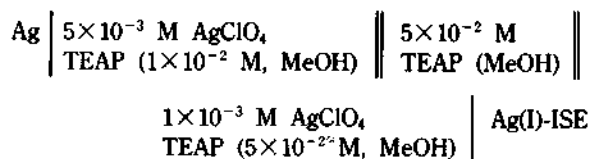


neral construction of the cell used for the measurements was as follows.



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.

Acknowledgement. This work has been supported in part by the Basic Science Research Institute Program, Ministry of Education of Korea (BSRI 92-305), and Non Directed Research Fund, Korea Research Foundation, 1992.

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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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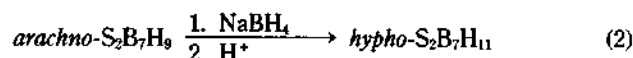
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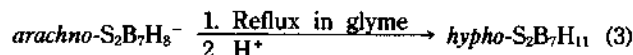
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Received March 15, 1993

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 2.¹² 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 on 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

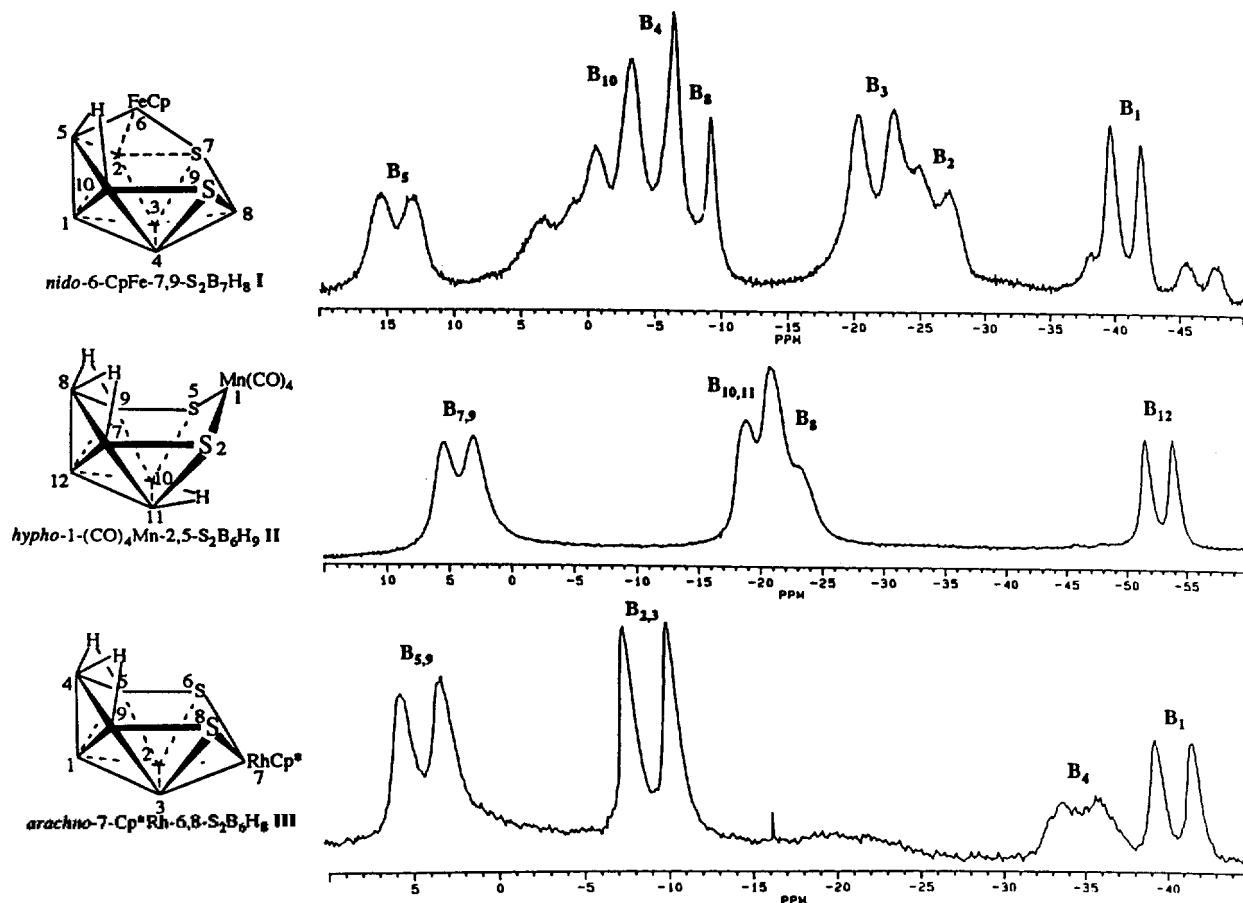
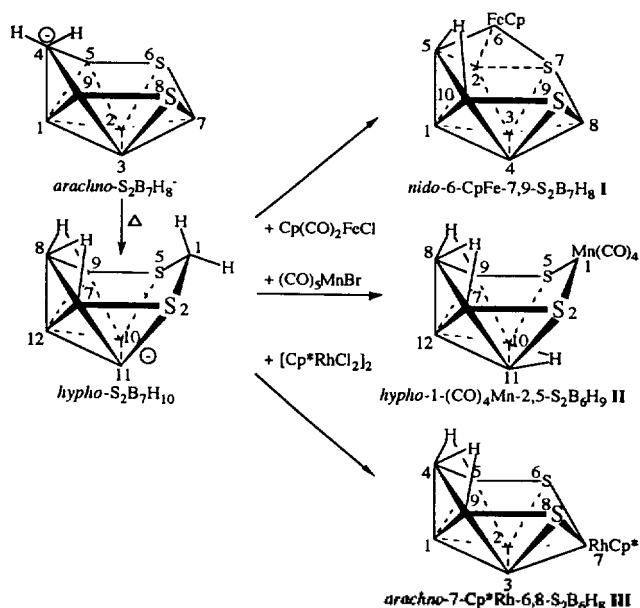


Figure 1. The 64.2-MHz ^{11}B -NMR spectrum of I, II, and III.

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 given 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^{*}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^{*}Co-6,8- $\text{S}_2\text{B}_6\text{H}_8$ ⁹ by Sneddon *et al.* Compound III is the Cp^{*}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^{*}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.

Acknowledgement. The present studies were supported in part by the Basic Science Research Institute program, Ministry of Education, 1992 and the Korea Science and Engineering Foundation (KOSEF 921-0300-030-2). We thank for Dr. Larry G. Sneddon for help in obtaining NMR results and for useful discussions and suggestions.

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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_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); 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 $^{11}\text{B}_6^{12}\text{C}_{10}^{1\text{H}}_{23}^{109}\text{Rh}_1^{32}\text{S}_2$ 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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Received April 9, 1993

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-