 1.2 (2)
no. of rflns collected	6363	5511
no. of ind reflns	5823 (R_{int} = 1.59%)	2639 (R_{int} = 4.95%)
no. of obsvd reflns	3696 ($F > 4.0\sigma(F)$)	1724 ($F > 4.0\sigma(F)$)
weighting scheme (w^{-1})	$\sigma^2(F) + 0.0009F^2$	$\sigma^2(F) + 0.0003F^2$
final R (obsd data), %	3.24	3.89
final R_w (obsd data), %	3.92	3.89
goodness of fit	0.94	1.05

Data reduction, structure solution, and refinement were carried out using the SHELXTL PLUS (VMS)[17] structure solution and refinement package. The structure of 2 was solved and refined in the monoclinic space group $P2_1/n$. In the case of 4, out of the two possible orthorombic space groups $Pmc2_1$ (No. 26) and $Pma2$ (No. 28) from the systematic absences, the former was selected on the basis of successful refinement and molecular geometry considerations. The structures were solved by the Patterson method and the remaining non-hydrogen atoms were located from subsequent difference Fourier maps. Full matrix least squares refinement was carried out by minimizing the function $w(F_o - F_c)^2$.

In the case of 2, the hydrogen atoms were located from the difference Fourier maps and were refined isotropically. The non-hydrogen atoms were refined anisotropically to convergence [R = 3.2% and R_w = 3.9% for 3696 observed reflections, $F > 4\sigma(F)$]. The final difference Fourier map had a maximum electron density of 0.7 e Å^{-3}.

In the case of 4, hydrogen atoms for the boron cage were located from difference Fourier maps and phenyl group hydrogens were calculated in their idealized positions. The atomic positions in the boron cage were idealized using the DFIX program,[17] and then rigid body refinement was carried out on the B_5H_8 motif. The structure was refined to convergence by the full matrix least squares method [R = 3.9% R_w = 3.9% for 1724 observed reflections, $F > 4\sigma(F)$]. The largest difference peak was at 0.8 Å from the Sn atom and had a maximum electron density of 1.42 e Å^{-3}.

Summaries of crystal data, intensity collection parameters, and final structure refinement parameters are presented in Table II. Refined positional parameters for the non-hydrogen atoms are listed in Tables III and IV, Figures 5–7 show the projection view and atom labeling schemes, and Tables V and VI list selected bond distances and angles for 2 and 4, respectively.

Results

The preparative reactions for the species 1–4 are summarized in Scheme I. If a solution of $K[B_5H_8]$ and $SnClPh_3$ in THF is stirred at 0 °C for 3–4 h, the ^{11}B and ^1H NMR spectra suggest the presence of a mixture of isomers and this is confirmed by the $^{119}Sn\{^1H\}$ NMR spectrum which is shown in Figure 2a. The spectrum clearly exhibits two 1:1:1:1 quartets and a broad single resonance. We will later show that the quartets arise from the 1-$(SnPh_3)B_5H_8$ and 2-$(SnPh_3)B_5H_8$ isomers, with the Sn atoms coupling to a ^{11}B atom ($I = {}^3/_2$), and the single broad resonance is due to a bridging Sn atom coupling to two ^{11}B atoms. The ^1H and ^{11}B NMR spectra are quite overlapped.

1-$(SnPh_3)B_5H_8$ (1). If the reaction mixture described above is stirred at 25 °C for 12 h in THF, a yellowish white solid is obtained which melts at 94–96 °C. The air-sen-

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[17] Sheldrick, G. M. Siemens Analytical X-ray Division, Madison, WI, 1990.

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for 2,3-μ-($SnPh_3$)B_5H_8 (2)

	x	*y*	*z*	*U*(eq)[a]
Sn	2039 (1)	1279 (1)	4834 (1)	46 (1)
C(1)	1762 (2)	1251 (3)	6248 (2)	47 (1)
C(2)	1410 (3)	74 (4)	6605 (3)	58 (1)
C(3)	1234 (3)	14 (5)	7527 (3)	70 (2)
C(4)	1411 (3)	1130 (5)	8092 (3)	69 (1)
C(5)	1758 (4)	2294 (5)	7747 (3)	76 (2)
C(6)	1930 (3)	2369 (4)	6828 (3)	64 (1)
C(7)	1980 (2)	−783 (3)	4325 (2)	46 (1)
C(8)	1135 (3)	−1246 (4)	3848 (3)	57 (1)
C(9)	1026 (3)	−2595 (5)	3574 (3)	66 (1)
C(10)	1758 (3)	−3507 (4)	3744 (3)	69 (2)
C(11)	2611 (3)	−3065 (4)	4212 (3)	73 (2)
C(12)	2720 (3)	−1722 (4)	4505 (3)	60 (1)
C(13)	979 (2)	2435 (3)	3989 (2)	49 (1)
C(14)	255 (3)	3067 (4)	4373 (3)	64 (1)
C(15)	−444 (3)	3808 (5)	3828 (4)	84 (2)
C(16)	−411 (4)	3917 (5)	2897 (4)	86 (2)
C(17)	309 (4)	3316 (5)	2503 (3)	82 (2)
C(18)	1002 (3)	2564 (4)	3037 (3)	67 (1)
B(1)	4430 (3)	3008 (5)	4922 (4)	68 (2)
B(2)	3244 (4)	3176 (5)	4830 (3)	60 (1)
B(3)	3786 (3)	1560 (4)	5012 (3)	56 (1)
B(4)	4480 (4)	1882 (5)	4077 (4)	72 (2)
B(5)	3924 (3)	3515 (5)	3885 (3)	61 (1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

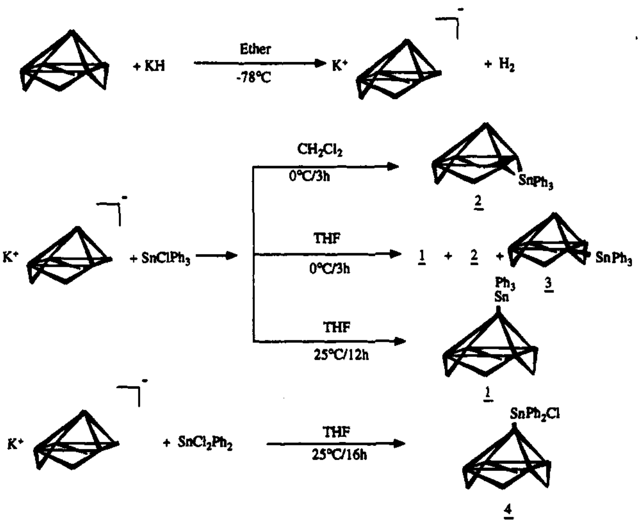
Table IV. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for 1-Sn($ClPh_2$)B_5H_8 (4)

