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Efficient Synthesis of *hypho*-2,5- $S_2B_7H_{11}$ and Preparation of New *nido*-, *arachno*-, and *hypho*-Metalladithiaborane Clusters Derived from Its Anion *hypho*- $S_2B_7H_{10}^-$

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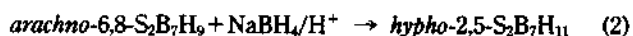
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Reaction of *arachno*- $S_2B_7H_8^-$ with either THF or 1,2-dimethoxyethane upon refluxing condition results in the formation of the previously known compound *hypho*- $S_2B_7H_{10}^-$. Protonation of *hypho*- $S_2B_7H_{10}^-$ with HCl/Et₂O generates *hypho*-2,5- $S_2B_7H_{11}$ in good yield. This *hypho*- $S_2B_7H_{10}^-$ anion has been employed to generate a series of new *nido*-, *arachno*-, and *hypho*-metalladithiaborane clusters. Reaction of the anion with $Cp(CO)_2FeCl$ results in direct metal insertion and the formation of a complex containing the general formula $(\eta^5-C_5H_5)FeS_2B_7H_8$. Spectroscopic studies of *nido*-6- $CpFe-7,9-S_2B_7H_8$ I demonstrated that compound I was shown to have a *nido*-type cage geometry derived from an octadecahedron missing one vertex, with the iron atom occupying the three-coordinate 6-position in the cage and the two sulfurs occupying positions on the open face of the cage. Reaction of *hypho*- $S_2B_7H_{10}^-$ with $CoCl_2/Li^+[C_5H_5]^-$ gave the previously known complex *arachno*-7- $CpCo-6,8-S_2B_7H_8$ II. Also, the reaction of the anion with $[Cp^*RhCl_2]_2$ gave the complex *arachno*-7- $Cp^*Rh-6,8-S_2B_7H_8$ III, the structure of which was shown to be that of complex II. The similarity of the NMR spectra of II and III suggest that III adopts cage structure similar to that previously confirmed for II. A series of 9-vertex *hypho* clusters in which the sulfur atoms are bridged by different species isoelectronic with a BH_3 unit, such as $HMn(CO)_4$ or SiR_2 have been prepared. Compounds IV, V, and VI are each $2n+4$ skeletal electron systems and would be expected according to skeletal electron counting theory to adopt *hypho*-type polyhedral structures derived from an icosahedron missing three vertices. The complex *hypho*-1- $(CO)_4Mn-2,5-S_2B_7H_8$ IV was obtained by the reaction of the anion with $(CO)_5MnBr$ and has been shown from spectroscopic data to consist of a $(CO)_4Mn$ fragment bound to the two sulfur atoms S_2 and S_5 of *hypho*- $S_2B_7H_{10}^-$. Also, similar *hypho*-type complexes *hypho*-1- $R_2Si-2,5-S_2B_7H_8$ ($R=CH_3$ V, $R=C_6H_5$ VI) have been prepared from the reaction of *hypho*- $S_2B_7H_{10}^-$ with R_2SiHCl .

Introduction

Previously *hypho*-2,5- $S_2B_7H_{11}$ was obtained from either the reaction of $BH_3 \cdot THF$ or $NaBH_4$ with *arachno*- $S_2B_7H_8^-$ or *arachno*-6,8- $S_2B_7H_9$ in moderate yield (24-33%) as shown in equation 1 and 2.^{1,2} The formation of *hypho*-2,5- $S_2B_7H_{11}$ was viewed as involving an initial interaction between the Lewis acid BH_3 and the base borane anion, followed by a cluster rearrangement.



We recently reported that the reaction of *arachno*-6,8- $S_2B_7H_9$

H_9^- anion with THF or 1,2-dimethoxyethane results in a rearrangement reaction to give good yields (40-47%) of the *hypho*- $S_2B_7H_{10}^-$ anion.³ This dithiaborane anion is a rare example of a $2n+8$ cluster system (26 skeletal electron, 9 cage atoms) and according to simple skeletal-electron counting theory⁴ should adopt a *hypho* cage geometry based on an icosahedron missing three vertices as shown in Figure 1. When the structures of *hypho*-2,5- $S_2B_7H_{11}$ and *arachno*-6,8- $S_2B_7H_9$ are compared, in complex *hypho*-2,5- $S_2B_7H_{11}$ the electron rich bridging $S-BH_2-S$ unit appears to be connected by conventional two-center, two-electron bonds, whereas the electron deficient six-boron unit adopts a configuration which favors multicenter interactions. Thus, these molecules can

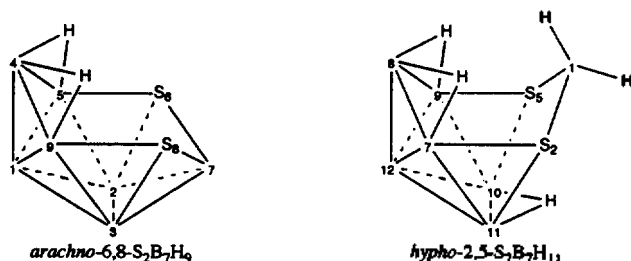


Figure 1. Structure of *arachno*-6,8- $S_2B_7H_9$ and *hypho*-2,5- $S_2B_7H_{11}$.

be described as having both classical and nonclassical portions. Owing to their open structure and "classical/nonclassical" hybrid natures,^{1,25} the reactivities of this *hypho*-dithiaborane might be expected to be intermediate between those observed for the polyhedral boranes and other types of clusters.

In this paper we wish to report on progress made towards the syntheses of *hypho*-2,5- $S_2B_7H_{11}$ and the formation of new metalladithiaborane complexes are discussed. Thus, we have now investigated these possibilities and report here the syntheses and characterizations of a unique series of eight- and nine-vertex dithiaborane clusters having *nido*-, *arachno*-, and *hypho*- skeletal electron counts.

Experimental Section

All Manipulation were carried out using standard high-vacuum or inert-atmosphere techniques described by Shriver.⁶

Methods and Materials. *arachno*-6,8- $S_2B_7H_9$ was prepared as reported previously.⁷ Oil-dispersed sodium hydride was obtained from Aldrich and was washed with hexane under a nitrogen atmosphere prior to use. The majority of solvents were of reagent grade and were used without further purification. Diethyl ether and THF were purified by distillation from lithium aluminum hydride, while 1,2-dimethoxyethane was further purified by distillation from sodium-benzophenone. Toluene was freshly distilled from sodium-benzophenone and methylene chloride was dried over calcium chloride. Anhydrous hydrogen chloride (HCl/Et_2O) and all other reagents were commercially obtained, as indicated, and used as received. $Cp(CO)_2FeCl$,⁸ $[(C_5(CH_3)_5)RhCl_2]_2$,⁹ and $Mn(CO)_5Br$ ¹⁰ were prepared by literature methods. $CoCl_2$ (Baker) was dehydrated under vacuum at 160 °C. Cyclopentadiene was freshly distilled from dicyclopentadiene (Aldrich). *n*-butyl lithium in hexane (Aldrich) was used as received. Chlorodimethylsilane and chlorodiphenylsilane were obtained from Huls America and distilled and degassed before use. Analytical thin-layer chromatography was conducted on 0.25 mm (5×10 cm) silica gel F-254 plates (Merck). Flash column chromatography was performed with silica gel (230-400 mesh, EM Science). Silica gel was obtained from J. T. Baker Co. and was dried before use. All reactions involving dithiaborane anion were carried out under nitrogen atmosphere.

