New Transition Metal Mediated Alkylation Reaction of *arachno*-$S_2B_7H_8$, Insertion Reaction of *arachno*-$S_2B_7H_8^-$ with $(CO)_5M$ $\{C(R_1)(R_2)\}$ (M=Cr, W; R_1=CH_3, C_6H_5; R_2=OCH_3, SC_6H_5): Synthesis and Characterization of *arachno*-4-RCH_2-6,8-$S_2B_7H_8$ (R=CH_3, IIa; C_6H_5, IIb)

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Good yield synthetic routes for the production of new B-alkyl-dithiaborane clusters are reported. The syntheses of the B-alkyl-dithiaboranes are based on the use of Fischer-type carbene reagents to activate the B-H bonds of dithiaborane for alkyl-addition reactions and are the first examples of transition-mediated reactions of dithiaborane to be reported. Thus, reactions employing *arachno*-$S_2B_7H_8^-$ and $(CO)_5M\{C(R_1)R_2\}$ (M=Cr, W; R_1=CH_3, C_6H_5; R_2=OCH_3, SC_6H_5) were found to yield the intermidiate anions I, $[(CO)_5M\{C(R_1)R_2(S_2B_7H_8)\}]^-$, which upon protonation gave the corresponding neutral, air-sensitive cluster *arachno*-4-RCH_2-6,8-$S_2B_7H_8$(R=CH_3, IIa; C_6H_5, IIb) range from 30 to 35% yield. Complexes IIa and IIb are isoelectronic with *arachno*-6,8-$S_2B_7H_9$ and, on the basis of the spectroscopic data, are proposed to adopt a similar *arachno* cage geometry in which an RCH_2 units are substituted to 4 position boron atom of the *arachno*-6,8-$S_2B_7H_9$.

Introduction

Transition-metal reagents are widely used in polyhedral borane chemistry to catalyze or promote a variety of transformation. Sneddon *et al.* previously showed that transition-metal reagents can be used to activate the B-H bonds in a variety of polyhedral boranes and carboranes, and that this activation can induce numerous important synthetic transitions such as acetylene addition,[1–6] olefin-borane coupling,[7] acetylene insertion,[8] and dehydrocoupling reactions.[9–11] We previously reported our preliminary results concerning the first metal-mediated alkylation reaction of a boron hydride, in which Fischer-type carbene complexes were found to promote the conversion of *arachno*-$S_2B_7H_8^-$ to the alkylated cage compound, *arachno*-4-RCH_2-6,8-$S_2B_7H_8$, in essentially quantitative yields under mild conditions.[12] In this paper we report full details of these and related reactions of a variety of Fischer-type carbene complexes with *arachno*-$S_2B_7H_8^-$.

Experimental

All manipulations were carried out using standard high-vacuum or inert atmosphere techniques described by Shriver.[13] *arachno*-6,8-$S_2B_7H_9$ was prepared as reported previously.[14] Oil-dispersed sodium hydride was obtained from Aldrich and was washed with hexane under a nitrogen atomosphere prior to use. The $(CO)_5Cr\{C(OCH_3)CH_3\}$,[15] $(CO)_5Cr\{C(OCH_3)C_6H_5\}$,[16] $(CO)_5Cr\{C(SC_6H_5)CH_3\}$,[17] $(CO)_5W\{C(OCH_3)CH_3\}$,[15] $(CO)_5W\{C-(OCH_3)C_6H_5\}$,[15] and $(CO)_5W\{C(SC_6H_5)CH_3\}$[18] were prepared according to the literature methods. Tetrahydrofuran 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 recieved.

^{11}B-NMR spectra at 160.5 and 64.2 MHz and ^{1}H-NMR spectra at 200 MHz were obtained on Bruker AM-500 and Bruker AF-200 spectrometers equipped with appropriate decoupling accessories. All [11]B chemical shifts are 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 from the lock solvent (99.5 %, C_6D_6) and then referenced to Me_4Si (0.0 ppm).

