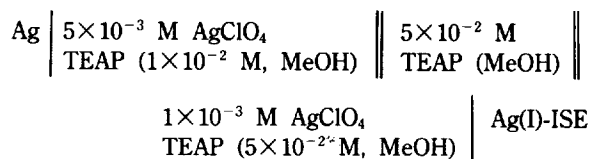


neral construction of the cell used for the measurements was as follows.



Titration were carried out in an all-glass cell thermostated to $25 \pm 0.1^\circ\text{C}$. Titrant was added from 5 to 10 mL microburets calibrated. The data were analyzed, using KINFIT4⁸ to fit the calibration curves for calculating the stability constants.

Extractions. The chloroform solution of the podand (5.0 mL, 3.0×10^{-3} M) and the aqueous solution of cation picrate (5.0 mL, 3.0×10^{-3} M) were placed in a volumetric flask, and the flask was shaken in thermostated incubator for 30 min at $25 \pm 0.2^\circ\text{C}$. The concentration of univalent cation picrate in the water phase was determined from its absorption at 356 nm.

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Thermal Reduction of *arachno*-S₂B₇H₈⁻ to *hypho*-S₂B₇H₁₀⁻ and Synthesis of New Metalladithiaborane Clusters Derived From *hypho*-S₂B₇H₁₀⁻.

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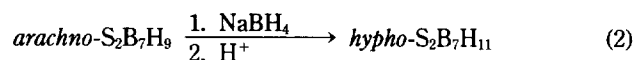
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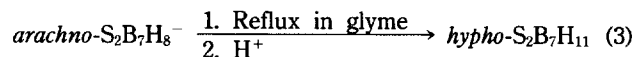
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Previously *hypho*-S₂B₇H₁₁ was obtained from either the reaction of BH₃·THF or NaBH₄ with *arachno*-6,8-S₂B₇H₈⁻ or *arachno*-6,8-S₂B₇H₉ in moderate yield as shown in Eq. 1 and 2.^{1,2} The formation of *hypho*-S₂B₇H₁₁ was viewed as involving an initial interaction between the Lewis acid BH₃ and the base borane anion, followed by a cluster rearrangement.



In this study we found that *arachno*-S₂B₇H₈⁻ has been thermally transformed to the corresponding *hypho*-S₂B₇H₁₀⁻ in excellent yields.³ Thus, the reaction was carried out during a period of overnight at refluxing condition and subsequent protonation gave the corresponding *hypho*-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 glyme solvent.



This procedure makes *hypho*-S₂B₇H₁₁ compound one of the most readily available thiaborane intermediate which can be used for further syntheses without purification. This dithiaborane has been identified by its mass spectrum, ¹H and ¹¹B-NMR spectra, and by comparison with an authentic sample.²

This high yield preparation of the *hypho*-S₂B₇H₁₀⁻ dithiaborane enabled us to use it for a convenient synthesis of a variety of new metalladithiaboranes. Thus, we have now investigated these possibilities and report here the syntheses and structural characterizations of a unique series of nine- and ten-vertex dithiaborane clusters derived from *hypho*-S₂B₇H₁₁.

Treatment of *hypho*-S₂B₇H₁₀⁻ with Cp(CO)₂FeCl in glyme at reflux temperature overnight resulted in the formation of an orange-yellow complex I (24% yield), under the condition of dry column chromatography on silicagel in *n*-hexane. Exact mass measurement supports the proposed composition of C₅H₅FeS₂B₇H₈.⁴ The ¹¹B-NMR spectrum shows evidence

