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# Synthesis of New Dithiacobaltaborane Clusters Derived from *arachno*-6,8-$S_2B_7H_9$

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A series of air-stable dithiacobaltaborane clusters has been isolated from either the reaction of the *arachno*-$S_2B_7H_8^-$ anion with cobalt chloride and pentamethylcyclopentadienide or the reaction of neutral *arachno*-6,8-$S_2B_7H_9$ with cobalt atoms and pentamethylcyclopentadiene. Thus, the reaction of *arachno*-$S_2B_7H_8^-$ with $CoCl_2$ and $C_5(CH_3)_5^-$ in THF gave, as the major products, the triple-decker compound *nido*-4,6-($\eta$-$C_5(CH_3)_5)_2Co_2$-3,5-$S_2B_2H_2$ (I) and the 11-vertex cluster *nido*-8,10-($\eta$-$C_5(CH_3)_5)_2Co_2$-7,9-$S_2B_7H_7$ (III). Also isolated in smaller amounts were a chlorine derivative of I, *nido*-1-Cl-4,6-($\eta$-$C_5(CH_3)_5)_2Co_2$-3,5-$S_2B_2H$ (II), two isomers of III, *nido*-3,10-($\eta$-$C_5(CH_3)_5)_2Co_2$-7,9-$S_2B_7H_7$ (IV) and *nido*-3,5-($\eta$-$C_5(CH_3)_5)_2Co_2$-7,9-$S_2B_7H_7$ (V), and the eight-boron cluster *nido*-8-($\eta$-$C_5(CH_3)_5$)Co-7,9-$S_2B_8H_8$ (VI). Other trace products of the reaction included the six-boron clusters *nido*-5,8-($\eta$-$C_5(CH_3)_5)_2Co_2$-6,9-$S_2B_6H_6$ (VII) and *arachno*-7-($\eta$-$C_5(CH_3)_5$)Co-6,8-$S_2B_6H_8$ (VIII). Compound III was found to isomerize at 250 °C to IV, which could then be converted to V at 300 °C. The reaction of cobalt atoms with *arachno*-6,8-$S_2B_7H_9$ in the presence of pentamethylcyclopentadiene gave VIII as the major product; however, a number of other clusters including I, V, VI, and $[(\eta\text{-}C_5(CH_3)_5)_2Co]^+[(SB_{10}H_{10})_2Co]^-$ were isolated in trace amounts.

## Introduction

A number of different types of metallathiaborane clusters containing a single sulfur cage atom have previously been reported;[1] however, there are only three examples of dithiametallaborane clusters known. These compounds, *nido*-6,8-($\eta$-$C_5H_5)_2Co_2$-7,9-$S_2B_5H_5$,[2] *arachno*-7-($\eta$-$C_5H_5$)Co-6,8-$S_2B_6H_8$,[2] and *nido*-4,6-($\eta$-$C_5H_5)_2Co_2$-3,5-$S_2B_2H_2$,[3] were previously synthesized in our laboratory via metal atom reactions involving either pentaborane(9) or hexaborane(10). Since a cage sulfur atom is a four-skeletal-electron donor (isoelectronic with $BH^{2-}$), the incorporation of two sulfur atoms into a boron hydride framework necessitates the formation of open-cage geometries. In addition, structural characterizations of the last two compounds mentioned above,[2,3] as well as the related complex ($\eta$-$C_5H_5$)$CoSe_2B_9H_9$ synthesized by Todd,[4] which contains two selenium cage atoms, have revealed several unique structural features and preferences that have not been observed in other isoelectronic cage systems.

The scarcity of dithiametallaborane complexes is undoubtedly due to the absence of dithiaborane clusters to serve as suitable starting materials. However, in 1977 Plešek, Heřmánek, and Janoušek reported[5] the high-yield synthesis of the first dithiaborane, *arachno*-6,8-$S_2B_7H_9$. This cluster, the structure of which is shown in Figure 1, contains both two sulfur atoms and two boron–boron-bridging hydrogens on the open face and would appear to be a versatile starting material for the generation of a range of new types of hybrid clusters. Surprisingly, however, the chemistry of this compound has been largely unexplored. We report here our studies of the reactions of *arachno*-6,8-$S_2B_7H_9$, using both conventional and metal atom techniques, which have led to the formation of a series of dithiacobaltaborane clusters.