	x	*y*	*z*	*U*(eq)[a]
Sn(1)	0	1773 (1)	0	46 (1)
Sn(2)	5000	−2851 (1)	−2522 (1)	46 (1)
Cl(1)	0	5487 (6)	40 (4)	81 (1)
Cl(2)	5000	843 (5)	−2469 (5)	84 (1)
C(1)	1082 (4)	1217 (13)	−713 (4)	47 (2)
C(2)	1427 (5)	2816 (15)	−1192 (5)	64 (3)
C(3)	2134 (7)	2448 (20)	−1644 (6)	92 (5)
C(4)	2502 (6)	577 (25)	−1626 (6)	93 (5)
C(5)	2174 (6)	−980 (19)	−1168 (7)	83 (4)
C(6)	1477 (5)	−663 (15)	−700 (5)	64 (3)
C(7)	6087 (4)	−3378 (12)	−3248 (4)	46 (2)
C(8)	6413 (6)	−1811 (15)	−3740 (5)	66 (3)
C(9)	7132 (7)	−2228 (17)	−4219 (6)	86 (4)
C(10)	7491 (6)	−4166 (17)	−4187 (5)	74 (4)
C(11)	7154 (5)	−5655 (18)	−3712 (5)	71 (4)
C(12)	6459 (4)	−5266 (15)	−3231 (5)	57 (3)
B(11)	0	788 (17)	1304 (4)	58 (5)
B(12)	−552	−937	1845	94 (5)
B(13)	−552	1770	2089	84 (5)
B(21)	5000	−3877 (16)	−1219 (4)	52 (4)
B(22)	4453	−5630	−690	93 (6)
B(23)	4460	−2941	−417	79 (4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

sitive species is soluble in CH_2Cl_2, $CHCl_3$, Me_2O, THF, and benzene and insoluble in pentane and hexane. NMR spectra suggest the presence of only one species, 1-($SnPh_3$)B_5H_8 (1). The ^{11}B NMR spectrum is shown in Figure 3a,b and clearly indicates that the $SnPh_3$ moiety is bonded to the apical 1-position, since the resonance which falls in the position expected for the apical B atom is a singlet, whereas the basal B atoms are seen as a doublet, due to coupling to the terminal H atom, with $J(^{11}B-^{1}H)$ = 164 Hz. As expected, the doublet collapses to a singlet on ^1H decoupling, as seen in Figure 3b. Also visible in Figure 3a,b are the ^{119}Sn satellites on the B(1) resonances with $J(^{11}B-^{119}Sn)$ = 1123 Hz. ^{119}Sn is the NMR-active isotope of tin ($I = {}^1/_2$), and it has a natural abundance of 8.58%. The ^{119}Sn NMR spectrum confirms that the species contains a Sn-containing moiety σ-bonded to a boron atom. The spectrum is given in Figure 2b, and it clearly shows a 1:1:1:1 quartet with $J(^{11}B-^{119}Sn)$ = 1117 Hz and a weaker 1:1:1:1:1:1:1 septet due to coupling of the ^{119}Sn atom to the ^{10}B nucleus (I = 3) with $J(^{10}B-^{119}Sn)$ = 391 Hz. The proton NMR spectrum is also consistent with the formulation as the 1-isomer. It exhibits a single broad resonance at δ = −2.30 ppm assigned to the four bridging hydrogens and a single 1:1:1:1 quartet, $J(^{11}B-^{1}H)$ = 160 Hz, at δ = 2.61 ppm, assigned to the four basal terminal H atoms. There is no resonance where an apical H atom would appear and the resonances arising from the phenyl hydrogen atoms are seen at δ = 7.24–7.48 ppm. Interestingly, the meta hydrogens couple to the ^{119}Sn atom, as

Scheme I



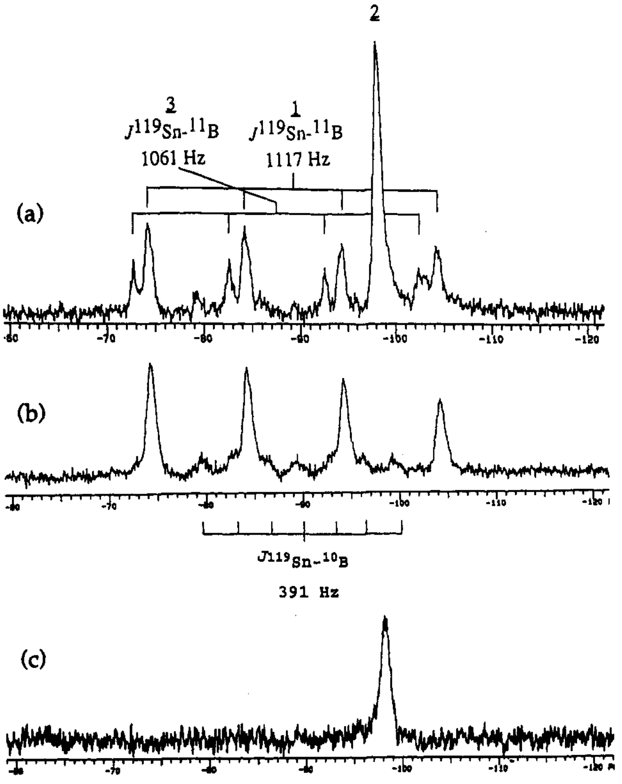


Figure 2. 111.7-MHz ^{119}Sn NMR spectra: (a) $^{119}Sn\{^1H\}$ spectrum of a mixture of 1-($SnPh_3$)B_5H_8 (1), 2,3-μ-($SnPh_3$)B_5H_8 (2), and 2-($SnPh_3$)B_5H_8 (3); (b) $^{119}Sn\{^1H\}$ spectrum of 1; (c) $^{119}Sn\{^1H\}$ spectrum of 2.

Table V. Selected Bond Lengths and Bond Angles for 2,3-μ-($SnPh_3$)B_5H_8 (2)

Bond Distances (Å)			
Sn–C(1)	2.138 (3)	Sn–C(7)	2.137 (3)
Sn–C(13)	2.140 (3)	Sn–B(2)	2.512 (5)
Sn–B(3)	2.467 (4)	B(1)–B(2)	1.674 (7)
B(1)–B(3)	1.691 (6)	B(1)–B(4)	1.654 (8)
B(1)–B(5)	1.664 (7)	B(1)–H(1A)	1.027 (47)
B(2)–B(3)	1.757 (6)	B(2)–B(5)	1.799 (7)
B(2)–H(2A)	1.080 (35)	B(2)–H(8A)	1.321 (43)
B(3)–B(4)	1.796 (8)	B(3)–H(3A)	0.910 (43)
B(3)–H(6A)	1.401 (63)	B(4)–B(5)	1.780 (7)
B(4)–H(4A)	1.014 (57)	B(4)–H(6A)	1.316 (61)
B(4)–H(7A)	1.275 (58)	B(5)–H(5A)	1.041 (42)
B(5)–H(7A)	1.290 (63)	B(5)–H(8A)	1.289 (43)