Physical Measurements. 1H NMR spectra at 200 MHz and ^{11}B NMR spectra at 64.2 MHz were obtained on a Bruker AM-200 Fourier transform spectrometer. All boron-11 chemical shifts were referenced to $BF_3 \cdot O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All proton

chemical shifts were measured relative to internal residual benzene^{-d} from the lock solvent (99.5% C_6D_6) and then referenced to Me_4Si (0.00 ppm). Two-dimensional COSY ^{11}B - 1H NMR experiments¹¹ were conducted with s-type selection parameters at 64.2 MHz. The sweep widths in the F_2 direction was 20000 Hz and in the F_1 direction 10000 Hz and a total of 128 increments (increment size 0.05 ms) was collected, with each slice having 512w F_2 data points. The data were zero-filled twice in the F_1 directions and subjected to 2D Fourier transformation with sine-bell apodization in both domains. A total of 128 scans for *hypho*-2,5- $S_2B_7H_{11}$, *hypho*- $S_2B_7H_{10}^-$, V, and VI and 256 scans for I, II, III, and IV were taken for each increment with a recycling time of 100 ms.

High- and low-resolution mass spectra were obtained on a VG Micromass 7070H mass spectrometer. All melting points were uncorrected. Elemental analyses were obtained from Schwazkopf Laboratories, Woodside, NY. Infrared spectra were obtained on a Perkin-Elmer 1430 spectrophotometer.

General procedure for the generation for *hypho*-2,5- $S_2B_7H_{11}$. A 100-mL round bottom flask fitted with a vacuum stopcock was charged with 0.45 g (3.0 mmol) of *arachno*-6,8- $S_2B_7H_9$ and ~0.10 g (4.2 mmol) of NaH. Tetrahydrofuran (20 mL) was distilled into the reaction flask *in vacuo*, and the flask was allowed to warm to room temperature, whereupon hydrogen gas was evolved. After gas evolution ceased (~1 h), the resulting yellow solution was filtered and concentrated and dried under vacuum. This yellow concentrate was transferred to a flask fitted with a reflux condenser, and 20 mL of predried suitable solvents were introduced. The solution was then heated at reflux. The reaction times required to reach completion was monitored by ^{11}B NMR. The solvent was removed *in vacuo* and the residue was dissolved in ~20 mL of methylene chloride. This suspension was maintained at -5 °C while 5 mL of 1 M HCl in Et_2O was added. The solution was stirred for 30 min and the methylene chloride layer then filtered. Subsequent vacuum sublimation of the resulting reaction mixture gave complex *hypho*-2,5- $S_2B_7H_{11}$.

Reaction of *arachno*- $S_2B_7H_9^-$ with Tetrahydrofuran. *arachno*-6,8- $S_2B_7H_9$ (0.45 g, 3.0 mmol), NaH (~0.10 g, 4.2 mmol), and tetrahydrofuran (~25 mL) were allowed to react according to the general procedure overnight. Analysis of the reaction mixture by ^{11}B NMR after stirring overnight at reflux temperature revealed that the starting material had been completely consumed and that resonances characteristic of *hypho*- $S_2B_7H_{10}^-$ anion were found. The anion was the sole product. Protonation followed by subsequent vacuum sublimation gave *hypho*-2,5- $S_2B_7H_{11}$ (0.18 g, 1.2 mmol). This corresponds to a 40% yield based on consumed *arachno*-6,8- $S_2B_7H_9$.

Reaction of *arachno*- $S_2B_7H_9^-$ with 1,2-dimethoxyethane. *arachno*-6,8- $S_2B_7H_9$ (0.45 g, 3.0 mmol), NaH (~0.10 g, 4.2 mmol), and 1,2-dimethoxyethane (~25 mL) were allowed to react according to the general procedure overnight. Analysis of the reaction mixture by ^{11}B NMR after stirring overnight at reflux temperature revealed that the starting material had been completely consumed and that resonances characteristic of *hypho*- $S_2B_7H_{10}^-$ anion were found. The anion was the sole product. Protonation followed by subsequent

vacuum sublimation gave *hypho*-2,5- $\text{S}_2\text{B}_7\text{H}_{11}$ (0.21 g, 1.4 mmol). This corresponds to a 47% yield based on consumed *arachno*-6,8- $\text{S}_2\text{B}_7\text{H}_9$.

Reaction of *arachno*- $\text{S}_2\text{B}_7\text{H}_8^-$ with Toluene. *arachno*-6,8- $\text{S}_2\text{B}_7\text{H}_9$ (0.45 g, 3.0 mmol), NaH (~0.10 g, 4.2 mmol), and toluene (~25 mL) were allowed to react according to the general procedure. After stirring overnight at reflux temperature, only the resonances characteristic of the starting complex *arachno*-6,8- $\text{S}_2\text{B}_7\text{H}_8^-$ anion were observed by ^{11}B NMR.

Synthesis of *nido*-6-CpFe-7,9- $\text{S}_2\text{B}_7\text{H}_8$ I. A sample of $\text{CpFe}(\text{CO})_2\text{Cl}$ (0.64 g, 3.0 mmol) was loaded into a 100 mL three necked 14/20 round bottom flask equipped with teflon coated magnetic stir bar, septum, vacuum adapter, and the flask was then degassed. 1,2-dimethoxyethane (~20 mL) was transferred at -78°C and on warming to room temperature gave a red solution. A solution of *hypho*- $\text{Na}^+\text{S}_2\text{B}_7\text{H}_{10}^-$ was prepared by the reaction *in vacuo* of excess NaH (~0.10 g, 4.2 mmol) with *hypho*-2,5- $\text{S}_2\text{B}_7\text{H}_{11}$ (0.46 g, 3.0 mmol) in 1,2-dimethoxyethane (~20 mL) at -20°C . A 20 mL sample of *hypho*- $\text{Na}^+\text{S}_2\text{B}_7\text{H}_{10}^-$ solution in 1,2-dimethoxyethane was added dropwise *via* syringe. The solution darkened to greenish black and the solution was stirred at reflux temperature 1 day. The 1,2-dimethoxyethane was evaporated under reduced pressure and the residue was extracted with hexane several times until the organic phase no longer remained red in color. The resulting dark red organic layer was dried, filtered, and concentrated under reduced pressure to afford the crude complex as brown-red solids. Purification *via* flash chromatography on silica using a 95/5 mixture of hexane/ CH_2Cl_2 as eluent gave 0.20 g of red-brown complex *nido*-6-CpFe-7,9- $\text{S}_2\text{B}_7\text{H}_8$ I (0.74 mmol, 25% yield): $R_f=0.31$ (hexane); mp=84–85 $^\circ\text{C}$; ^{11}B NMR (64.2 MHz, ppm, C_6D_6) 14.2 (d, B_5 , $J_{\text{BH}}=150$ Hz), -2.0 (d, B_{10} , $J_{\text{BH}}=180$ Hz), -4.9 (d, B_4 , $J_{\text{BH}}=200$ Hz), -8.0 (d, B_6 , $J_{\text{BH}}=170$ Hz), -21.8 (d, B_3 , $J_{\text{BH}}=180$ Hz), -26.1 (d, B_2 , $J_{\text{BH}}=150$ Hz), -40.8 (d, B_1 , $J_{\text{BH}}=150$ Hz); 2D ^{11}B - ^{11}B COSY NMR (64.2 MHz, ppm, C_6D_6 , ^{11}B spin-decoupled) B_5 - B_2 , B_5 - B_1 , B_{10} - B_1 , B_4 - B_3 , B_4 - B_1 , B_3 - B_2 , B_3 - B_1 , B_2 - B_1 ; ^1H NMR (200.13 MHz, ppm, C_6D_6 , ^{11}B spin-decoupled) 3.9 (s, CH of C_5H_5), -1.6 (s, BHB); IR spectrum (KBr pellet, cm^{-1}) 3120 w, 2580 m, 2560 m, 2520 m, 2360 w, 2350 w, 1440 w, 1430 w, 1270 w, 1030 m, 990 m, 980 w, 920 w, 880 w, 850 w, 840 w, 820 w, 800 w, 770 w, 760 w, 700 w, 650 w, 610 w, 570 w, 540 w, 500 w, 410 w, 380 w. Anal. Calcd for $\text{B}_7\text{C}_5\text{Fe}_1\text{H}_{13}\text{S}_2$: C, 22.34; H, 4.88; Found: C, 22.40; H, 4.90; Exact mass calcd for $^{11}\text{B}_7^{12}\text{C}_5^{56}\text{Fe}_1^{1}\text{H}_{13}^{32}\text{S}_2$ 270.0456, found 270.0480.