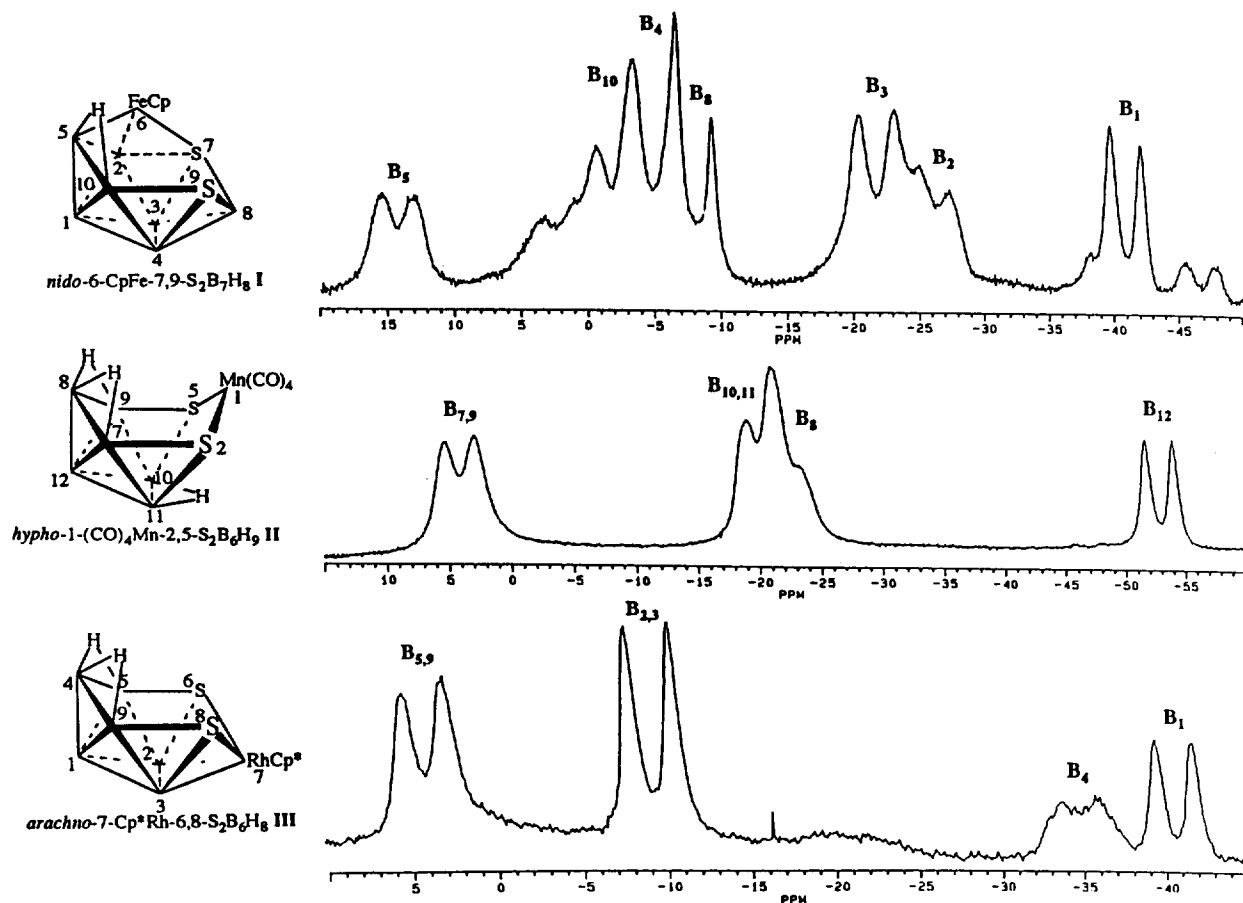
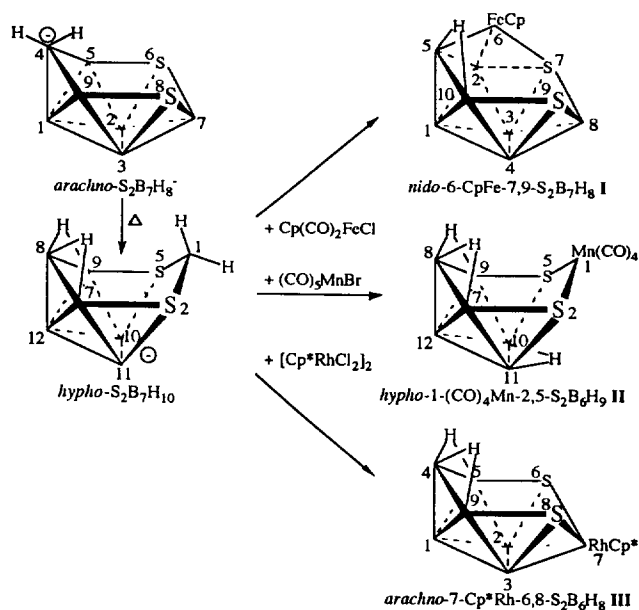


Figure 1. The 64.2-MHz ^{11}B -NMR spectrum of I, II, and III.

for a lack of symmetry, and the 2-D ^{11}B - ^{11}B NMR spectra show connectivities supporting the structure shown in Figure 1. The ^1H -NMR spectrum of I contains an upfield resonance at -1.6 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- $\text{S}_2\text{B}_7\text{H}_8$ I structure shown is the most plausible.