Bond Angles (deg)			
C(1)–Sn–C(7)	108.5 (1)	C(1)–Sn–C(13)	111.3 (1)
C(7)–Sn–C(13)	107.4 (1)	C(1)–Sn–B(2)	102.4 (1)
C(7)–Sn–B(2)	133.5 (1)	C(13)–Sn–B(2)	92.3 (1)
C(1)–Sn–B(3)	101.4 (1)	C(7)–Sn–B(3)	97.9 (1)
C(13)–Sn–B(3)	128.7 (1)	B(2)–Sn–B(3)	41.3 (1)
Sn–C(1)–C(2)	119.3 (3)	Sn–C(1)–C(6)	122.6 (3)
Sn–C(7)–C(8)	118.4 (2)	Sn–B(7)–C(12)	123.7 (2)
Sn–C(13)–C(14)	120.5 (3)	Sn–C(13)–C(18)	121.3 (3)
B(2)–B(1)–B(3)	62.9 (3)	B(2)–B(1)–B(4)	97.9 (3)
B(3)–B(1)–B(4)	64.9 (3)	B(2)–B(1)–B(5)	65.2 (3)
B(3)–B(1)–B(5)	98.1 (3)	B(4)–B(1)–B(5)	64.9 (3)
B(2)–B(1)–H(1A)	126.6 (31)	B(3)–B(1)–H(1A)	127.1 (29)
B(4)–B(1)–H(1A)	135.3 (31)	B(5)–B(1)–H(1A)	134.4 (28)
Sn–B(2)–B(1)	126.9 (3)	Sn–B(2)–B(3)	67.9 (2)
B(1)–B(2)–B(3)	59.0 (3)	Sn–B(2)–B(5)	124.1 (3)
B(1)–B(2)–B(5)	57.1 (3)	B(3)–B(2)–B(5)	90.9 (3)
Sn–B(2)–H(2A)	91.0 (19)	B(1)–B(2)–H(2A)	128.9 (17)
B(3)–B(2)–H(2A)	135.5 (19)	B(5)–B(2)–H(2A)	132.0 (19)
Sn–B(2)–H(8A)	89.3 (18)	B(1)–B(2)–H(8A)	101.1 (19)
B(3)–B(2)–H(8A)	105.3 (18)	B(5)–B(2)–H(8A)	45.7 (19)
H(2A)–B(2)–H(8A)	113.5 (25)	Sn–B(3)–B(1)	128.7 (3)
Sn–B(3)–B(2)	70.7 (2)	B(1)–B(3)–B(2)	58.1 (3)
SN–B(3)–B(4)	124.8 (3)	B(1)–B(3)–B(4)	56.5 (3)
B(2)–B(3)–B(4)	89.9 (3)	Sn–B(3)–H(3A)	90.4 (27)
B(1)–B(3)–H(3A)	133.2 (25)	B(2)–B(3)–H(3A)	143.9 (29)
B(4)–B(3)–H(3A)	125.6 (28)	Sn–B(3)–H(6A)	84.9 (26)
B(1)–B(3)–H(6A)	99.4 (23)	B(2)–B(3)–H(6A)	99.0 (22)
B(4)–B(3)–H(6A)	46.6 (25)	H(3A)–B(3)–H(6A)	110.0 (35)
B(1)–B(4)–B(3)	58.5 (3)	B(1)–B(4)–B(5)	57.8 (3)
B(3)–B(4)–B(5)	90.2 (3)	B(1)–B(4)–H(4A)	126.8 (28)
B(3)–B(4)–H(4A)	137.0 (28)	B(5)–B(4)–H(4A)	130.5 (28)
B(1)–B(4)–H(6A)	105.0 (27)	B(3)–B(4)–H(6A)	50.7 (28)
B(5)–B(4)–H(6A)	99.5 (24)	H(4A)–B(4)–H(6A)	120.5 (37)
B(1)–B(4)–H(7A)	101.3 (28)	B(3)–B(4)–H(7A)	100.9 (28)
B(5)–B(4)–H(7A)	46.4 (28)	H(4A)–B(4)–H(7A)	116.7 (40)
H(6A)–B(4)–H(7A)	72.7 (37)	B(1)–B(5)–B(2)	57.7 (3)
B(1)–B(5)–B(4)	57.3 (3)	B(2)–B(5)–B(4)	89.0 (3)
B(1)–B(5)–H(5A)	137.7 (21)	B(2)–B(5)–H(5A)	138.3 (23)
B(4)–B(5)–H(5A)	132.6 (23)	B(1)–B(5)–H(7A)	100.1 (26)
B(2)–B(5)–H(7A)	100.2 (28)	B(4)–B(5)–H(7A)	45.7 (25)
H(5A)–B(5)–H(7A)	100.3 (35)	B(1)–B(5)–H(8A)	103.1 (19)
B(2)–B(5)–H(8A)	47.2 (19)	B(4)–B(5)–H(8A)	104.6 (18)
H(5A)–B(5)–H(8A)	110.2 (28)	H(7A)–B(5)–H(8A)	80.5 (32)
B(3)–H(6A)–B(4)	82.7 (33)	B(4)–H(7A)–B(5)	87.9 (36)
B(2)–H(8A)–B(5)	87.2 (25)		

Table VI. Selected Bond Lengths and Bond Angles for 1-Sn($ClPh_2$)B_5H_8 (4)

Bond Distances (Å)			
Sn(1)–C(1)	2.387 (4)	Sn(1)–C(1)	2.136 (7)
Sn(1)–B(11)	2.182 (7)	Sn(1)–C(1A)	2.136 (7)
Sn(2)–Cl(2)	2.376 (4)	Sn(2)–C(7)	2.151 (7)
Sn(2)–B(21)	2.189 (6)	Sn(2)–C(7A)	2.151 (7)
B(11)–B(12)	1.671	B(11)–B(13)	1.671
B(11)–B(12A)	1.671 (1)	B(11)–B(13A)	1.671 (1)
B(12)–B(13)	1.783	B(12)–H(12)	1.020
B(12)–H(15)	1.381	B(12)–H(16)	1.315
B(12)–B(12A)	1.805 (1)	B(13)–H(13)	1.032
B(13)–H(14)	1.288	B(13)–H(16)	1.315
B(13)–B(13A)	1.805 (1)	H(14)–B(13A)	1.288 (1)
H(15)–B(12A)	1.380 (1)	B(21)–B(22)	1.670
B(21)–B(23)	1.671	B(21)–B(22A)	1.670 (1)
B(21)–B(23A)	1.671 (1)	B(22)–B(23)	1.783
B(22)–H(22)	1.016	B(22)–H(25)	1.248
B(22)–H(26)	1.315	B(22)–B(22A)	1.791 (1)
B(23)–H(23)	1.024	B(23)–H(24)	1.158
B(23)–H(26)	1.315	B(23)–B(23A)	1.768 (1)
H(24)–B(23A)	1.153 (1)	H(25)–B(22A)	1.245 (1)