Two-dimensional COSY ^{11}B-^{11}B-NMR experiments[19] were conducted with s-type selection parameters at 64.2 MHz for **IIa**. 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 256 scans was 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. Infrared spectra were obtained on a Perkin-Elmer 1430 spectrophotometer.

Reaction of *arachno*-$S_2B_7H_8^-$ with $(CO)_5Cr\{C(OCH_3)CH_3\}$. A 100 m*l* 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 ~0.1 g (4.2 mmol) of NaH. Tetrahydrofuran (~ 25 m*l*) was distilled into the reaction flask *in vacuo*, and the flask was allowed to warm to ~ −20°C, whereupon H_2 gas was evolved. After gas evolution ceased (~2 h), the resulting yellow solution was filtered. This yellow solution was transferred to a three-neck flask fitted with a dropping funnel and reflux condenser. To this solution 0.80 g (3.2 mmol) of $(CO)_5Cr\{C(OCH_3)CH_3\}$ in THF was added at −78°C and allowed to warm slowly to room temperature and continued overnight. The solution gradually turned dark brown, sug-

gesting the formation of a chromathiaborane complex. Analysis of the reaction mixture by ^{11}B-NMR after stirring overnight at room temperature revealed that the starting material had been completely consumed and that resonances characteristic of anion **Ia** [(CO)$_5$Cr{C(CH$_3$)(OCH$_3$)(S$_2$B$_7$H$_8$)}]$^-$ were found. The anion **Ia** was the sole product.

Generation and Spectral Characterization of Ia. A standard 5-mm NMR tube adapted for alternate high vacuum-inert atmosphere operation was used for generation and of **Ia**. Typically 0.03 mmol of Na$^+$S$_2$B$_7$H$_8^-$ was placed in the NMR tube and dissolved in 0.3 m*l* of tetrahydrofuran-d$_8$ at -78°C. Th· solution was degased by a freeze-pump-thaw cycle. Transfer of (CO)$_5$Cr{C(OCH$_3$)CH$_3$}(0.4 mmol) to the cooled reaction mixture (-78°C) followed by mixing resulted in a rapid and usually quantitative formation of the brown solution of **Ia**. The NMR tube was then frozen, evacuated, and sealed at liquid N$_2$ temperature. The tube was allowed to warm to room temperature. The complex was characterized by ^{1}H and ^{11}B-NMR spectroscopy. ^{11}B-NMR (160.5 MHz, ppm, CD$_3$CN) 11.3 (d, $J_{BH}=160$ Hz), 8.4 (d, $J_{BH}=145$ Hz), -7.0 (d, $J_{BH}=145$ Hz), -8.8 (d, $J_{BH}=145$ Hz), -16.8 (d, $J_{BH}=130$ Hz), -21.5 (s), -42.6 (d, $J_{BH}=130$ Hz), ^{1}H-NMR (200.13 MHz, ppm, tetrahydrofuran-d$_8$) 3.6 (br, OCH$_3$), 1.0 (br, CH$_3$), -0.5 (br, B-H-B), -10.3 (br, M-H).