In contrast to the preceding reaction, treatment of *hypho*- $\text{S}_2\text{B}_7\text{H}_{10}^-$ with $(\text{CO})_5\text{MnBr}$ in glyme afforded a yellow complex II in 28% yield. Mass spectral analysis and the NMR data⁵ correspond well to the *hypho*-1-(CO) $_4\text{Mn}$ -2,5- $\text{S}_2\text{B}_6\text{H}_9$ II structure. Thiaborane of the formula, $(\text{CO})_4\text{MnS}_2\text{B}_6\text{H}_9$ II 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*-1- CH_2 -2,5- $\text{S}_2\text{B}_6\text{H}_8$.² The ^{11}B -NMR spectra of II and *hypho*-1- CH_2 -2,5- $\text{S}_2\text{B}_6\text{H}_8$ ² have similar feature and support the structure proposed in Figure 1 showing four doublets of relative intensities 2:2:1:1. The assignment for II give in the Figure also agrees with 2D ^{11}B - ^{11}B COSY NMR experiments. The 200 MHz ^1H -NMR spectrum of II strongly supports the proposed formulation, showing two distinct types of bridging hydrogens in a relative ratio of 2:1. Upon boron decoupling one broad BH bridging hydrogen resonances collapse to a triplet arising from two terminal B-H hydrogens.

Reaction of *hypho*- $\text{S}_2\text{B}_7\text{H}_{10}^-$ with $[\text{Cp}^*\text{RhCl}_2]_2$ in glyme produced a red species and the mass spectrum of which is consistent with a monometallic *arachno*-7-Cp $^*\text{Rh}$ -6,8- $\text{S}_2\text{B}_6\text{H}_8$ com-



plex III. The spectral data⁶ are consistent with those found for *arachno*-7-CpCo-6,8- $\text{S}_2\text{B}_6\text{H}_8$ ^{7,8} and *arachno*-7-Cp $^*\text{Co}$ -6,8- $\text{S}_2\text{B}_6\text{H}_8$ ⁹ by Sneddon *et al.* Compound III is the Cp $^*\text{Rh}$ analogue of the previously characterized clusters *arachno*-7-CpCo-6,8- $\text{S}_2\text{B}_6\text{H}_8$ ^{7,8} and *arachno*-7-Cp $^*\text{Co}$ -6,8- $\text{S}_2\text{B}_6\text{H}_8$ ⁹ and is the only compound isolated in the above reaction which retained two bridging hydrogens. The compound thus adopts the *arachno*-

structure, shown in Figure 1, which is based on an octadecahedron missing two adjacent vertices.

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, it is surprising that complex II is the only product of the $(\text{CO})_5\text{MnBr}$ reaction since its formation requires degradation of the starting *hypho*- $\text{S}_2\text{B}_7\text{H}_{10}^-$. The reaction of $[\text{Cp}^*\text{RhCl}_2]_2$ with *hypho*- $\text{S}_2\text{B}_7\text{H}_{10}^-$ also resulted in cage degradation, and gave the six-boron cluster *arachno*-7-Cp* Rh -6,8- $\text{S}_2\text{B}_6\text{H}_8$ III. Thus the reaction leading to the formation of the compounds involves either the direct insertion or the degradative insertion of a metal atom to the cage-framework.

The work presented here has resulted in the production of a variety of new metalladithiaborane clusters with cage framework compositions including S_2B_6 and S_2B_7 . These results also suggest that an even wider range of metalladithiaborane clusters are possible.