Bond Angles (deg)			
Cl(1)–Sn(1)–C(1)	100.5 (2)	Cl(1)–Sn(1)–B(11)	105.3 (3)
C(1)–Sn(1)–B(11)	117.5 (2)	Cl(1)–Sn(1)–C(1A)	100.5 (2)
C(1)–Sn(1)–C(1A)	112.0 (3)	B(11)–Sn(1)–C(1A)	117.5 (2)
Cl(2)–Sn(2)–C(7)	100.2 (2)	Cl(2)–Sn(2)–B(21)	105.5 (3)
C(7)–Sn(2)–B(21)	117.9 (2)	Cl(2)–Sn(2)–C(7A)	100.2 (2)
C(7)–Sn(2)–C(7A)	111.5 (3)	B(21)–Sn(2)–C(7A)	117.9 (2)
Sn(1)–C(1)–C(2)	120.2 (6)	Sn(1)–C(1)–C(6)	122.0 (6)
Sn(2)–C(7)–C(8)	120.7 (6)	Sn(2)–C(7)–C(12)	120.0 (5)
Sn(1)–B(11)–B(12)	133.5 (2)	Sn(1)–B(11)–B(13)	127.6 (2)
B(12)–B(11)–B(13)	64.5	Sn(1)–B(11)–B(12A)	133.5 (2)
B(12)–B(11)–B(12A)	65.4 (1)	B(13)–B(11)–B(12A)	98.8 (1)
Sn(1)–B(11)–B(13A)	127.6 (2)	B(12)–B(11)–B(13A)	98.8 (1)
B(13)–B(11)–B(13A)	65.4 (1)	B(12A)–B(11)–B(13A)	64.5 (1)
B(11)–B(12)–B(13)	57.8	B(11)–B(12)–H(12)	142.7
B(13)–B(12)–H(12)	134.5	B(11)–B(12)–H(15)	105.3
B(13)–B(12)–H(15)	127.5	H(12)–B(12)–H(15)	90.8
B(11)–B(12)–H(16)	104.8	B(13)–B(12)–H(16)	47.3
H(12)–B(12)–H(16)	98.8	H(15)–B(12)–H(16)	113.6
B(11)–B(12)–B(12A)	57.3 (1)	B(13)–B(12)–B(12A)	90.0 (1)
H(12)–B(12)–B(12A)	135.3 (1)	H(15)–B(12)–B(12A)	49.2 (1)
H(16)–B(12)–B(12A)	113.8 (1)	B(11)–B(13)–B(12)	57.8
B(11)–B(13)–H(13)	142.9	B(12)–B(13)–H(13)	122.9
B(11)–B(13)–H(14)	100.5	B(12)–B(13)–H(14)	102.8
H(13)–B(13)–H(14)	113.9	B(11)–B(13)–H(16)	104.8
B(12)–B(13)–H(16)	47.3	H(13)–B(13)–H(16)	88.7
H(14)–B(13)–H(16)	91.0	B(11)–B(13)–B(13A)	57.3 (1)
B(12)–B(13)–B(13A)	90.0 (1)	H(13)–B(13)–B(13A)	146.6 (1)
H(14)–B(13)–B(13A)	45.5 (1)	H(16)–B(13)–B(13A)	113.8 (1)
B(13)–H(14)–B(13A)	89.0 (1)	B(12)–H(15)–B(12A)	81.6 (1)
B(12)–H(16)–B(13)	85.4	Sn(2)–B(21)–B(22)	133.4 (2)
Sn(2)–B(21)–B(23)	128.6 (2)	B(22)–B(21)–B(23)	64.5
Sn(2)–B(21)–B(22A)	133.4 (2)	B(22)–B(21)–B(22A)	64.8 (1)
B(23)–B(21)–B(22A)	97.9 (1)	Sn(2)–B(21)–B(23A)	128.6 (2)
B(22)–B(21)–B(23A)	97.9 (1)	B(23)–B(21)–B(23A)	63.9 (1)
B(22A)–B(21)–B(23A)	64.5 (1)	B(21)–B(22)–B(23)	57.8
B(21)–B(22)–H(22)	138.2	B(23)–B(22)–H(22)	140.3
B(21)–B(22)–H(25)	98.4	B(23)–B(22)–H(25)	128.3
H(22)–B(22)–H(25)	89.3	B(21)–B(22)–H(26)	104.8
B(23)–B(22)–H(26)	47.3	H(22)–B(22)–H(26)	106.4
H(25)–B(22)–H(26)	120.3	B(21)–B(22)–B(22A)	57.6 (1)
B(23)–B(22)–B(22A)	89.6 (1)	H(22)–B(22)–B(22A)	130.1 (1)
H(25)–B(22)–B(22A)	44.0 (1)	H(26)–B(22)–B(22A)	112.2 (1)
B(21)–B(23)–B(22)	57.7	B(21)–B(23)–H(23)	138.0
B(22)–B(23)–H(23)	117.6	B(21)–B(23)–H(24)	95.4
B(22)–B(23)–H(24)	100.3	H(23)–B(23)–H(24)	124.9
B(21)–B(23)–H(26)	104.7	B(22)–B(23)–H(26)	47.3
H(23)–B(23)–H(26)	87.3	H(24)–B(23)–H(26)	91.4
B(21)–B(23)–B(23A)	58.1 (1)	B(22)–B(23)–B(23A)	90.4 (1)
H(23)–B(23)–B(23A)	151.9 (1)	H(24)–B(23)–B(23A)	40.1 (1)
H(26)–B(23)–B(23A)	112.7 (1)	B(23)–H(24)–B(23A)	99.8 (1)
B(22)–H(25)–B(22A)	91.8 (1)	B(22)–H(26)–B(23)	85.4

indicated in Table I, with $^3J(^{119}Sn-^1H) = 46.5$ Hz. Infrared spectra and mass spectra are consistent with the formulation of 1; however we were unable to grow crystals suitable for X-ray structural analysis. Elemental analysis gave inconclusive results, however, since the species is very air sensitive and also quite thermally and light sensitive; this is not surprising. There was no evidence, from examination of the crude reaction product, that any other isomers of $SnPh_3B_5H_8$ were present, and it is assumed that the formation of 1 in 61% yield represents the exclusive borane product. Table I gives all the NMR data including those from ^{13}C spectra, and Figure 1 compares the 70-eV mass spectrum with that calculated for the ion cluster $[B_5SnC_{12}H_{18}]^+$, that is $[M - Ph]^+$, using a program for the calculation of isotopic distributions from molecular formula, which includes 13 Sn isotopes and 2 B isotopes.[18]

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[18] 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.