## Experimental Section

All manipulations were carried out using standard high-vacuum or inert-atmosphere techniques as described by Shriver.[6]

**Materials.** $CoCl_2\cdot 6H_2O$ (Baker) was dehydrated under vacuum at 160 °C. Pentamethylcyclopentadiene[7] and *arachno*-6,8-$S_2B_7H_9$[5] were prepared by using standard methods. Toluene and tetrahydrofuran were freshly distilled from sodium benzophenone. Sodium hydride (Aldrich) and *n*-butyllithium in hexanes (Aldrich) were used as received. Preparative thin-layer chromatography was conducted on 0.5 mm (20 × 20 cm) silica gel F-254 plates (Merck). 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). The Chromatotron (7924T) was purchased from Harrison Research, Palo Alto, CA. Preparative 2-mm rotors were prepared by using silica gel PF-254 with $CaSO_4\cdot{}^1/_2H_2O$ (EM Science) and oven-dried prior to use.

**Physical Measurements.** Boron-11 NMR spectra at 160.5 and 64.2 MHz were obtained on Bruker AM-500 and AF-500 spectrometers, respectively, equipped with the appropriate decoupling accessories. Proton NMR spectra at 250 and 200 MHz were obtained on Bruker WM-250 and AP-200 spectrometers, respectively. All boron-11 chemical shifts are referenced to $BF_3\cdot O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. Proton chemical shifts were referenced to internal solvent from the lock solvents used (99.0% $CD_2Cl_2$) and then referenced to tetramethylsilane.

Two dimensional $^{11}B$–$^{11}B$ NMR experiments[8] (Table I) were performed with s-type selectrion parameters at 160.5 MHz for III–VI and at 64.2 MHz for II and VIII. For III, IV, and VI the sweep width in the $F_2$ direction was 25 000 Hz and in the $F_1$ direction was 12 500 Hz. A total of 256 increments (increment size 0.04 ms for III, IV, and VI and 0.05 ms for V) were collected, each slice having 512W $F_2$ data points for III, V, and VI and 1K data points for IV. For II, V, and VIII the sweep width in the $F_2$ direction was 20 000 Hz and in the $F_1$ direction was 10 000 Hz. A total of 128 increments (increment size of 0.05 ms) were collected, each slice having 256W $F_2$ data points for II and 512W data points for VIII. The data were zero-filled twice for II, III, V, VI, and VIII and once for IV in the $F_1$ directions and subjected to 2D Fourier transformation with sine-bell apodization in both domains. A total of 800 scans for III, 300 for IV and V, 700 for VI, 2000 for II, and 2000 for VIII were taken for each increment with a recycling time of 100 ms each.

High- and low-resolution mass spectra were obtained on a VG Micromass 7070H mass spectrometer. Infrared spectra were obtained on a Perkin-Elmer 1310 spectrophotometer. All melting points are uncorrected.

**Reaction of $Li^+[C_5(CH_3)_5]^-$, $CoCl_2$, and $Na^+S_2B_7H_8^-$.** A solution of $Li^+[C_5(CH_3)_5]^-$ was prepared by the addition, under $N_2$, of 15 mmol of *n*-butyllithium in hexane (1.6 M, 9.4 mL) to a stirred sample of $C_5(CH_3)_5H$ (2.00 g, 14.7 mmol) at 0 °C over a 5-min period. The reaction was maintained at 0 °C for ~4–5 h, after which time the reaction mixture appeared as a viscous yellow slurry. To this reaction vessel was attached a side arm containing anhydrous $CoCl_2$ (2.73 g, 21.0 mmol). The hexane was vacuum-evaporated, the flask immersed in liquid nitrogen, and THF (20 mL) condensed into the flask. The mixture was warmed to room temperature to dissolve the salt, and $CoCl_2$ was added