Synthesis of *arachno*-7-CpCo-6,8- $\text{S}_2\text{B}_6\text{H}_8$ II. A solution of $\text{Li}^+[\text{C}_5\text{H}_5]^-$ was prepared by the addition, under N_2 , of 4.2 mmol of *n*-butyl lithium in hexane (1.6 M, 2.6 mL) to a stirred sample of C_5H_6 (0.27 g, 4.1 mmol) at 0°C over 5-min period. The reaction was maintained at 0°C for ~1 h after which time the reaction mixture appeared as a viscous yellow slurry. To this reaction vessel was attached a side arm containing anhydrous CoCl_2 (0.78 g, 6.0 mmol). The hexane was vacuum evaporated, the flask immersed in liquid nitrogen, and THF (~20 mL) condensed into the reaction flask. The mixture was warmed to room temperature to dissolve the salt, and the CoCl_2 was added in small portions. A slightly exothermic reaction produced a dark olive-green solution after stirring for 2 h. During this time

a solution of $\text{Na}^+\text{S}_2\text{B}_7\text{H}_{10}^-$ was prepared separately by the reaction *in vacuo* of excess NaH with *hypho*-2,5- $\text{S}_2\text{B}_7\text{H}_{11}$, (0.46 g, 3.0 mmol) in THF (~30 mL) at -20°C . After 2 h evolution of H_2 had ceased, indicating completion of the reaction. The $\text{Na}^+\text{S}_2\text{B}_7\text{H}_{10}^-$ solution was next transferred to a dropping funnel which was then attached to the flask containing $\text{CoCl}_2/\text{Li}^+[\text{C}_5\text{H}_5]^-$ mixture. The $\text{Na}^+\text{S}_2\text{B}_7\text{H}_{10}^-$ solution was added dropwise to the reaction mixture which was maintained at -78°C . After 2 h the solution was allowed to warm gradually to room temperature, which caused the solution to change to dark brown. The reaction mixture was opened to the air and filtered through a medium porosity glass frit. The solvent was removed under vacuum and the residue extracted from CH_2Cl_2 . Evaporation of the solvents under reduced pressure gave a crude product consisting of a mixture of compounds. This material was purified by flash chromatography on silica (hexane/ CH_2Cl_2 , 95/5) to afford 0.29 g (1.1 mmol, 37%) of complex *arachno*-7-CpCo-6,8- $\text{S}_2\text{B}_6\text{H}_8$ II as a purple solid: $R_f=0.25$ (hexane/benzene, 9/1); mp=149 $^\circ\text{C}$ decomposed; ^{11}B NMR (64.2 MHz, ppm, C_6D_6) 5.0 (d, $\text{B}_{5,9}$, $J_{\text{BH}}=160$ Hz), -9.8 (d, $\text{B}_{2,3}$, $J_{\text{BH}}=170$ Hz), -34.0 (dt, B_4 , $J_{\text{BH}}=150$ Hz), -40.2 (d, B_1 , $J_{\text{BH}}=140$ Hz); 2D ^{11}B - ^{11}B COSY NMR (64.2 MHz, ppm, C_6D_6 , ^{11}B spin-decoupled) $\text{B}_{5,9}$ - B_1 , $\text{B}_{2,3}$ - B_1 , B_4 - B_1 ; ^1H NMR (200.13 MHz, ppm, C_6D_6 , ^{11}B spin-decoupled) 5.3 (s, CH of C_5H_5), -1.56 (s, BHB); IR spectrum (KBr pellet, cm^{-1}) 3110 w, 2923 m, 2855 sh, 2535 vs, 2221 w, 1890 w, 1322 m, 1047 m, 993 s, 950 m, 897 m, 857 sh, 818 m, 788 m, 735 m, 525 br, 421 br. Anal. Calcd for $\text{B}_6\text{C}_5\text{H}_{13}\text{Co}_1\text{S}_2$: C, 23.01; H, 5.02; Found: C, 23.11; H, 5.08; Exact mass calcd for $^{11}\text{B}_6^{12}\text{C}_5^{59}\text{H}_{13}^{59}\text{Co}_1^{32}\text{S}_2$ 262.0346, found 262.0353.

Synthesis of *arachno*-7-CpRh-6,8- $\text{S}_2\text{B}_6\text{H}_8$ III. A solution of $\text{Na}^+\text{S}_2\text{B}_7\text{H}_{10}^-$ was prepared by the reaction *in vacuo* of excess NaH with *hypho*-2,5- $\text{S}_2\text{B}_7\text{H}_{11}$, (0.46 g, 3.0 mmol) in THF (~30 mL) at -20°C as described above. To this solution of $\text{Na}^+\text{S}_2\text{B}_7\text{H}_{10}^-$ was added 0.93 g (1.5 mmol) of $[(\text{C}_5(\text{CH}_3)_5)\text{RhCl}_2]_2$. The resulting mixture was stirred at room temperature overnight and then concentrated *in vacuo*, affording an oily, red residue, which was taken up in 50 mL of hexanes and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by flash chromatography (hexane/diethyl ether, 95/5) on silica to separate 0.27 g (0.72 mmol, 24%) of a dark red complex *arachno*-7-CpRh-6,8- $\text{S}_2\text{B}_6\text{H}_8$ III, which was air-stable solid: $R_f=0.76$ (benzene); mp=90–92 $^\circ\text{C}$; ^{11}B NMR (64.2 MHz, ppm, C_6D_6) 3.9 (d, $\text{B}_{5,9}$, $J_{\text{BH}}=160$ Hz), -9.4 (d, $\text{B}_{2,3}$, $J_{\text{BH}}=170$ Hz), -35.0 (dt, B_4 , $J_{\text{BH}}=130$ Hz), -40.8 (d, B_1 , $J_{\text{BH}}=130$ Hz); 2D ^{11}B - ^{11}B COSY NMR (64.2 MHz, ppm, C_6D_6 , ^{11}B spin-decoupled) $\text{B}_{5,9}$ - B_1 , $\text{B}_{2,3}$ - B_1 , B_4 - B_1 ; ^1H NMR (200.13 MHz, ppm, C_6D_6 , ^{11}B spin-decoupled) 0.3 (s, CH_3 of $\text{C}_5(\text{CH}_3)_5$), -0.7 (s, BHB); IR spectrum (KBr pellet, cm^{-1}) 2960 s, 2920 s, 2860 s, 2570 w, 2550 w, 2530 w, 1470 m, 1420 w, 1380 m, 1270 m, 1200 w, 1100 m, 1030 m, 910 w, 880 w, 810 s, 750 w, 670 w, 580 w, 420 w, 410 w. Anal. Calcd for $\text{B}_6\text{C}_{10}\text{H}_{23}\text{Rh}_1\text{S}_2$: C, 32.01; H, 6.18; Found: C, 32.22; H, 6.23; Exact mass calcd for $^{11}\text{B}_6^{12}\text{C}_{10}^{1}\text{H}_{23}^{103}\text{Rh}_1^{32}\text{S}_2$ 376.0849, found 376.0855.