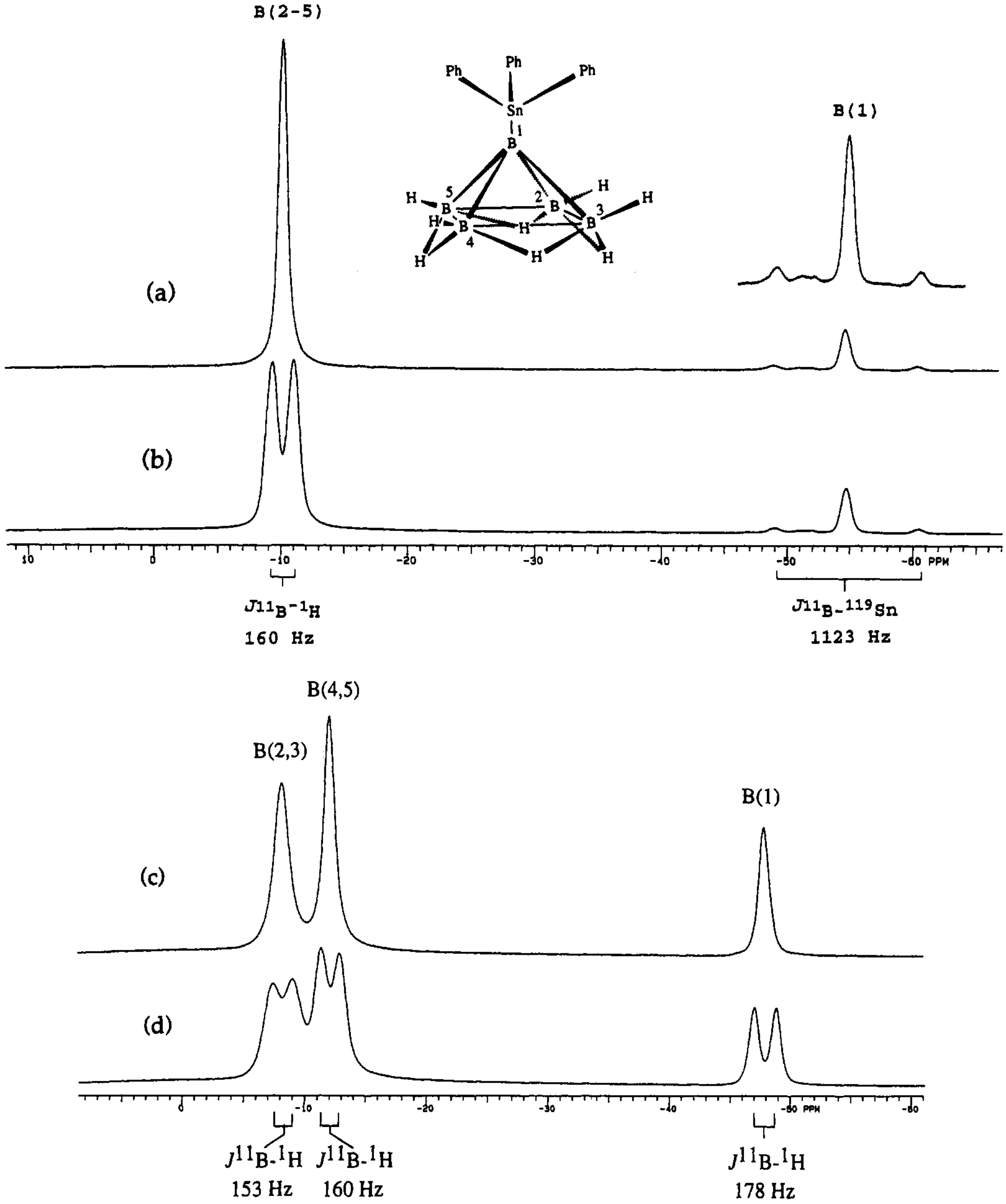

Figure 3. 96.3-MHz ^{11}B NMR spectra for 1-$(SnPh_3)B_5H_8$ (1) and 2,3-μ-$(SnPh_3)B_5H_8$ (2): (a) $^{11}B\{^1H\}$ spectrum of 1; (b) ^{11}B spectrum of 1; (c) $^{11}B\{^1H\}$ spectrum of 2; (d) ^{11}B spectrum of 2.

The agreement is very good. The cutoff at m/z 341 for $[^{11}B_5{}^{124}Sn^{12}C_{12}{}^{1}H_{18}]^+$ is correct, and the differences between the calculated and observed spectra are due to the very small relative intensity of the parent ion cluster. The relative intensity of the molecular ion is very low, about 5% of that for the $[M - Ph]^+$ ion cluster, and the fit between the observed and calculated data was poor, presumably due to errors introduced by baseline noise; thus the $[M - Ph]^+$ ion was selected for analysis. Minor differences between the mass spectra we observe for 1, 2, and 4 and the calculated ones are understandable when one considers that the loss of H is not taken into consideration in the calculations. The use of monoisotopic spectra does not improve the fit since the mass spectral fragmentation pattern of B_5H_9 and that of a B_5H_8 moiety bonded to a $SnPh_3$ moiety are unlikely to be identical.

2,3-μ-$(SnPh_3)B_5H_8$ (2) is formed if the above reaction is allowed to proceed in CH_2Cl_2 at 0 °C for 3 h. A white solid is obtained which melts at 139–141 °C with decomposition. Its solubility properties are similar to those for 1, but the colorless crystals appear to be air stable for extended periods when pure. Elemental analysis and mass spectra are consistent with the formula, and NMR spectra strongly indicate that the species is 2,3-μ-$(SnPh_3)B_5H_8$. The ^{11}B NMR spectrum, shown in Figure 3c,d, exhibits two doublets of equal area in the basal region and an upfield doublet, all of which collapse to singlets on proton-decoupling. This spectrum is strongly suggestive of the μ-isomer which should distinguish two groups of two equivalent basal boron atoms. On the other hand, the 2-isomer would show three resonances in an area ratio 1:2:1 for the basal borons. The pair of resonances at lower field is assigned to B(2,3) which are bonded to the Sn atom, by analogy with related systems. The ^{119}Sn NMR spectrum exhibits a broad single resonance at δ = −93.3 ppm with fwhm = 108 Hz, as indicated in Figure 2c. This single resonance suggests that the Sn atom is not bonded to a single B atom but that it is bridging two B atoms as it would in 2,3-μ-$(SnPh_3)B_5H_8$. The ^1H NMR spectrum shown in Figure 4a also supports this formulation. There are two broad resonances in the bridging region in the area ratio 2:1, as expected if the $SnPh_3$ moiety occupies one of

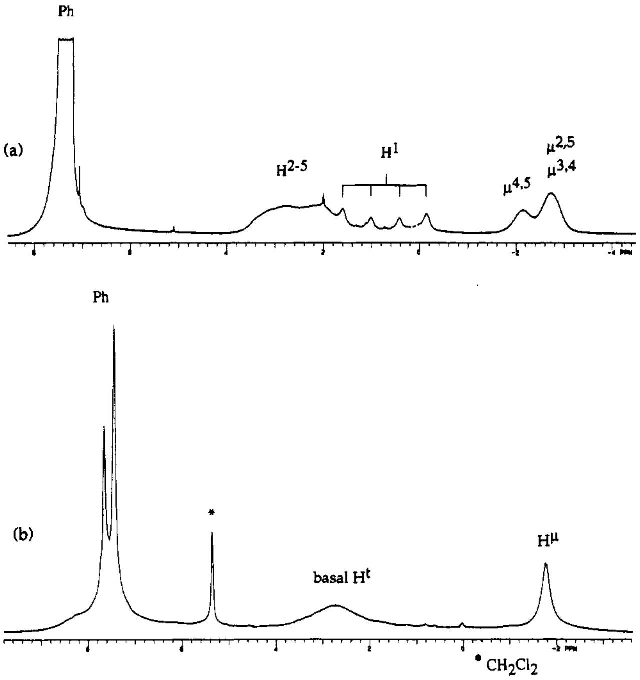

Figure 4. 300-MHz ^1H NMR spectra for 1-$(SnClPh_2)B_5H_8$ (**4**) and 2,3-μ-$(SnPh_3)B_5H_8$ (**2**): (a) ^1H spectrum of **2** at 25 °C; (b) ^1H spectrum of **4** at -90 °C.

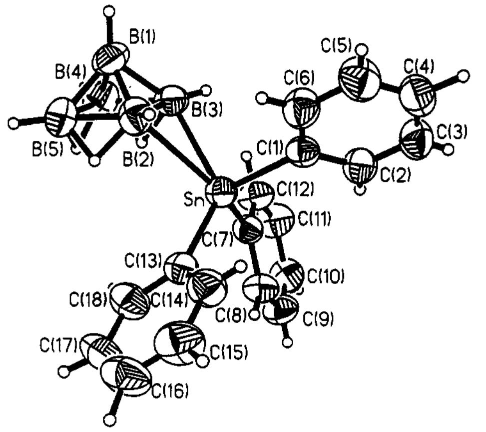

Figure 5. Projection view of 2,3-μ-$(SnPh_3)B_5H_8$ (**2**). The thermal ellipsoids are drawn at the 50% probability level.

the four bridging sites in the B_5H_9 molecule. Also visible in the proton spectrum is a quartet at $\delta = 0.67$ ppm, which sharpens at higher temperatures, suggestive of a proton bonded to the apical boron atom, B(1). Downfield are overlapping quartets which are assigned to the basal terminal H atoms. They broaden significantly at lower temperatures due to thermal decoupling whereas the apical resonance is affected much less. The more symmetrical environment of the apical proton renders it less susceptible to quadrupolar thermal decoupling. The phenyl H atoms are observed in the expected region and the ^{13}C NMR spectra are well-resolved and are quite normal.