Attempted Protonation of Ia. A 0.45 g (3.0 mmol) sample of *arachno*-6,8-S$_2$B$_7$H$_9$ was used to generate a solution of the sodium salt of **Ia** as described above. Tetrahydrofuran was then vacuum-evaporated and the resulting brown solid suspended in 30 m*l* of methylene chloride. To this suspension was added dropwise 5 m*l* of anhydrous 1 M HCl in Et$_2$O at -5°C. The solution was stirred for 30 min and the methylene chloride layer then filtered. The material eluting from methylene chloride was found to be a single product with the trace amount of (CO)$_5$Cr{C(OCH$_3$)CH$_3$}. Subsequent separation was performed by flash chromatography with hexane to give 0.18 g (1.01 mmol) of *arachno*-4-CH$_3$CH$_2$-6,8-S$_2$B$_7$H$_8$ **IIa**. This corresponds to a 34% yield based on consumed *arachno*-6,8-S$_2$B$_7$H$_9$. ^{11}B-NMR (64.2 MHz, ppm, C$_6$D$_6$) 2.0 (d, B$_{5,9}$, $J_{BH}=155$ Hz), -5.7 (d, B$_7$, $J_{BH}=170$ Hz), -22.2 (d, B$_{2,3}$ $J_{BH}=180$ Hz), -24.6 (s, B$_4$), -49.0 (d, B$_1$, $J_{BH}=150$ Hz); ^{1}H-NMR (200.13 MHz, ppm, C$_6$D$_6$, ^{11}B spin decoupled) 0.9 (t, CH$_3$), 0.7 (q, CH$_2$), -1.2 (br, BHB); exact mass calcd for ^{11}B$_7$^{12}C$_2$^{1}H$_{11}$^{32}S$_2$ 176.0954, found 176.1007; $R_f=0.98$ in Hexance; IR spectrum (KBr pellet, cm^{-1}) 2950m, 2920w, 2860w, 2570s, 1455w, 1255m, 1090m, br, 1050w, 1020m, br, 925w, 900w, 850w, 800m, 750w, 695w, 590w.

Reaction of *arachno*-S$_2$B$_7$H$_8^-$ with (CO)$_5$Cr{C(OCH$_3$)C$_6$H$_5$}. In a typical experiment, a solution of Na$^+$S$_2$B$_7$H$_8^-$ was prepared by the reaction *in vacuo* of excess NaH ($\sim$0.1 g, 4.2 mmol) with *arachno*-6,8-S$_2$B$_7$H$_9$ (0.45 g, 3.0 mmol) in THF (-25 m*l*) at ~ -20°C. The solution was transferred to a three-neck flask fitted with a dropping funnel and reflux condenser. To this solution 1.0 g (3.2 mmol) of (CO)$_5$Cr{C(OCH$_3$)C$_6$H$_5$} in THF was added at -78°C and allowed to warm slowly to room temperature and continued overnight. Again, the solution gradually turned dark brown, suggesting the formation of a chromathiaborane complex. ^{11}B-NMR spectra taken at this point confirmed the exclusive formation of **Ib** [(CO)$_5$Cr{C(C$_6$H$_5$)(OCH$_3$)(S$_2$B$_7$H$_8$)}]$^-$. The solvent was removed *in vacuo* and the residue dissolved in 20 m*l* of methylene chloride. This suspension was maintained at -5

°C while 5 m*l* of 1 M HCl in Et$_2$O was added. The solution was stirred for 30 min and the methylene chloride layer then filtered. Subsequent TLC separation of the resulting reaction mixture gave 0.21 g (0.9 mmol) of *arachno*-4-C$_6$H$_5$CH$_2$-6,8-S$_2$B$_7$H$_8$ **IIb**. This corresponds to a 30% yield based on consumed *arachno*-6,8-S$_2$B$_7$H$_9$. ^{11}B-NMR (64.2 MHz, ppm, C$_6$D$_6$) 2.6 (d, B$_{5,9}$ $J_{BH}=160$ Hz), -5.8 (d, B$_7$, $J_{BH}=170$ Hz), -21.2 (d, B$_{2,3}$, $J_{BH}=190$ Hz), -25.1(s, B$_4$), -48.1 (d, B$_1$, $J_{BH}=150$ Hz); ^{1}H-NMR (200.13 MHz, ppm, C$_6$D$_6$) 7.15 (m, CH of C$_6$H$_5$), 7.10 (m, CH of C$_6$H$_5$), 6.98 (m, CH of C$_6$H$_5$), 2.11 (s, CH$_2$), -1.1 (broad, BHB); exact mass calcd for ^{11}B$_7$^{12}C$_7$^{1}H$_{13}$^{32}S$_2$ 238.1110, found 238.1082; Rf=0.42 in Hexane; IR spectrum (KBr pallet, cm^{-1}) 3070w, 3020w, 2920w, 2890w, 2570s, 2360 w, 1600w, 1495m, 1450w, 1380w, 1260w, 1070w, 1030s, 1000w, 980w, 970w, 940w, 900w, 860m, 800w, 755m, br, 740m, br, 700s, 670w, 650w, 620w, 600w, 530w, 485w, 470w.