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**Table I.** $^{11}B$ NMR Data

| compd[a] | $\delta$ (*J*, Hz) | cross peaks[c] |
|---|---|---|
| *nido*-4,6-$(Cp^*)_2Co_2$-3,5-$S_2B_2H_2$ (I) | 23.5 (153) [B1,2] | |
| *nido*-1-Cl-4,6-$(Cp^*)_2Co_2$-3,5-$S_2B_2H$ (II) | 33.3 (s) [B1], 23.0 (br) [B2] | B1–B2 (s)[b] |
| *nido*-8,10-$(Cp^*)_2Co_2$-7,9-$S_2B_7H_7$ (III) | 35.9 (122) [B11], 34.0 (135) [B6], 17.1 (130) [B5], 4.3 (138) [B2], −9.1 (139) [B1], −16.5 (153) [B3], −18.5 (161) [B4] | B11–B6 (s), B6–B2 (s), B6–B1 (s), B5–B1 (s), B2–B1 (m), B1–B3 (m), B1–B4 (w), B3–B4 (m) |
| *nido*-3,10-$(Cp^*)_2Co_2$-7,9-$S_2B_7H_7$ (IV) | 17.3 (144) [B11], 11.7 (120) [B8], 10.9 (120) [B6], −0.8 (157) [B2], −3.0 (157) [B4], −14.9 (157) [B5], −19.8 (137) [B1] | B11–B6 (s), B8–B4 (m), B6–B2 (s), B6–B5 (w), B6–B1 (m), B2–B1 (s), B4–B1 (s), B5–B1 (s) |
| *nido*-3,5-$(Cp^*)_2Co_2$-7,9-$S_2B_7H_7$ (V) | 25.8 (130) [B11], 17.1 (141) [B6], 16.0 (141) [B1], 5.6 (149) [B2], 1.6 (135) [B4], −5.4 (133) [B10], −30.6 (116) [B8] | B11–B6 (s),[d] B11–B10 (s), B6–B2 (m),[d] B6–B10 (s),[d] B1–B2 (m),[d] B1–B6,[e] B1–B4 (s)[d] |
| *nido*-8-Cp*Co-7,9-$S_2B_8H_8$ (VI) | 6.2 (164) [B1], 4.8 (164) [B10,11], −2.3 (138) [B3,4], −16.6 (169) [B2,5], −26.9 (146) [B6] | B1–B3,4 (s), B1–B2,5 (s), B1–B6 (s),[d] B10,11–B6 (s), B2,5–B6(s) |
| *nido*-5,8-$(Cp^*)_2Co_2$-6,9-$S_2B_6H_6$ (VII) | 24.8 (160), 21.9 (134), 19.7 (137) | |
| *arachno*-7-$(Cp^*)$Co-6,8-$S_2B_6H_8$ (VIII) | 5.1 (145) [B5,9], −8.0 (175) [B2,3], −34.6 (145) [B4], −39.6 (160) [B1] | B5,9–B1 (s), B2,3–B1 (s), B4–B1 (s)[b] |

[a] At 160.5 MHz unless otherwise noted. [b] 64.2 MHz. [c] Abbreviations: s, strong; m, medium; w, weak. [d] Due to the coincidental overlap of resonances, resolution of individual cross peaks with other borons is not possible. [e] Individual resonances are too overlapped to allow resolution of possible cross peaks between these borons.

**Table II.** $^{1}H$ NMR Data[a]

| compd[b] | $\delta$ (assignt) | compd[b] | $\delta$ (assignt) |
|---|---|---|---|
| I[c] | 1.58 ($CH_3$) | V | 1.68 ($CH_3$), 1.67 ($CH_3$) |
| II | 1.58 ($CH_3$) | VI | 1.75 ($CH_3$) |
| III | 1.73 ($CH_3$), 1.62 ($CH_3$) | VII | 1.83 ($CH_3$), 1.71 ($CH_3$) |
| IV | 1.72 ($CH_3$), 1.63 ($CH_3$) | VIII | 1.74 ($CH_3$), −1.64 (BHB, 2) |

[a] $CD_2Cl_2$ solution. [b] At 250 MHz unless otherwise noted. [c] 200 MHz.