The crystal structure determination confirmed that **2** is 2,3-μ-$(SnPh_3)B_5H_8$. A projection view of the structure is displayed in Figure 5. It clearly indicates that the Sn atom occupies a bridging position and has replaced one of the bridging H atoms in B_5H_9. The $SnPh_3$ moiety is well below the basal plane of the square pyramid. Figure 6 shows the atom-numbering scheme for **2**. The isolation of **1** and **2** allowed us to assign NMR spectra of mixtures containing the third isomer, 2-$(SnPh_3)B_5H_8$ (**3**). Thus we have good data for all three isomers of a new substituted pentaborane(9).

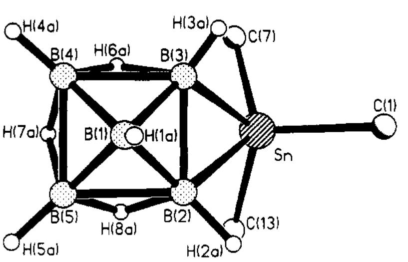

Figure 6. Figure indicating the atomic numbering scheme for 2,3-μ-$(SnPh_3)B_5H_8$ (**2**).

1-$(ClSnPh_2)B_5H_8$ (4) is obtained if the procedure described for the preparation of **1** is employed in the reaction of $K[B_5H_8]$ with $SnCl_2Ph_2$. The species is light orange in color, and it melts at 87–90 °C. It appears to be air sensitive, and its solubility properties are similar to those for **1** and **2**. The species is also thermally and light sensitive, similar to **1**, and thus elemental analysis was unsatisfactory, but mass spectral data provided an excellent fit with the calculated data, as indicated in Figure 1. The molecular ion is not observed but the expected loss of C_6H_5, by α-cleavage adjacent to the halogen atom, stabilizes the $[M - C_6H_5]^+$ ion and the data in Figure 1 are for the $[Sn(ClPh)B_5H_8]^+$ ion. Boron-11 and proton NMR spectra are similar to those for **1**, and they are listed in Table I along with ^{119}Sn and ^{13}C spectra. The $^{119}Sn\{^1H\}$ NMR spectra again exhibit the quartet and septet due to $^{119}Sn-^{11}B$ and $^{119}Sn-^{10}B$ coupling, respectively, and the ^{119}Sn satellites are clearly visible in the ^{11}B spectra. The proposed formulation of **4** was confirmed by the crystal structure. The unit cell contains two crystallographically unique molecules, each with a mirror plane containing Sn, Cl, B(1), and two of the bridging H atoms. The plane bisects the B_5 cage and lies on the midpoint of two opposite B–B bonds in the basal plane. The structures of the two molecules in the unit cell are given in Figure 7.

Since we obtained both **1** and **4** as exclusive products of the prolonged reaction of the Sn chloride with $K[B_5H_8]$ in THF, we repeated the work of Gaines involving the reaction between the $[B_5H_8]^-$ anion and $SnClMe_3$ in ether. We find that the exclusive product of the reaction is 2,3-μ-$(SnMe_3)B_5H_8$ (**5**) and continuous stirring of the reaction mixture at 0 or 25 °C does not result in the formation of either the 2- or 1-isomers of **5**. Furthermore, just as Gaines had observed, attempts to isomerize **5** by treatment with 2,6-lutidine or hexamethylenetetramine resulted only in cage degradation, as did attempts to prepare the 2-isomer by conducting the reaction in $CDCl_3$.

Discussion

We believe that I is the first example of a pyramidal borane with a tin atom bonded to the apical boron atom. We presume that the reaction proceeds via the initial formation of the bridge-substituted species 2,3-μ-$(SnPh_3)B_5H_8$. Such reactions are well documented and several examples exist in which the smaller group 14 element-containing moieties replace a bridging hydrogen atom in B_5H_9.[2a,5a,6,9,12] In these latter systems, the bridge-substituted isomer rearranges, in the presence of base, to form the 2-substituted species which is thermodynamically much more stable.[5a,11] Gaines, in a series of elegant experiments, has demonstrated that, in the presence of base, an equilibrium between the 2- and 1-substituted species exists and that, for several of the systems studied heretofore, the 2-substituted isomer appears to be the thermodynamically stable product and the rearrangement takes place without scission of the B–substit-

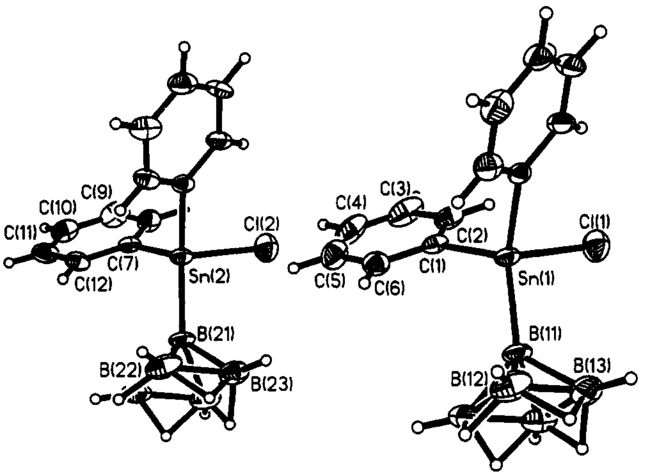

Figure 7. Projection view of the two unqiue molecules in the unit cell of 1-$(SnClPh_2)B_5H_8$ (4), showinng the atomic numbering scheme. The thermal elipsoids are drawn at the 50% probability level.

uent bond.[11b,c] These workers also found that 2,3-μ-$(SiMe_3)B_5H_8$ rearranges irreversibly to 2-$(SiMe_3)B_5H_8$ and that the latter is converted to the 1-isomer in the presence of very strong bases such as hexamethylenetetramine or at elevated temperatures but that the final equilibrium mixture contains a 4:1 mixture of the 1- and 2-isomers respectively.[12] A recent theoretical study by McKee and Lipscomb[19] suggests different mechanisms for the rearrangement at room temperature under base catalysis conditions and the high-temperature process, but our results shed no light on these suggestions. In the case of 2,3-μ-$(SnMe_3)B_5H_8$, the species is reported not to isomerize to the 2-isomer but some degradation does occur.[9b] However we understand that the species was not studied to any great extent.[20] We repeated the experiments with 2,3-μ-$(SnMe_3)B_5H_8$ and confirmed that it indeed does not rearrange when treated with ethers, 2,6-lutidine, or hexamethyltetramine but that degradation occurs.