Reaction of *arachno*-S$_2$B$_7$H$_8^-$ with (CO)$_5$Cr{ C(SC$_6$-H$_5$)CH$_3$}. In an analogous reaction, 0.45 g (3 mmol) of *arachno*-6,8-S$_2$B$_7$H$_9$, $\sim$0.1 g (4.2 mmol) of NaH, and 1.1 g (3.4 mmol) of (CO)$_5$Cr{C(SC$_6$H$_5$)CH$_3$} were reacted in $\sim$30 m*l* of THF *in vacuo*. The reaction mixture was initially warmed to -20°C whereupon the solution also gradually turned brown. The reaction was then allowed to react at 0°C for 1 h. The solution was stirred for another 18 h at room temperature, resulting in a color change to dark brown. ^{11}B-NMR spectra taken at this point indicated that the starting material had been completely consumed and that the new anion was the sole product. Protonation with HCl followed by extraction with hexane gave yellow solid. Further purification can be achieved by flash chromatography using hexane elution gave 0.18 g (1.0 mmol) of *arachno*-4-CH$_3$CH$_2$-6,8-S$_2$B$_7$H$_8$ **IIa**. This corresponds to a $\sim$33% yield based on consumed *arachno*-6,8-S$_2$B$_7$H$_9$.

Reaction of *arachno*-S$_2$B$_7$H$_8^-$ with (CO)$_5$W{C(OCH$_3$)CH$_3$}. In an analogous reaction, 0.45 g (3 mmol) of *arachno*-6,8-S$_2$B$_7$H$_8$, $\sim$0.1 g (4.2 mmol) of NaH, and 1.2 g (3.1 mmol) of (CO)$_5$W{C(OCH$_3$)CH$_3$} were reacted in $\sim$30 m*l* of THF *in vacuo*. The reaction mixture was initially warmed to -20 °C whereupon the solution also gradually turned dark red. The reaction was then allowed to react at 0°C for 1 h. The solution was stirred for another 18 h at room temperature, resulting in a color change to dark brown. ^{11}B-NMR spectra taken at this point indicated that the starting material had been completely consumed and that the new anion was the sole product. Protonation with HCl followed by extraction with hexane gave yellow solid. Work up of the product, in a similar manner to that described above gave 0.19 g (1.1 mmol) of *arachno*-4-C$_2$H$_5$-6,8-S$_2$B$_7$H$_8$ **IIa**. This corresponds to a $\sim$36% yield based on consumed *arachno*-6,8-S$_2$B$_7$H$_9$.

Reaction of *arachno*-S$_2$B$_7$H$_8^-$ with (CO)$_5$W{C(OCH$_3$)C$_6$H$_5$}. In an analogous reaction, 0.45 g (3 mmol) of *arachno*-6,8-S$_2$B$_7$H$_9$, $\sim$0.1 g (4.2 mmol) of NaH, and 1.42 g (3.2 mmol) of (CO)$_5$W{C(OCH$_3$)C$_6$H$_5$} were reacted in $\sim$30 m*l* of THF *in vacuo*. The reaction mixture was initially warmed to -20°C whereupon the solution also gradually turned dark red. The reaction was then allowed to react at 0°C for 1 h. The solution was stirred for another 18 h at room temperature, resulting in a color change to dark brown. ^{11}B-NMR spectra taken at this point indicated that the starting material had been completely consumed and that the new anion was the sole product. Protonation with HCl followed by extraction
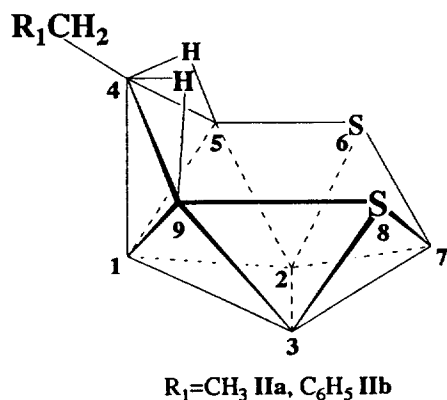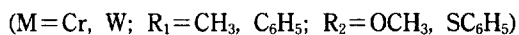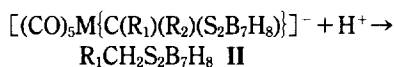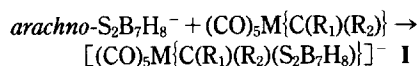
Alkylation Reaction of Arachno-S₂B₇H₈⁻