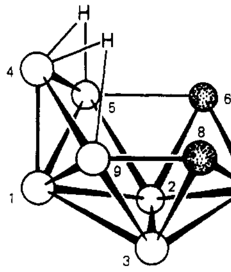

**Figure 1.** Proposed structure and numbering for *arachno*-6,8-$S_2B_7H_9$.

**Table III.** IR Data ($cm^{-1}$)[a]

| | |
|---|---|
| I | 2950 (s), 2920 (s), 2855 (s), 2480 (m), 1463 (s), 1455 (s), 1380 (s), 1020 (s), 910 (w), 890 (w), 755 (s), 720 (w), 620 (w), 590 (w), 460 (m, br), 380 (w) |
| II | 2970 (m), 2950 (m), 2900 (s), 2850 (m), 2480 (s), 1490 (w), 1445 (s, br), 1375 (s), 1155 (w), 1070 (m), 1020 (s), 940 (s), 915 (s), 835 (s), 795 (w), 750 (s), 590 (m), 540 (w), 518 (s), 440 (s), 385 (w), 365 (w) |
| III | 2960 (s, sh), 2920 (s), 2850 (s), 2560 (m), 2520 (m), 2470 (w), 1460 (m), 1380 (m), 1260 (w), 1020 (m), 910 (w), 890 (w), 800 (m, br), 550 (w), 500 (w), 450 (w), 400 (w), 355 (w) |
| IV | 2970 (w), 2950 (w), 2910 (m), 2850 (w), 2550 (s, sh), 2540 (s), 2520 (s), 2510 (s), 2490 (s), 2480 (s), 2460 (s), 1490 (w), 1450 (m, br), 1430 (w), 1375 (s), 1070 (w), 1020 (m), 970 (m), 930 (w), 850 (w), 800 (w), 760 (w), 730 (w), 620 (w), 430 (w), 390 (w), 365 (w), 350 (w) |
| V | 2980 (w), 2950 (w), 2910 (m), 2850 (w), 2550 (s), 2510 (s), 2480 (s), 2460 (s, sh), 1450 (s), 1430 (w), 1380 (m, sh), 1370 (s), 1360 (w), 1260 (w), 1155 (w), 1070 (w), 1020 (s), 980 (s), 935 (w), 920 (w), 900 (w), 880 (w), 865 (w), 840 (w), 820 (w), 740 (w), 680 (w), 620 (w), 535 (w), 470 (w), 450 (w), 380 (w), 340 (w), 320 (w) |
| VI | 2980 (w), 2960 (w), 2920 (m), 2540 (s), 1495 (w), 1450 (m, br), 1430 (w), 1380 (s), 1075 (w), 1020 (s), 1000 (m), 990 (s), 965 (w), 935 (w), 900 (w), 890 (w), 850 (m), 800 (m), 750 (m), 720 (m), 700 (w), 670 (w), 630 (m), 610 (w), 560 (w), 540 (w), 510 (w), 485 (w), 450 (w), 430 (w), 390 (w), 355 (w), 330 (m), 300 (w), 280 (w) |
| VII | 2960 (m), 2920 (s), 2850 (m), 2530 (m), 2490 (s), 2450 (m), 2430 (m), 1735 (w), 1460 (m), 1430 (w), 1375 (s), 1260 (s), 1095 (s), 1075 (m), 1020 (s), 915 (w), 880 (w), 800 (s), 750 (w), 620 (w), 500 (w), 400 (w), 380 (w) |
| VIII | 2990 (w), 2960 (w), 2920 (m), 2850 (w), 2560 (s), 2540 (s), 2520 (s), 2515 (s, sh), 2500 (s), 2060 (w), 1490 (w), 1465 (w), 1455 (w), 1440 (w), 1428 (w), 1375 (s), 1260 (m), 1160 (w), 1095 (w), 1075 (w), 1055 (m), 1020 (m), 1005 (s), 960 (m), 905 (m), 870 (m), 832 (w), 800 (m), 765 (w), 735 (m), 705 (w), 680 (w), 635 (w), 628 (w), 588 (m), 535 (m), 510 (w), 490 (w), 462 (m), 445 (w), 422 (w), 405 (w), 385 (w), 365 (w), 340 (w), 330 (w) |

[a] KBr pellets. Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; br, broad.