Synthesis of *hypho*-1-(CO) $_4\text{Mn}$ -2,5- $\text{S}_2\text{B}_6\text{H}_8$ IV. A solution of $\text{Na}^+\text{S}_2\text{B}_7\text{H}_{10}^-$ was prepared by the reaction *in vacuo* of excess NaH with *hypho*-2,5- $\text{S}_2\text{B}_7\text{H}_{11}$, (0.46 g, 3.0 mmol) in THF (~30 mL) at -20°C as described above. To this solution of $\text{Na}^+\text{S}_2\text{B}_7\text{H}_{10}^-$ was added 0.83 g (3.0 mmol) of $(\text{CO})_5\text{MnBr}$. The reaction mixture was stirred for 3 h at

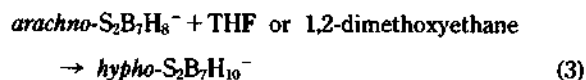
ambient temperature. After the reaction, THF was removed under reduced pressure and the brown residue was extracted with hexane several times, until the organic layer lost its yellow color. The resulting yellow hexane layer was dried and evaporated to give a garnet solid. Purification of this crude material was performed by flash chromatography on silica (hexane/CH₂Cl₂, 95/5) to give 0.26 g (0.85 mmol, 28%) of yellow complex *hypho*-1-(CO)₄Mn-2,5-S₂B₆H₈ IV; *R*_f=0.57 (hexane); mp=95-96 °C; ¹¹B NMR (64.2 MHz, ppm, C₆D₆) 4.0 (d, B_{7,9}, *J*_{BH}=150 Hz), -20.1 (d, B_{10,11}, *J*_{BH}=130 Hz), -22.1 (dt, B₈, *J*_{BH}=120 Hz), -52.8 (d, B₁₂, *J*_{BH}=150 Hz); 2D ¹¹B-¹¹B COSY NMR (64.2 MHz, ppm, C₆D₆, ¹¹B spin-decoupled) B_{7,9}-B₈, B_{7,9}-B₁₂, B_{10,11}-B₁₂, B₈-B₁₂; ¹H NMR (200.13 MHz, ppm, C₆D₆, ¹¹B spin-decoupled) -0.6 (t, BHB), -1.6 (s, BHB); IR spectrum (KBr pellet, cm⁻¹) 2970 w, 2940 w, 2910 w, 2860 w, 2600 m, 2590 m, 2580 m, 2560 m, 2100 s, 2010 s, 1980 s, 1960 s, 1550 w, 1470 w, 1460 w, 1270 w, 1100 w, 1060 w, 1010 m, 990 m, 870 m, 850 w, 820 w, 770 w, 740 w, 700 w, 670 m, 640 m, 620 m, 450 m, 430 m. Anal. Calcd for B₆C₄H₉MnO₄S₂: C, 15.75; H, 2.97. Found: C, 15.83; H, 2.99; Exact mass calcd for ¹¹B₆¹²C₄¹H₉⁵⁵Mn¹⁶O₄³²S₂ 305.9878, found 305.9901.

Synthesis of *hypho*-1-(CH₃)₂Si-2,5-S₂B₆H₈ V. Airless flasks (100 mL and 250 mL) were flame dried and filled with argon. A 35% oil dispersed NaH (0.29 g) was placed into the 100 mL flask, and the oil was removed by washing with freshly distilled hexane (3×10 mL) and removing *via* syringe. After drying the clean NaH under vacuum to produce 0.10 g (4.2 mmol), 30 mL of dry diethyl ether was introduced into the reaction flask; which was cooled to -20 °C. 0.46 g of *hypho*-2,5-S₂B₇H₁₁ (3.0 mmol) was added to the suspension, and the reaction mixture was stirred for 30 min at -20 °C and for 2 h at room temperature, until evolution of H₂ stopped. The resulting solution of Na⁺S₂B₇H₁₀⁻ was transferred *via* cannular into an addition funnel attached to the 250 mL Airless flask, which contained a solution of chlorodimethylsilane (0.33 g, 3.5 mmol) and triethylamine (~0.5 mL) in 80 mL diethyl ether, and then the Na⁺S₂B₇H₁₀⁻ solution was added dropwise at -78 °C. This mixture was stirred at room temperature for 24 h, during which time the solution color slowly changed from yellow to white. The reaction volatiles were then removed *in vacuo* below 0 °C to afford an yellow oil. The residue was taken up in 50 mL of hexanes and then the suspension was quickly filtered on alumina to remove excess chlorodimethylsilane. The filtrate was concentrated *in vacuo* to give a waxy material, which was sublimed at 30-40 °C (0.01 mmHg) to afforded 0.16 g (0.82 mmol, 27%) of *hypho*-1-(CH₃)₂Si-2,5-S₂B₆H₈ V as a air-sensitive white solid: mp=42-44 °C; ¹¹B NMR (64.2 MHz, ppm, C₆D₆) -7.0 (d, B_{7,9}, *J*_{BH}=160 Hz), -25.0 (d, B_{10,11}, *J*_{BH}=150 Hz), -34.9 (d, B₁₂, *J*_{BH}=145 Hz), -55.0 (dt, B₈, *J*_{BH}=160 Hz); 2D ¹¹B-¹¹B COSY NMR (64.2 MHz, ppm, C₆D₆, ¹¹B spin-decoupled) B_{7,9}-B₁₂, B_{7,9}-B₈, B_{10,11}-B₁₂, B₁₂-B₈; ¹H NMR (200.13 MHz, ppm, C₆D₆, ¹¹B spin-decoupled) 0.3 (s, CH₃ of Si(CH₃)₂), -1.6 (s, BHB); IR spectrum (KBr pellet, cm⁻¹) 2960 w, 2930 w, 2850 w, 2560 s, 2550 s, 2520 s, 2500 s, 1420 m, br, 1390 m, br, 1380 w, 1370 w, 1315 s, 1260 w, 1100 w, br, 1010 m, 995 m, 975 m, 935 w, 875 w, 850 w, 810 w, 730 m, 705 w, 660 m, 610 w, 550 w, 520 w, 505 w, 485 m. Found: C, 12.36; H, 7.28; Exact mass calcd for ¹¹B₆¹²C₂¹H₁₄³²S₂²⁸Si₁ 196.0861, found 196.0848.