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R₁CH₂

R₁=CH₃ IIa, C₆H₅ IIb

Figure 1. Proposed structure for *arachno*-4-RCH₂-6,8-S₂B₇H (II).

with hexane gave yellow solid. The reaction was worked up in the manner described above to give a material which was separated by flash chromatography by using hexane gave 0.20 g (0.8 mmol) of *arachno*-4-C₆H₅CH₂-6,8-S₂B₇H₈ **IIb**. This corresponds to a 28% yield based on consumed *arachno*-6,8-S₂B₇H₉.

Reaction of *arachno*-S₂B₇H₈⁻ with (CO)₅W{C(SC₆H₅)CH₃}. In an analogous reaction, 0.45 g (3 mmol) of *arachno*-6,8-S₂B₇H₉, ~0.1 g (4.2 mmol) of NaH, and 1.5 g (3.3 mmol) of (CO)₅W{C(SC₆H₅)CH₃} were reacted in ~30 ml of THF *in vacuo*. The reaction mixture was initially warmed to −20 °C whereupon the solution also gradually turned dark red. The reaction was then allowed to react at 0°C for 1 h. The solution was stirred for another 18 h at room temperature, resulting in a color change to dark brown. ¹¹B-NMR spectra taken at this point indicated that the starting material had been completely consumed and that the new anion was the sole product. Protonation with HCl followed by extraction with hexane gave yellow solid. Subequent separation was performed by flash chromatography with hexane to give 0.17 g (1.0 mmol) of *arachno*-4-CH₃CH₂-6,8-S₂B₇H₈ **IIa**. This corresponds to a ~32% yield based on consumed *arachno*-6,8-S₂B₇ H₉.

Results and Discussion

The reaction of a variety of Fischer-type carbene complexes with *arachno*-S₂B₇H₈⁻ were explored, and all reactions were found to proceed at moderate temperature, be highly selective, and give good yields of alkylated cage products. Thus, the reaction of the *arachno*-S₂B₇H₈⁻ anion with the Fischer-type carbene complexes, (CO)₅M{C(R₁)(R₂)}(M=Cr, W; R₁=CH₃, C₆H₅; R₂=OCH₃, SC₆H₅), followed by protonation of the resulting anion **I** with the anhydrous HCl resulted in the formation of compound **II**, which was isolated as an air-sensitive, white crystalline product in good yield:

arachno-S₂B₇H₈⁻ + (CO)₅M{C(R₁)(R₂)} →
　　[(CO)₅M{C(R₁)(R₂)(S₂B₇H₈)}]⁻ **I**

[(CO)₅M{C(R₁)(R₂)(S₂B₇H₈)}]⁻ + H⁺ →
　　R₁CH₂S₂B₇H₈ **II**

(M=Cr, W; R₁=CH₃, C₆H₅; R₂=OCH₃, SC₆H₅)

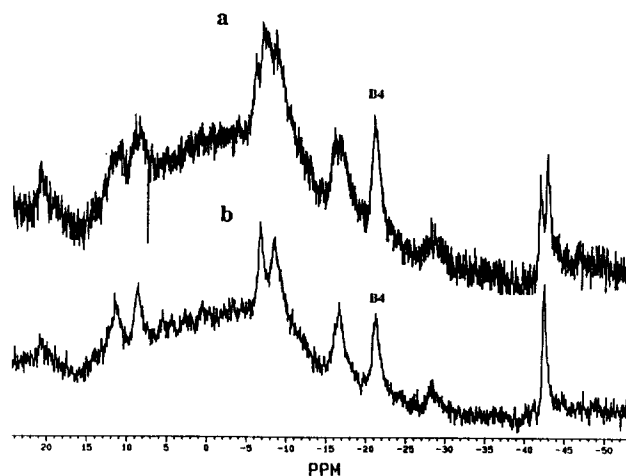The reaction was found to proceed at room temperature