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- In a typical experiment, a solution of $\text{Na}^+\text{S}_2\text{B}_7\text{H}_8^-$ was prepared by the reaction *in vacuo* of excess NaH (~0.1 g, 4.2 mmol) with *arachno*-6,8- $\text{S}_2\text{B}_7\text{H}_9$ (0.45 g, 3.0 mmol) in dimethoxyethane (~25 mL) at ~-20°C. The solution was allowed to warm slowly to room temperature and refluxed overnight. ^{11}B -NMR spectra taken at this point confirmed the exclusive formation of *hypho*- $\text{S}_2\text{B}_7\text{H}_{10}^-$. The solvent was removed *in vacuo* and the residue 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 0.21 g (0.9 mmol) of *hypho*- $\text{S}_2\text{B}_7\text{H}_{11}$. This corresponds to a 67.5% yield based on consumed *arachno*-6,8- $\text{S}_2\text{B}_7\text{H}_9$.
- ^{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_8 , $J_{\text{BH}}=170$ 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); Exact mass calcd for $^{11}\text{B}_7^{12}\text{C}_5^{56}\text{Fe}_1^{1\text{H}}^{32}\text{S}_2$ 270.0456, found 270.0895; $R_f=0.31$ in Hexane; Mp=84-85°C; IR spectrum (KBr pellet, cm^{-1}) 3120w, 2580m, 2560m, 2520m, 2360w, 2350w, 1440w, 1430w, 1270w, 1030m, 990m, 980w, 920w, 880w, 850w, 840w, 820w, 800w, 770w, 760w, 700w, 650w, 610w, 570w, 540w, 500w, 410w, 380w.
- ^{11}B -NMR (64.2 MHz, ppm, C_6D_6) 4.0 (d, $\text{B}_{7,9}$, $J_{\text{BH}}=150$ Hz), -20.1 (d, $\text{B}_{10,11}$, $J_{\text{BH}}=130$ Hz), -22.1 (dt, B_8 , $J_{\text{BH}}=120$ Hz), -52.8 (d, B_{12} , $J_{\text{BH}}=150$ Hz); 2D ^{11}B - ^{11}B COSY NMR (64.2 MHz, ppm, C_6D_6 , ^{11}B spin-decoupled) $\text{B}_{7,9}$ - B_8 , $\text{B}_{7,9}$ - B_{12} , $\text{B}_{10,11}$ - B_{12} , B_8 - B_{12} ; ^1H -NMR (200.13 MHz, ppm, C_6D_6 , ^{11}B spin-decoupled) -0.6 (t, BHB), -1.6 (s, BHB); Exact mass calcd for $^{11}\text{B}_6^{12}\text{C}_4^{1\text{H}}_9^{55}\text{Mn}_1^{16}\text{O}_4^{32}\text{S}_2$ 305.9881, found 305.9001; $R_f=0.57$ in hexane; Mp=95-96°C; IR spectrum (KBr pellet, cm^{-1}) 2970w, 2940w, 2910w, 2860w, 2600m, 2590m, 2580m, 2560m, 2100s, 2020s, 2000s, 1980s, 1960s, 1940w, 1550w, 1470w, 1460w, 1270w, 1100w, 1060w, 1010m, 990m, 870m, 850w, 820w, 770w, 740w, 700w, 670m, 620m, 450m, 430m.
- ^{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); Exact mass calcd for $^{11}\text{B}_6^{12}\text{C}_{10}^{1\text{H}}_{23}^{103}\text{Rh}_1^{32}\text{S}_2$ 376.0854, found 376.9014; $R_f=0.76$ in Benzene; Mp=90-92°C; IR spectrum (KBr pellet, cm^{-1}) 2960s, 2920s, 2860s, 2570w, 2550w, 2530w, 1470m, 1420w, 1380m, 1270m, 1200w, 1100m, 1030m, 910w, 880w, 810s, 750w, 670w, 580w, 420w, 410w.
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Preparation of N-Carboethoxymethyl-C-alkyl(or aryl)nitrones and Their 1,3-Dipolar Cycloaddition to Alkenes

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Nitrones are valuable synthetic intermediates and excellent 1,3-dipoles. They have been utilized for the synthesis of various nitrogen containing biologically active compounds, e.g., alkaloids¹ and β -lactams². Preparation of nitrones has usually been achieved either by condensation of aldehydes with hydroxylamines³ or by oxidation of *N,N*-dialkylhydroxylamines⁴.

During the examination of various 1,3-dipolar cycloadducts as the possible starting materials for the construction of carbapenem skeleton, we thought that it would be interesting to develop a method for the preparation of *N*-carboethoxymethyl nitrones (2). Examination of literature did not reveal any reported method. Recently, we found that *N*-carboethoxyme-