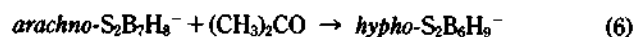
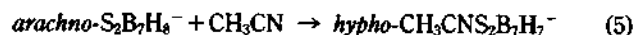
Synthesis of *hypho*-1-(C₆H₅)₂Si-2,5-S₂B₆H₈ VI. 3 mmol diethyl ether solution of Na⁺S₂B₇H₁₀⁻, 0.88 g (4.0 mmol) of chlorodiphenylsilane, and ~0.5 mL of triethylamine in diethyl ether (~80 mL) at 0 °C were allowed to react according to the previous procedure for 24 h to give a crude product consisting of complex *hypho*-1-(C₆H₅)₂Si-2,5-S₂B₆H₈ VI. Filtration and removal of the solvent at 0 °C afforded an yellow product. The yellow oil was taken up in *ca.* 10 mL of toluene and cooled to -78 °C resulting in deposition of a white crystalline solid. The liquid was decanted, and the solid was recrystallized from hexanes at -78 °C to afford 0.35 g (1.1 mmol, 37%) of complex VI: mp=50-51 °C; ¹¹B NMR (64.2 MHz, ppm, C₆D₆) -7.0 (d, B_{7,9}, *J*_{BH}=160 Hz), -25.0 (d, B_{10,11}, *J*_{BH}=150 Hz), -34.9 (d, B₁₂, *J*_{BH}=145 Hz), -55.0 (dt, B₈, *J*_{BH}=160 Hz); 2D ¹¹B-¹¹B COSY NMR (64.2 MHz, ppm, C₆D₆, ¹¹B spin-decoupled) B_{7,9}-B₁₂, B_{7,9}-B₈, B_{10,11}-B₁₂, B₁₂-B₈; ¹H NMR (200.13 MHz, ppm, C₆D₆, ¹¹B spin-decoupled) 7.7 (d, C₆H₅ of Si(C₆H₅)₂), 7.4 (m, C₆H₅ of Si(C₆H₅)₂), -1.6 (s, BHB); IR spectrum (KBr pellet, cm⁻¹) 3070 w, 3050 w, 2570 s, 2480 m, 2420 s, 1940 w, 1860 w, 1810 w, 1740 w, 1600 s, 1580 m, 1540 w, 1460 w, 1140 m, 1050 s, 1035 m sh, 1005 s, 975 w, 960 w, 915 w, 870 m, 835 w sh, 825 m, 765 w, 740 m, 735 w, 680 m, 660 w, 640 w, 460 m. Anal. Calcd for B₆C₁₂H₁₈S₂Si₁: C, 45.13; H, 5.68. Found: C, 45.32; H, 5.73; Exact mass calcd for ¹¹B₆¹²C₁₂¹H₁₈³²S₂²⁸Si₁ 320.1173, found 320.1196.

Results and Discussion

In this study we found that *arachno*-S₂B₇H₈⁻ has been thermally transformed to the corresponding *hypho*-S₂B₇H₁₀⁻ in good yield.³ Thus, the reaction was carried out during a period of overnight at refluxing condition and subsequent protonation gave the corresponding *hypho*-2,5-S₂B₇H₁₁ in a good yield. It has been noted that the conversion of *arachno*-S₂B₇H₈⁻ to *hypho*-S₂B₇H₁₀⁻ was varied with the solvent used and the best conversion was observed when *arachno*-S₂B₇H₈⁻ was refluxed in 1,2-dimethoxyethane solvent.



The formation of *hypho*-S₂B₇H₁₀⁻ from the reaction of *arachno*-S₂B₇H₈⁻ with either THF or 1,2-dimethoxyethane was quite unexpected. Such reactions may be viewed as involving an initial interaction between the B7 boron in the *arachno*-6,9-S₂B₇H₈ framework (Figure 1) and nucleophilic solvents. Since B7 boron atom sits between the two electronegative sulfur atoms, it is apparently activated for attack by nucleophiles, and rearrangement followed by disproportionation reactions can result. Such a unique reactivity exhibited by the B7 boron in the *arachno*-6,9-S₂B₇H₈ framework has been observed by reaction of *arachno*-S₂B₇H₈⁻ with either nitriles¹² or ketones² as shown in equation 5 and 6.



However, it was also found that reaction of the anion with non-nucleophilic solvents such as toluene did not yield *hy*