Figure 2. ¹¹B-NMR spectra (160.5 MHz) of **Ia**. Spectrum b is proton spin decoupled.

to give the unstable metallathiaborane intermediate **I**. These compounds can be obtained quantitatively in all reactions described above but decomposes rapidly in solution above −30°C. The new compounds would be [(CO)₅M{C(R₁)(R₂)(S₂B₇-H₈)}]⁻ supported by ¹¹B-NMR data. The ¹¹B-NMR spectrum at 160.5 MHz, shown in Figure 2, consists of seven resonances of equal intensity. All the resonances are split into B-H coupled doublet except for the resonance at −21.5 ppm which appears as a singlet in the proton coupled spectrum. A complex ¹H-NMR spectrum of **I** is obtained at room temperature. The extremely complex and broad spectrum (25°C) precludes structural assignment for **I**. However, broad highfield absorption observed at −10.3 ppm may indicate the presence of the metal hydride complex. Thus, the proposed structure for complex **I** is that of a substituted *arachno*-6,8-S₂B₇H₉ system in which the carbene complex fragments has substituted for a boron vertex in a 4-boron atom.

We had hoped that the addition of a cationic carbene complexes[20,21] to **I** would lead to the corresponding neutral metal complexes. However, we found that the addition of [Cp(CO)₂ Fe{C(CH₃)(OCH₃)}]⁺BF₄⁻ to **I** did not give the desired product but rather decomposed material.

It was also found that *in situ* reaction of the anion **I** with anhydrous HCl in methylene chloride resulted in the good yield formation of the alkylated derivatives of *arachno*-6,8-S₂B₇H₉ **II**. Exact mass measurements support the proposed composition of CH₃CH₂S₂B₇H₈ **IIa** and C₆H₅CH₂S₂B₇H₈ **IIb**. Thiaborane of the formulas, RCH₂-S₂B₇H₈ (R=CH₃, **IIa**, C₆H₅, **IIb**) would be arachno skeletal electron systems (9 cage atoms and 12 skeletal electron pairs) and would be expected to adopt an open cage geometries found in *arachno*-6,8-S₂B₇H₉.

The ¹¹B-NMR spectra of **IIa** and **IIb** (Figure 3) have several similar features and support the structures proposed in Figure 1. Both spectra show four doublets of relative intensities 2 : 1 : 2 : 1 : 1, with the resonances at −24.6 ppm in **IIa** and −25.1 ppm in **IIb**, exhibited singlet consistent with their assignment to the boron (B4) in each cage which is bonded to alkyl substituents. The assignment for **II** given in Figure 1 also agree with 2D ¹¹B-¹¹B COSY NMR experiments (Figure 4), which show cross peaks arising from all adjacent borons, except between those borons on the pentagonal face. Since
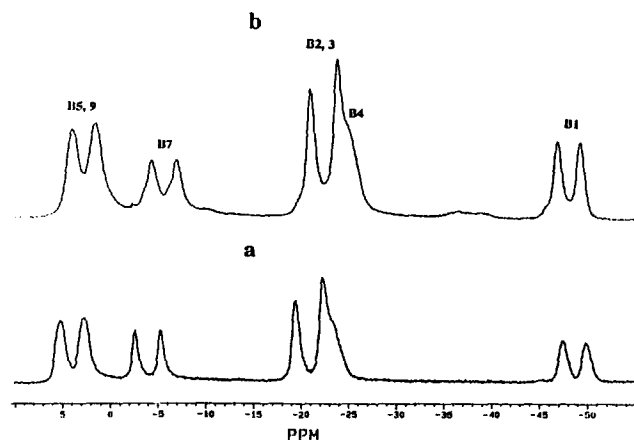
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Figure 3. ^{11}B-NMR spectra (64.2 MHz) of **IIa** (a) and **IIb** (b).