In the case of the $SnPh_3$-substituted species, the $SnPh_3$ moiety is apparently sufficiently sterically hindered to render the 2-isomer much less stable than the 1-isomer. Thus initial formation of the bridging isomer is followed by isomerization to the 2-isomer, and after 12 h, the product is exclusively 1-$(SnPh_3)B_5H_8$, the thermodynamically more stable isomer. If the ^{119}Sn NMR spectrum is run at ambient temperature, after stirring the $SnClPh_3$/$K[B_5H_8]$ mixture at 0 °C for 5 h, the spectrum contains two quartets and a broad resonance. The spectrum suggests that all three isomers, 2,3-μ-$(SnPh_3)B_5H_8$, 2-$(SnPh_3)B_5H_8$, and 1-$(SnPh_3)B_5H_8$, are present. Quartets would arise from Sn bonded terminally to ^{11}B ($I = {}^3/_2$), and although one might ideally expect a septet from a Sn atom bridging two borons, experience indicates that resolution of the septet is typically missing for boranes and that broad resonances are observed.[21] This observation of a mixture of two terminally bonded and one bridge-bonded Sn derivative supports our conclusion that the process proceeds as 2,3-μ-$(SnPh_3)B_5H_8 \rightarrow$ 2-$(SnPh_3)B_5H_8 \rightarrow$ 1-$(SnPh_3)B_5H_8$. The amount of 2-$(SnPh_3)B_5H_8$ present is quite small, and our conclusion is that this species is the least thermodynamically stable species and that it only forms when there is a kinetic pathway provided by the Lewis base. Electronic effects on the relative stabilities of the three isomers of $SiH_3B_5H_8$ have been studied by theoretical calculations and also photoelectronic spectroscopy.[22] The conclusions were that the 2-isomer is favored for highly electronegative substituents, while the 1-isomer is favored by substituents with low electronegativities that are π-acceptors or π-donors. Tin certainly fits this category although the d-orbitals may be too diffuse to participate in such bonding. We feel that, in this case, steric effects probably contribute substantially such that the equilibrium mixture contains only 1-isomer.

We also report the first observation of ^{119}Sn–^{11}B coupling in a pyramidal borane both for 1 and 4. There are several reports in the literature of ^{119}Sn NMR spectra of tin bonded to boron.[23,24] The magnitudes of the $J(^{119}Sn$–$^{11}B)$ values range from 554 to 1007 Hz,[24] so our values of 1117 Hz for 1 and 1272 Hz for 4, although the highest values reported, so far, are clearly within the normal range. This is confirmed by our observation of ^{119}Sn satellites in the ^{11}B NMR spectra which give values of 1123 and 1270 Hz for 1 and 4, respectively. It is well estblished that resonances involving nuclei with quadrupole moments are substantially broadened due to quadrupolar relaxation.[25] For pyramidal boranes, the more highly symmetrical apical borons provide the least favorable environment for such relaxation and the relaxation times are the longest.[26] Thus it is not unexpected that we were able to observe ^{119}Sn–^{11}B coupling only for the apical resonance.

Our failure to obtain crystals suitable for structure determination of 1 was mitigated by the isolation of 4, 1-$(ClSnPh_2)B_5H_8$. NMR spectra were very similar to those for 1, and the crystal structure, shown in Figure 7, unambiguously identifies it as the 1-isomer. The unit cell contains two independent molecules, both of which contain a plane of symmetry which passes through the apical B(1)–Sn–Cl plane and bisects two basal B–B bonds. The geometry of the cage is essentially that of B_5H_9,[27] with apex to base distances slightly shorter than in B_5H_9, but the B–B distances in the basal plane essentially the same. The B–Sn distances in the two molecules, 2.182 and 2.189 Å, respectively, are shorter than the sum of the covalent radii of Sn (1.40 Å) and B (0.88 Å).[28] These distances are also shorter than those in the only comparable system, bis(1,2-dimethyl-*o*-carboran-9-yl)dimethyltin (2.221 and 2.224 Å).[29] In the latter system, the tin atom bridges two different carboranyl polyhedra and the carborane moieties probably withdraw electron density from the boron atoms to a greater extent than do the pentaboranyl moieties.

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1 and 4 represent examples of a very small class of molecules, the 1-substituted group 14 derivatives of nido-pyramidal boranes, and 4 is the only structurally characterized one. The 1-(SiH_3)-, 1-($SiMe_3$)-,[12] and 1-($SiClR_2$)B_5H_8[30] species have been isolated, as have 1-($SiMe_3$)B_6H_9 and 1-($GeMe_3$)B_6H_9,[31] the last two by an unusual boron insertion reaction of the corresponding pentaboranyl anions. The species 1 and 4 are the first examples of tin atoms σ-bonded to boron in a polyhedral cage. We expect that the isolation of 1 and 4 and the observation of ^{119}Sn NMR spectra and coupling auger well for future chemistry of nido-pyramidal boranes, especially tin derivatives.

The isolation of 2,3-μ-($SnPh_3$)B_5H_8 (2) as the exclusive product of the reaction between $SnClPh_3$ and K[B_5H_8] in CH_2Cl_2 is not surprising. The presence of a Lewis base, in this case the THF solvent, is necessary for the isomerization of 2,3-μ-$MR_3B_5H_8$ (M = group 14 element) species.[9b] The base presumably coordinates to the most electrophilic position, a basal B atom, and the cage opens to form a transient arachno cluster. The cluster then loses the base such that either the substituent or a proton occupies the bridging site. Since bases catalyze μ to 2 rearrangements in B_5H_9, the 2-isomer must be the more thermodynamically stable. The use of a noncoordinating solvent such as CH_2Cl_2 removes the kinetically accessible pathway for the rearrangement, and thus 2,3-μ-($SnPh_3$)B_5H_8 (2) is the exclusive product formed in 53% yield. The formula of the species is established by elemental analysis and mass spectra. NMR spectra, especially the ^{119}Sn{^{1}H} spectrum which exhibits a broad single resonance at δ = −98.3 ppm, quite distinct from the quartet resonances we assign to terminally bonded tin atoms, indicate that this is the bridging isomer, and this conclusion is confirmed by the X-ray structure determination.

As seen in Figures 5 and 6, the $SnPh_3$ moiety occupies a bridging site such that it replaces a proton between B(2) and B(3) and may be considered as a pseudo-hydrogen, thus bonding to the cage by a three-center, two-electron bond. The structure is similar to that previously determined for 1-Br-2,3-μ-($SiMe_3$)B_5H_8,[32] and the much larger central bridging atom (covalent radii: Sn, 1.40 Å; Si, 1.17 Å) has little effect on the dimensions of the boron cage. The B(2)–B(3) distance, 1.757 (6) Å, is shortened from the basal B–B bond distance in B_5H_9, 1.830 (5) Å, and it is shorter than the hydrogen-bridged B–B distances in 2. This is also observed for silicon-,[32] beryllium-,[7b] and boron-bridged[33] pentaborane derivatives for which X-ray structures have been determined. The B_{apex}–B_{base} distances are shorter on the side containing the Sn bridge, that is B(1)–B(2 or 3), than they are on the other side of the pyramid, B(1)–B(4 or 5), and the H atom bonded to B(1) is tilted slightly toward the edge containing the Sn atom, as has been noted for 2,3-μ-(9-BBN)B_5H_8[33] and 2,3-μ-(BeCp)B_5H_8.[7b] The B–Sn distances, 2.512 (5) and 2.467 (4) Å, are quite long and are comparable to those which involve Sn bonds to B atoms wherein both atoms are part of a polyhedral cluster. In the latter, the known Sn–B distances range from 2.377[34] to 2.751 Å[35]. The length of the Sn–B bonds in 2 reflect that they are two-center, three-electron interactions. There is only one known B–Sn bond length in a system wherein both atoms are not vertices in a polyhedral cluster, bis(1,2-dimethyl-*o*-carboran-9-yl)dimethyltin,[29] and the bond distances are 2.221 and 2.224 Å, respectively, much shorter than those in 2 and also those for intrapolyhedral B–Sn bonds.[34-36] The only real analogue of 2, 1-Br-2,3-μ-($SiMe_3$)B_5H_8 contains a plane of symmetry through B(1), the $SiMe_3$ moiety, and the bisector of B(2)–B(3) and B(4)–B(5). This is not the case for 2 since, for steric reasons, the phenyl groups cannot be oriented so as to render two of them equivalent and the third one either exactly on or perpendicular to the plane.