Table 1. NMR Data

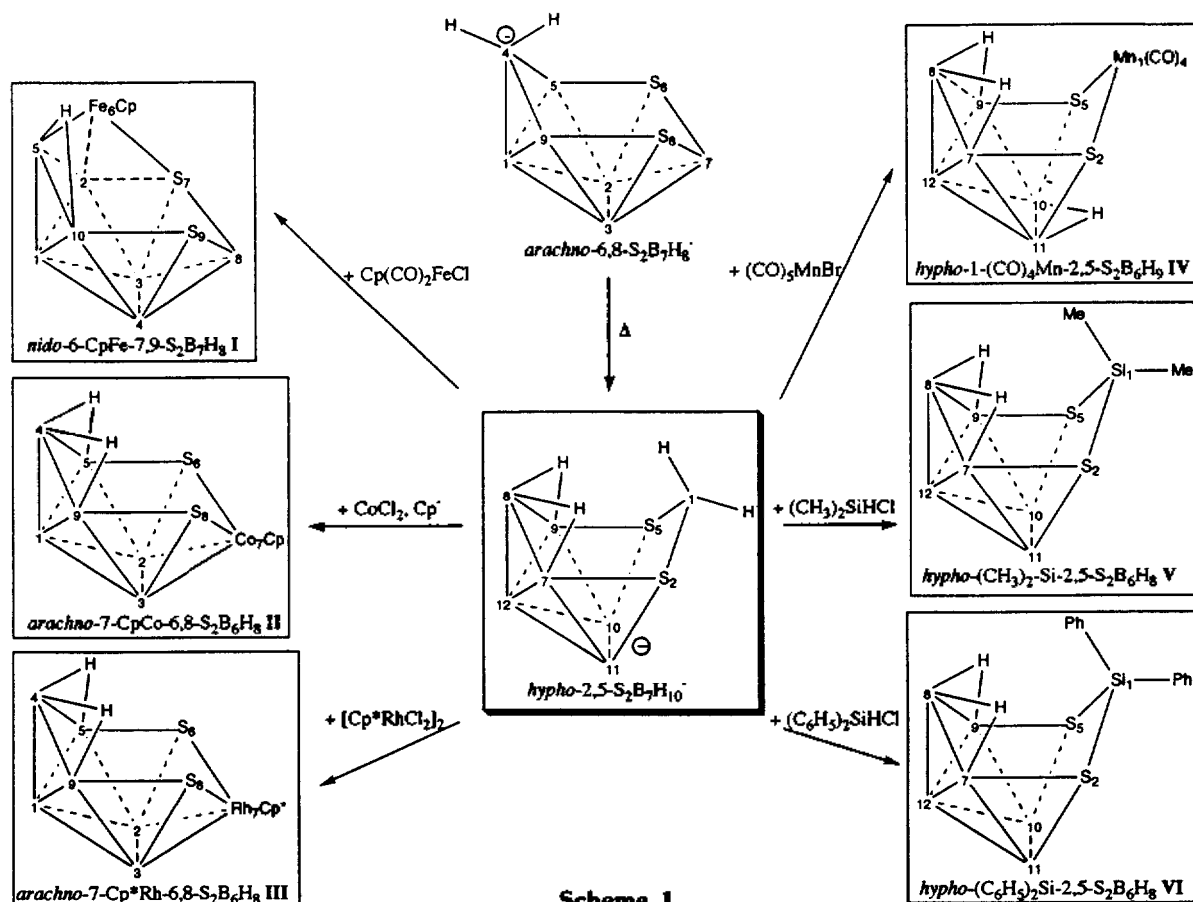
compd	nucleus	δ , ppm (multiplicity, assignment, J (Hz))
<i>nido</i> -6-CpFe-7,9- $S_2B_7H_8$ I ^{a,hr}	^{11}B	14.2 (d, B_9 , J_{BH} 150 Hz), -2.0 (d, B_{10} , J_{BH} 180 Hz), -4.9 (d, B_4 , J_{BH} 200 Hz), -8.0 (d, B_8 , J_{BH} 170 Hz), -21.8 (d, B_3 , J_{BH} 180 Hz), -26.1 (d, B_2 , J_{BH} 150 Hz), -40.8 (d, B_1 , J_{BH} 150 Hz)
	^{11}B - ^{11}B	observed crosspeaks: B_5 - B_2 ; B_5 - B_1 ; B_{10} - B_1 ; B_4 - B_3 ; B_4 - B_1 ; B_3 - B_2 ; B_3 - B_1 ; B_2 - B_1
	1H	3.9 (s, CH of C_5H_5), -1.6 (s, BHB)
	^{11}B	5.0 (d, $B_{5,9}$, J_{BH} 160), -9.8 (d, $B_{2,3}$, J_{BH} 170), -34.0 (dt, B_4 , J_{BH} 150), -40.2 (d, B_1 , J_{BH} 140)
<i>arachno</i> -7-CpCo-6,8- $S_2B_6H_8$ II ^{a,hr}	^{11}B - ^{11}B	observed crosspeaks: $B_{5,9}$ - B_1 , $B_{2,3}$ - B_1 , B_4 - B_1
	1H	5.3 (s, CH of C_5H_5), -1.56 (s, BHB)
	^{11}B	3.9 (d, $B_{5,9}$, J_{BH} 160), -9.4 (d, $B_{2,3}$, J_{BH} 170), -35.0 (dt, B_4 , J_{BH} 130), -40.8 (d, B_1 , J_{BH} 130)
	^{11}B - ^{11}B	observed crosspeaks: $B_{5,9}$ - B_1 ; $B_{2,3}$ - B_1 ; B_4 - B_1
<i>arachno</i> -7-Cp*Rh-6,8- $S_2B_6H_8$ III ^{a,hr}	1H	0.3 (s, CH_3 of $C_5(CH_3)_5$), -0.7 (s, BHB)
	^{11}B	2.6 (dd, $B_{7,9}$, J_{BH} 160), -11.5 (t, B_1 , J_{BH} 130), -22.2 (dd, $B_{10,11}$, J_{BH} 145), -23.1 (dt, B_8 , J_{BH} 175), -54.6 (d, B_{12} , J_{BH} 155)
	^{11}B - ^{11}B	observed crosspeaks: $B_{7,9}$ - B_{12} ; $B_{10,11}$ - B_{12} ; B_8 - B_{12}
	$^1H\{^{11}B\}$	-0.47 (t, BHB, J_{HH} 8), -1.48 (s, BHB)
<i>hypho</i> -2,5- $S_2B_7H_{11}$ ^{a,hr}	^{11}B	-5.8 (t, B_1 , J_{BH} 120), -6.3 (d, $B_{7,9}$, J_{BH} 150), -24.2 (d, $B_{10,11}$, J_{BH} 150), -34.8 (d, B_{12} , J_{BH} 130), -53.7 (dt, B_8 , J_{BH} 150)
	^{11}B - ^{11}B	observed crosspeaks: $B_{7,9}$ - B_{12} ; $B_{7,9}$ - B_8 ; $B_{10,11}$ - B_{12} ; B_{12} - B_8
	$^1H\{^{11}B\}$	-0.70 (s, BHB)
	^{11}B	4.0 (d, $B_{7,9}$, J_{BH} 150), -20.1 (d, $B_{10,11}$, J_{BH} 130), -22.1 (dt, B_8 , J_{BH} 120), -52.8 (d, B_{12} , J_{BH} 150)
<i>hypho</i> -1-(CO) ₄ Mn-2,5- $S_2B_6H_9$ IV ^{a,hr}	^{11}B - ^{11}B	observed crosspeaks: $B_{7,9}$ - B_8 ; $B_{7,9}$ - B_{12} ; $B_{10,11}$ - B_{12} ; B_8 - B_{12}
	$^1H\{^{11}B\}$	-0.6 (t, BHB, J_{HH} 10), -1.6 (s, BHB)
	^{11}B	-3.4 (d, $B_{7,9}$, J_{BH} 200), -24.6 (d, $B_{10,11}$, J_{BH} 180), -34.7 (d, B_{12} , J_{BH} 190), -54.8 (dt, B_8 , J_{BH} 170)
	^{11}B - ^{11}B	observed crosspeaks: $B_{7,9}$ - B_{12} ; $B_{7,9}$ - B_8 ; $B_{10,11}$ - B_{12} ; B_{12} - B_8
<i>hypho</i> -1-(CH ₃) ₂ Si-2,5- $S_2B_6H_9$ V ^{a,hr}	$^1H\{^{11}B\}$	0.3 (s, CH_3 of $Si(CH_3)_2$), -1.7 (s, BHB)
	^{11}B	-3.1 (d, $B_{7,9}$, J_{BH} 200), -25.1 (d, $B_{10,11}$, J_{BH} 190), -34.6 (d, B_{12} , J_{BH} 185), -54.1 (dt, B_8 , J_{BH} 165)
	^{11}B - ^{11}B	observed crosspeaks: $B_{7,9}$ - B_{12} ; $B_{7,9}$ - B_8 ; $B_{10,11}$ - B_{12} ; B_{12} - B_8
	$^1H\{^{11}B\}$	7.7 (d, C_6H_5 of $Si(C_6H_5)_2$), 7.4 (m, C_6H_5 of $Si(C_6H_5)_2$), -1.6 (s, BHB)

^aAll complexes were run in C_6D_6 . ^bChemical shifts are relative to external $BF_3 \cdot O(C_2H_5)_2 = 0.00$ ppm. Positive sign indicates a downfield shifts. ^cAll chemical shifts are measured from the proton-decoupled spectra; because of the heavy overlapping of peaks coupling constants are given only when a doublet is defined.