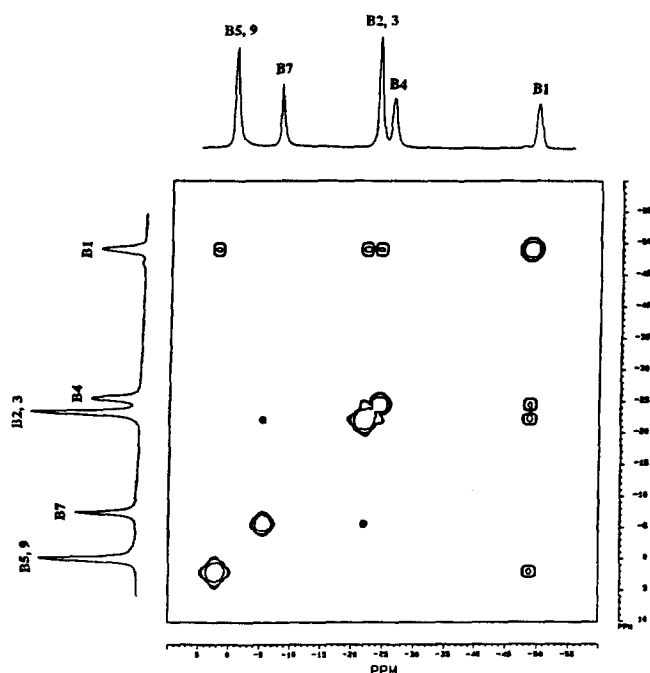**Figure 4.** The 64.2 MHz 2D ^{11}B-NMR spectrum (proton-spin decoupled) of *arachno*-4-CH$_3$CH$_2$-6,8-S$_2$B$_7$H$_8$ (**IIa**). The spectrum at the top is the normal 1D ^{11}B proton-spin-decoupled spectrum.

these borons are bridged by either hydrogen[19b,c] or sulfur atoms,[22] cross peaks are not expected.

The 200 MHz ^{1}H-NMR spectrum of **IIa** strongly supports the proposed formulation, showing two alkyl CH in a relative ratio of 2:3 and one distinct type of bridging hydrogens. Upon boron decoupling these broad CH resonances collapse to a triplet and quartet arising from an ethyl group. Also, in agreement with the proposed structure, the 200 MHz ^{1}H-NMR spectrum of **IIb** exhibits broad resonance for B-H protons as well as resonances expected for the benzylic protons.

It has been found that insertion reaction is one of the characteristic feature of Fischer-type carbene complexes. So far, carbene ligands insert into the silicone-,[23] germanium-,[24] and tin-hydrogen[25] bonds. In contrast, there is no known example for the insertion of a metal coordinated carbene into a B-H bond. It should be noted that a typical B-H bond
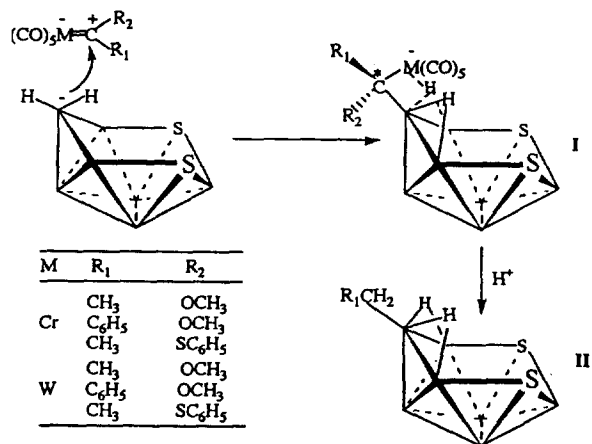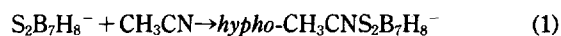

Figure 5. Possible reaction sequence leading to the formation of **II** from the reaction of *arachno*-6,8-S$_2$B$_7$H$_8$$^-$ with (CO)$_5$M{C(R$_1$) (R$_2$)}(M = Cr, W; R$_1$ = CH$_3$, C$_6$H$_5$; R$_2$ = OCH$_3$, SC$_6$H$_5$).

energy is similar to that for an analogous Si-H bond.[26] This means that insertion reactions involving boron hydrides occur under similar conditions.