The position of the Sn atom, well below the basal plane of the B_5H_8 moiety, clearly suggests that it is not a vertex of a six-membered polyhedron but that it simply replaces the bridging H atom. Several other analogous systems have been characterized structurally. They include the B, Be, and Si species mentioned previously and also the coinage-metal derivatives 2,3-μ-[(PPh_3)$_2$Cu]B_5H_8[37] and 2,3-μ-(PPh_3Au)B_5H_8.[38] The dihedral angle between the B(2–5) basal plane of the cage and the B(2)–B(3)–Sn plane for 2 is 53.0°, comparable to the corresponding angles in the B, Be, Si, Cu, and Au systems which are 52, 56.18, 51.7, 52, and 54.2°, respectively. These systems are all very similar to 2, although the Cu atom formally possess 16 electrons and the Au atoms possesses only 14. The external dihedral angles between the B(1)–B(2)–B(3) face and the B(2)–B(3)–M face are all close to 180°. On the other hand, the analogous angles for 2,3-μ-(PPh_2)B_5H_8 which has been structurally characterized[10e] are 22.5 and 148°, respectively, as expected since the P atom is a three-electron donor and thus forms two two-center, two-electron bonds with B(2) and B(3).

Conclusions

We have discovered that a bulky group 14 substituent, either $SnPh_3$ or $SnPh_2Cl$, may be inserted into a bridging position in pentaborane(9) and that the selection of solvent determines which isomer is formed. In THF, the reaction proceeds via formation of the 2,3-μ- and the 2-isomers, to form the 1-isomer, 1-($SnPh_3$)B_5H_8, exclusively if enough time is allowed, suggesting that the 1-isomer is by far the most stable. Previously, it was thought that such isomerizations did not occur for Sn derivatives. The use of noncoordinating solvents allows the formation of only the 2,3-μ-isomer. Thus we have observed all three possible isomers of ($SnPh_3$)B_5H_8. The species were characterized by NMR spectroscopy and X-ray crystallography. We have determined the first crystal structure, with the exception of halogeno species, of a main-group element bonded to the apical boron in a pyramidal borane and also the structure of the kinetically stable 2,3-μ-isomer. ^{119}Sn NMR spectra of the various products allowed, for the first time, the observation of ^{11}B– and ^{10}B–^{119}Sn coupling in compounds involving tin σ-bonded to boron in a polyhedral borane and of ^{119}Sn "satellites" in ^{11}B NMR spectra. These latter measurements provide a potential new handle for

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the characterization of tin atoms in cluster molecules.

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Supplementary Material Available: Tables of anisotropic thermal parameters, coordinates of the hydrogen atoms, and complete bond lengths and angles for 2 and 4 (7 pages). Ordering information is given on any current masthead page.

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Reactivity of Tervalent Titanium Compounds $(\eta^5\text{-}C_5Me_5)_2TiR$ (R = Me, Et): Insertion versus β-Hydrogen Transfer and Olefin Extrusion. Preparation of the Paramagnetic Titanium Alkoxide, Iminoacyl, Acyl, Vinyl, and Azomethide Complexes $(\eta^5\text{-}C_5Me_5)_2TiX$ and Oxidation of These with $PbCl_2$ to the Diamagnetic Tetravalent Derivatives $(\eta^5\text{-}C_5Me_5)_2Ti(X)Cl$

Gerrit A. Luinstra, Johannes Vogelzang, and Jan H. Teuben*

Groningen Center for Catalysis and Synthesis, Department of Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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The paramagnetic, tervalent titanium alkyls Cp^*_2TiR (1, R = Me; 2, R = Et) were compared in their behavior toward a range of reactive molecules. These 15-electron, d^1 systems appear to be weak Lewis acids, reluctant to form adducts. Only for 1 and $Me_3CC{\equiv}N$ could an instable adduct $Cp^*_2TiR{\cdot}L$ be isolated. With active-hydrogen-containing substrates HX (X = $O_2C(H)Me_2$, OEt, $C{\equiv}CMe$), Cp^*_2TiX and RH were produced. Polar, unsaturated molecules like $Me_3CN{\equiv}C$, CO, and paraformaldehyde inserted to give $Cp^*_2Ti\{\eta^2\text{-}C(R){=}NCMe_3\}$, $Cp^*_2Ti\{\eta^2\text{-}C(O)R\}$, and $Cp^*_2TiOCH_2R$ for both 1 and 2. Apolar unsaturated substrates did not insert into the Ti—C bond with the exception of $MeC{\equiv}CMe$, which reacted with 1 to produce the vinyl compound $Cp^*_2TiC(Me){=}CMe_2$. A striking difference between 1 and 2 was found in their reaction with CO_2, $Me_3CC{\equiv}N$, $Me_2C{=}O$, and $RC{\equiv}CR^1$ (R, R^1 = Me, Ph). While 1 either gave a normal insertion (CO_2 and $MeC{\equiv}CMe$) or adducts (Me_2CO, $Me_3CC{\equiv}N$) or did not react ($PhC{\equiv}CPh$), 2 lost ethene and gave compounds that appared to be products of insertion into a Ti—H bond, $Cp^*_2TiO_2CH$, $Cp^*_2TiN{=}C(H)CMe_3$, $Cp^*_2TiOC(H)Me_2$, and $Cp^*_2TiC(R){=}C(H)R^1$. Facile β-hydrogen transfer from the ethyl ligands was also observed in the reaction of 2 with olefins $CH_2{=}CHR$ (R = Me, Ph) to give ethene and $Cp^*_2TiCH_2CH_2R$. This reaction is reversible and equilibrium constants could be determined. Ground-state differences between 2 and $Cp^*_2TiCH_2CH_2R$ were found to be 9 (2) (R = Me) and 7 (2) $kJ{\cdot}mol^{-1}$ (R = Ph). Isotope-labeling experiments showed that liberation of ethene and formation of the new insertion products proceed via an intermediate hydride, Cp^*_2TiH. The kinetic preference for insertion of an unsaturated substrate into the Ti—H bond relative to insertion into the Ti—C bond, in combination with a rapid equilibrium between ethene elimination and reinsertion causes 2 to react in most cases as a hydride, and explains the striking difference in reactivity between 1 and 2. The products of 1 and 2 with various substrates were also characterized as their monochloride derivative $Cp^*_2Ti(R)Cl$ after quantitative oxidation with $PbCl_2$. Comparison of spectroscopic data gives information about the specific coordination of ligand R in both Cp^*_2TiR and $Cp^*_2Ti(R)Cl$ and shows that the Lewis acidity of the metal center increases substantially on oxidation to Ti(IV).

Introduction

Early-transition-metal (group 3–5) and lanthanide compounds Cp^x_2MR (Cp^x: $\eta^5\text{-}C_5R_{5-x}H_x$, x = 0–5; R = H, alkyl, aryl) are highly reactive species.[1] The group 3 and lanthanide derivatives are electronically and sterically very unsaturated 14-electron, d^0 systems. They are strong Lewis acids, which leads to coordination of solvent molecules (ethers) and, sometimes, even of salt molecules.[2] Solvent- and salt-free complexes often satisfy their need for electron density by forming (intramolecular) π or agostic interac-

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