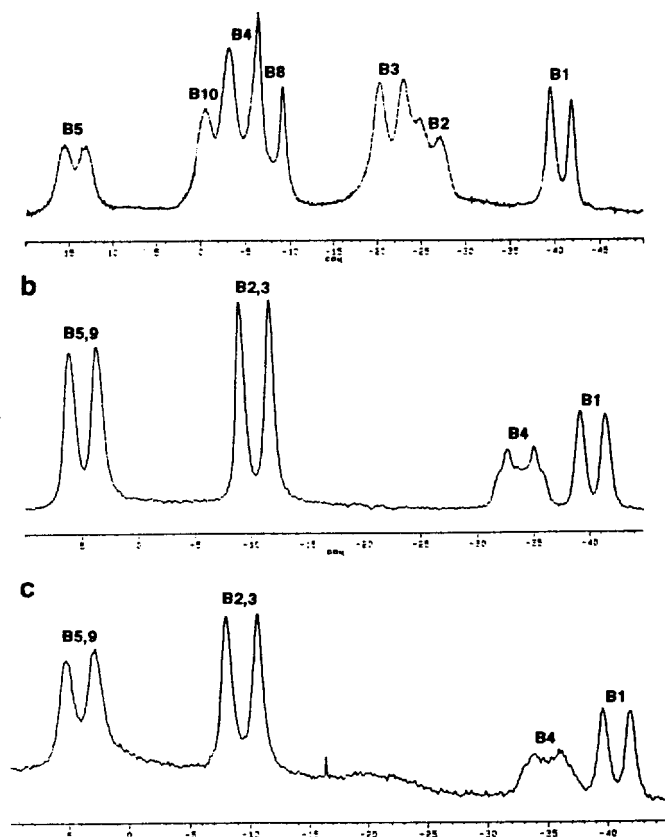
pho- $S_2B_7H_{10}^-$ but instead resulted in extensive decomposition upon prolonged refluxing condition. The above observations suggest that in *arachno*- $S_2B_7H_8^-$ system B7 boron appears to play a unique role and is activated for attack by nucleophile to generate *hypho*- $S_2B_7H_{10}^-$. This procedure makes *hypho*-2,5- $S_2B_7H_{11}$ compound one of the most readily available thiaaborane intermediate which can be used for further syntheses without purification. This dithiaaborane has been identified by its mass spectrum, 1H and ^{11}B NMR spectra (Table 1), and by comparison with an authentic sample.²

This high yield preparation of the dithiaaborane *hypho*- $S_2B_7H_{10}^-$ enabled us to use it for a convenient synthesis of a variety of new metalladithiaaboranes. Thus, we have now investigated these possibilities and report here the syntheses and structural characterizations of a unique series of nine- and ten-vertex dithiaaborane clusters derived from *hypho*-2,5- $S_2B_7H_{11}$.

Treatment of *hypho*- $S_2B_7H_{10}^-$ with $Cp(CO)_2FeCl$ in 1,2-dimethoxyethane at reflux temperature 1 day resulted in the formation of a red-brown complex I (25% yield). Exact mass measurement supports the proposed composition of $C_5H_5FeS_2B_7H_8$. Dithiaaborane of the formula, $C_5H_5FeS_2B_7H_8$ would be nido skeletal electron systems (10 cage atoms and 12 skeletal electron pairs) and would be expected to adopt an open cage geometries found in *nido*-9-(PPh₃)₂Pt-6- SB_6H_{10} ¹³ and *nido*-5,8-(Cp*Co)₂-6,9- $S_2B_6H_6$.¹⁴ The ^{11}B NMR spectrum at 64.2 MHz, shown in Figure 2a, consists of seven resonances of equal intensity showing evidence for a lack of symmetry. The assignment for I given in Scheme 1 also agrees with 2-D ^{11}B - ^{11}B COSY NMR experiment (Table 1), which show cross peaks arising from all adjacent borons, except between those borons bridged by either hydrogen^{11bc} or sulfur atoms.¹⁵ For such boron atoms cross peaks are not expected. The 1H NMR spectrum of I contains an upfield resonance at -1.6



Scheme 1.

Figure 2. The 64.2-MHz ^{11}B NMR spectrum of I, II, and III.

ppm, consistent with the presence of one bridging hydrogen. Of all possible structural arrangements being in agreement with the NMR spectral result, only the *nido*-6- $CpFe$ -7,9- $S_2B_7H_8$ I structure shown in Scheme 1 is the most plausible.

The reaction of *hypho*- $S_2B_7H_{10}^-$ and $Li^+C_5H_5^-$ with $CoCl_2$ produced compound II. Compound II is air stable and its compositions were established by exact mass measurements. The major product of the reaction was identified as known *arachno*-7- $CpCo$ -6,8- $S_2B_6H_8$ II, based on a comparison of its spectral data with that of the previously characterized compound II.¹⁶

Reaction of *hypho*- $S_2B_7H_{10}^-$ with $[Cp^*RhCl_2]_2$ in THF produced a red species and the mass spectrum of which is consistent with a monometallic *arachno*-7- Cp^*Rh -6,8- $S_2B_6H_8$ complex III. The spectral data are consistent with those found for *arachno*-7- $CpCo$ -6,8- $S_2B_6H_8$ II and *arachno*-7- Cp^*Co -6,8- $S_2B_6H_8$ by Sneddon.¹⁴ Compound III is the Cp^*Rh analogue of the previously characterized clusters *arachno*-7- $CpCo$ -6,8- $S_2B_6H_8$ II and *arachno*-7- Cp^*Co -6,8- $S_2B_6H_8$ and is the only compound isolated in the above reaction which retained two bridging hydrogens. The compound thus adopts the *arachno*-structure, shown in Scheme 1, which is based on an octadecahedron missing two adjacent vertices.

In contrast to the preceding reaction, treatment of *hypho*- $S_2B_7H_{10}^-$ with $(CO)_5MnBr$ in THF afforded a yellow complex IV in 28% yield. Elemental analysis and exact mass measurements support the proposed composition of $(CO)_4MnS_2B_6H_8$. If the compound is considered a nine-vertex cluster, composed of six boron, two sulfur, and one manganese atoms, then

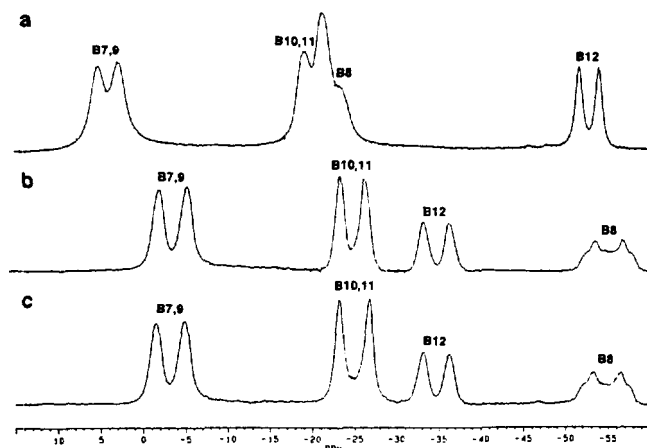


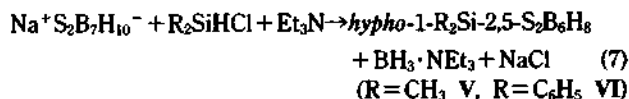
Figure 3. The 64.2-MHz ^{11}B NMR spectrum of IV, V, and VI.

according to skeletal-electron counting procedures,⁴ the compound would contain 26 skeletal electrons and fall into the *hypho* electronic class. IV would therefore be isoelectronic in a cluster sense with *hypho*-2,5- $S_2B_7H_{11}^{2-}$ and *hypho*-1,2,5-(η^6 - C_6Me_6) $RuClS_2B_6H_9^5$ and should adopt a similar structure derived from an icosahedron by removing three vertices.