Previously, *arachno*-S$_2$B$_7$H$_8$$^-$ was found to insert into a variety of polarizable organic compounds[27] such as nitriles and ketones to generate the corresponding *hypho*-CH$_3$CNS$_2$B$_7$H$_8$$^-$ [28] and *hypho*-S$_2$B$_6$H$_9$$^-$ as shown in Eq. (1) and (2),[29] respectively.

$$S_2B_7H_8^- + CH_3CN \rightarrow hypho\text{-}CH_3CNS_2B_7H_8^- \qquad (1)$$

$$S_2B_7H_8^- + (CH_3)_2CO \rightarrow hypho\text{-}S_2B_6H_9^- \qquad (2)$$

The result of the reactions above suggests that *arachno*-S$_2$B$_7$H$_8$$^-$ anion might also readily attack other polarized multiple bonds. Indeed, we have found that *arachno*-S$_2$B$_7$H$_8$$^-$ anion readily reacts with Fischer-type carbene complexes at room temperature. Similar to the reactions with nitriles and ketones, cage B-H insertion results in the production of new alkyl substituted thiaboranes, *arachno*-4-RCH$_2$-6,8-S$_2$B$_7$H$_8$ (R = CH$_3$, **IIa**; C$_6$H$_5$, **IIb**), in good yield.

All of the insertion reactions studied make use of electrophilic carbene complexes (CO)$_5$M{C(R$_1$)(R$_2$)}(M = Cr, W; R$_1$ = CH$_3$, C$_6$H$_5$; R$_2$ = OCH$_3$, SC$_6$H$_5$). These species react with *arachno*-S$_2$B$_7$H$_8$$^-$ at room temperature, below those required for ligand dissociation. In addition, no boron containing side products are observed. All available evidence points to direct reaction of these metal carbene complexes with *arachno*-S$_2$B$_7$ H$_8$$^-$ without prior formation of carbene-borane complexes *via* ligand substitution.

Although the mechanism of the reactions reported herein have not been determined, the above observations suggest that the reaction with *arachno*-S$_2$B$_7$H$_8$$^-$ may involve steps analogous to those given in Eq. (1) and (2) to yield a metallathiaborane complex, which could then undergo protonation to produce alkylated products.

Thus, the formation of **IIa** and **IIb** suggests that the reaction route as illustrated in Figure 5 is involved. We postulate that the mechanism involves the reaction of *arachno*-S$_2$B$_7$H$_8$$^-$ with the polarized metal-carbon bond of (CO)$_5$M{C(R$_1$)(R$_2$)} to form an intermediate complex of (CO)$_5$M{C(R$_1$)(R$_2$)(S$_2$B$_7$H$_8$)}$^-$ **I**, which is the expected insertion product. The ^{11}B-NMR

spectrum of I shows seven resonances, where the peak at -21.5 ppm exhibits a singlet upon proton coupling. This splitting pattern arises from the attachment at the 4-position of arachno-$S_2B_7H_8{}^-$ to the assymetric center of $(CO)_5M\{C(R_1)(R_2)\}$. This proposed reaction sequence is entirely speculative and additional detailed studies will be required before an exact reaction mechanism can be confirmed; however, it is clear that the intermediate I appears to play a unique role in all reactions discussed above.

The work described above was very important since it demonstrated not only that Fischer-type carbene complexes could be used to promote insertion reactions involving boron hydrides, but also that such reactions could lead to high yield, selective functionalization. Furthermore, these results suggest that nucleophilic arachno-$S_2B_7H_8{}^-$ may be able to attack other polarized metal-carbon bonds providing a new synthetic route to cage carbon dithiaborane clusters.

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