Except for the B1 boron resonance at -11.5 ppm in *hypho*-2,5- $S_2B_7H_{11}$ (Table 1) the ^{11}B NMR spectra of IV (Figure 3a) and *hypho*-2,5- $S_2B_7H_{11}$ have similar feature and support the structures proposed in Scheme 1, showing four doublets of relative intensities 2:2:1:1. The assignment for IV given in the Scheme 1 also agrees with 2D ^{11}B - ^{11}B COSY NMR experiments (Table 1), which show cross peaks arising from all adjacent borons, except between those borons on the pentagonal face. Since these borons are bridged by either hydrogen or sulfur atoms, cross peaks are not expected. The 200 MHz 1H NMR spectrum of IV is shown in Table 1 and strongly supports the proposed formulation, showing two distinct types of bridging hydrogens in a 1:2 ratio. The bridge resonance at -0.6 ppm shows broad structure characteristic of a bridge hydrogen located between two equivalent boron atoms (B10 and B11). Upon boron decoupling this resonance collapses to a triplet ($J_{HH}=10$ Hz) arising from coupling to the two terminal B-H hydrogens attached to B10 and B11.

Alternatively, IV may be regarded as an exopolyhedrally substituted *hypho*- $S_2B_6H_9^-$ cluster. The $(CO)_4Mn$ fragment, or the BH_2 fragment in *hypho*-2,5- $S_2B_7H_{11}$ (i.e. *hypho*-1- BH_2 -2,5- $S_2B_6H_9$), could then be considered as an exopolyhedral bridging unit having localized two-center, two-electron bonding interactions with the two sulfur cage atoms.

A wide range of 9-vertex *hypho* clusters in which atoms are bridged by different species isoelectronic with a HMn $(CO)_4$ unit, such as R_2Si ($R=CH_3$, C_6H_5), should be possible. Thus, similar *hypho*-type complexes *hypho*-1- R_2Si -2,5- $S_2B_6H_9$ ($R=CH_3$ V, $R=C_6H_5$ VI) have been prepared from the reaction of *hypho*-2,5- $S_2B_7H_{10}^{2-}$ with R_2SiHCl as shown in equation 7.



The composition of V and VI was established by both ele-

mental analysis and mass spectral analysis. Since compounds V and VI are isoelectronic with IV similar structures are proposed, as shown in Scheme 1. Thiaborane of the formula, $R_2SiS_2B_6H_8$ would be *hypho* skeletal electron systems (9 cage atoms and 13 skeletal electron pairs) and would be expected to adopt an open-cage geometries found in *hypho*-2,5- $S_2B_7H_{10}^{2-}$ (i.e. *hypho*-1- BH_2 -2,5- $S_2B_6H_8^-$) and *hypho*-1- CH_2 -2,5- $S_2B_6H_8^2$. The ^{11}B NMR spectra (Figure 3b and 3c) of V and VI show four doublets of relative intensities 2:2:1:1, with the resonances at -54.8 ppm in V and -54.1 ppm in VI, further split into triplets ($J=\sim 65$ Hz and $J=\sim 60$ Hz, respectively) consistent with their assignment to boron (B8) in each cage, which is bonded to two bridging hydrogens. Except for the B1 boron resonance at -5.8 ppm in *hypho*-1- BH_2 -2,5- $S_2B_6H_8^-$ (Table 1) the ^{11}B NMR spectra of V, VI, and *hypho*-1- BH_2 -2,5- $S_2B_6H_8^-$ have similar feature and support the structures proposed in Scheme 1, indicating the absence of a bridging hydrogen between B10 and B11. The boron atom assignment for V and VI given in the Scheme 1 also agrees with 2D ^{11}B - ^{11}B COSY NMR experiments. Also, in agreement with the proposed structure, the 200-MHz ^{11}B spin-decoupled 1H NMR spectra of V and VI show only one type of bridge hydrogen as well as methyl and phenyl resonances, which are attributed to the protons on the sulfur-bridging R_2Si units.

The relative chemical shifts of the boron resonances in the spectra of previously characterized 9-vertex *hypho* clusters *hypho*-1- BH_2 -2,5- $S_2B_6H_9$ and *hypho*-1- BH_2 -2,5- $S_2B_6H_8^-$, and of the analogous resonances arising from the borons in the pyramidal boron fragments of IV-VI discussed below, are of special interest since they are highly diagnostic of their structures. Thus, IV and *hypho*-1- BH_2 -2,5- $S_2B_6H_9$ exhibit similar spectra in which the B8 resonance appears near -23 ppm and the apical B12 resonance near -54 ppm and are proposed to have structures that contain a dithiaborane fragment with three boron-boron bridging hydrogens. Compounds V, VI, and *hypho*-1- BH_2 -2,5- $S_2B_6H_8^-$ also exhibit similar spectral features in which the B8 resonance appears near -54 ppm and the apical B12 resonance near -34 ppm and are each proposed to have structures in which one boron-boron edge is unsubstituted.

In summary, as demonstrated by the results discussed above, the *hypho*- $S_2B_7H_{10}^{2-}$ anion exhibits different types of reactivity, centered at the sulfur and bridge hydrogens, respectively, and may thus exhibit a variety of bonding configuration with respect to metal coordination. Thus, the formation of the complex I can be envisaged as the direct insertion of the metal atom above the B(5,9,8,1) face of the anion with the loss of two hydrogens, followed by the rearrangement of the cage-framework. However, the reactions leading to the formation of the compounds II-VI involve the degradative insertion of a metal atom to the cage-framework. It is significant that each of the new metalladithiaborane complexes II-VI contain the same number of boron atoms and retain the basic hexaborane (10) boron frameworks, respectively. Although the exact mechanism of the formation is unknown, all of these compounds appear to have resulted from the abstraction of B1 boron atom from the parent borane *hypho*- $S_2B_7H_{10}^{2-}$ accompanied by a substitution of metal atom units to the two sulfurs.

Finally, it should also be noted that compounds V and

VI are the first two examples of main-group metal containing dithiaborane clusters. The isolation of V and VI illustrates that $hypho-S_2B_7H_{10}^-$ may be used in future to incorporate even larger numbers and types of main-group metal atoms into dithiaborane cage systems resulting in the production of new classes of hybrid clusters.

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Synthesis and Properties of Novel Pt(II)-containing Polyphosphazenes

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Poly(dichlorophosphazene) having low molecular weight ($M_w \sim 10^4$) was synthesized by the thermal reaction of hexachlorocyclotriphosphazene in the presence of excess $AlCl_3$ (>2%) as catalyst. Using the poly(dichlorophosphazene), poly[bis(ethylglycino)phosphazene], poly[bis(glycinemethylamido)phosphazene], and poly[(glycinemethylamido)(methylamino)phosphazene] were prepared. Diammineplatinum(II) complex cation was introduced into these derivatized phosphazene polymers, and the resultant polymers containing the platinum(II) moiety were characterized by means of elemental analysis, IR and NMR spectroscopies, and then subjected to *in vitro* and *in vivo* assays of antitumor activity.

Introduction

Hydrolytically sensitive polyphosphazenes¹⁻³ are recently attracting a remarkable attention because of their potential applicability to biomedical materials⁴⁻¹⁵ such as substrates for drug delivery systems and absorbable suturing materials.

Polyphosphazenes are polymers with an inorganic back-

bone consisting of alternating nitrogen and phosphorous atoms linked by alternating single and double bonds. Starting from the poly(dichlorophosphazene) a variety of polymers with variable properties can be prepared by nucleophilic substitution with various organic groups. Allcock and co-workers^{1,2,16} who extensively explored the field of polyphosphazenes reported that polyphosphazenes substituted with amino