in small portions. A slightly exothermic reaction produced a dark olive green solution after stirring for 2 h. During this time a solution of $Na^+S_2B_7H_8^-$ was prepared separately by the reaction in vacuo of excess NaH with *arachno*-6,8-$S_2B_7H_9$ (0.90 g, 6.0 mmol) in THF (~50 mL) at ~−20 °C. After 2 h evolution of $H_2$ had ceased, indicating completion of the reaction. The $S_2B_7H_8^-$ solution was next transferred to a dropping funnel, which was then attached to the flask containing the $CoCl_2$/$Li^+[C_5(CH_3)_5]^-$ mixture. The $S_2B_7H_8^-$ 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 greenish brown. The solvent was removed under vacuum and the residue extracted with $CH_2Cl_2$. This solution was filtered, concentrated, and separated into three crude components via flash column chromotography. Elution with hexane gave a green compound, which was further purified by recrystallization with a methylene chloride and cold pentane mixture: *nido*-8,10-$(Cp^*)_2Co_2$-7,9-$S_2B_7H_7$ (III); $R_f$ 0.96 (50% hexane in benzene solution); green; yield 220 mg (0.41 mmol, 7.8%); mp 300 °C (with sublimation). Mass measurement (amu): calcd for $^{12}C_{20}{}^{1}H_{37}{}^{32}S_2{}^{11}B_7{}^{59}Co^2$, 536.1652; found, 536.1735. Anal. Calcd for $C_{20}H_{37}S_2B_7Co_2$: C, 44.88; H, 6.98. Found: C, 44.30; H, 6.74. The second band from the column was further separated by TLC on silica gel using a 50% hexane in benzene solution. The resultant separation yielded two products. *nido*-5,8-$(Cp^*)_2Co_2$-6,9-$S_2B_6H_6$ (VII): $R_f$ 0.91; dark brown; yield 2 mg ($3.8 \times 10^{-3}$ mmol, 0.06%); mp ~215 °C. Mass measurement (amu): calcd for $^{12}C_{20}{}^{1}H_{36}{}^{32}S_2{}^{11}B_6{}^{59}Co_2$, 524.148; found, 524.127. *arachno*-7-Cp*Co-6,8-$S_2B_6H_8$ (VIII): yield 2 mg ($6 \times 10^{-3}$ mmol, 0.1%). (See following reaction for characterization data.) The third band from the column was separated again by flash column chromatography with a 10% benzene in hexane solution to give a purple crystalline material. Sequential separation of this material with the Chromatotron using a 20% benzene in hexane solution gave five boron-containing products. *nido*-3,5-$(Cp^*)_2Co_2$-7,9-$S_2B_7H_7$ (V): $R_f$ 0.76 (50% hexane in benzene solution); brownish yellow; yield 65 mg (0.12 mmol, 2.0%); mp 295 °C (with sublimation). Mass measurement (amu): calcd for $^{12}C_{20}{}^{1}H_{37}{}^{32}S_2{}^{11}B_7{}^{59}Co_2$, 536.1652; found, 536.1666. Anal. Calcd for $C_{20}H_{37}S_2B_7Co_2$: C, 44.88; H, 6.98. Found: C, 44.31; H, 6.84. *nido*-1-Cl-4,6-$(Cp^*)_2Co_2$-3,5-$S_2B_2H$ (II): $R_f$ 0.73 (50% hexane in benzene solution); dark blue; yield 35 mg (0.068 mmol, 1.1%); mp 255 °C. Mass measurement (amu): calcd for $^{12}C_{20}{}^{1}H_{31}{}^{32}S_2{}^{37}Cl{}^{11}B_2{}^{59}Co_2$, 512.0424; found, 512.0400. *nido*-3,10-$(Cp^*)_2Co_2$-7,9-$S_2B_7H_7$ (IV): $R_f$ 0.71 (50% hexane in benzene solution); purple, yield 48 mg (0.09 mmol, 1.5%); mp 293–295 °C (with sublimation). Mass measurement (amu): calcd for $^{12}C_{20}{}^{1}H_{37}{}^{32}S_2{}^{11}B_7{}^{59}Co_2$: 536.1652; found, 536.1556. *nido*-8-Cp*Co-7,9-$S_2B_8H_8$ (VI): $R_f$ 0.70; yellow; yield 46 mg (0.13 mmol, 2.2%); mp 180 °C. Mass measurement (amu): calcd for $^{12}C_{10}{}^{1}H_{23}{}^{32}S_2{}^{11}B_8{}^{59}Co$ 354.1318; found, 354.1357. Anal. Calcd for $C_{10}H_{23}S_2B_8Co$: C, 34.04; H, 6.58. Found: C, 35.24; H, 6.84. *nido*-4,6-$(Cp^*)_2Co_2$-3,5-$S_2B_2H_2$ (I): $R_f$ 0.66; purple; yield 558 mg (1.17 mmol, 19.5%); mp undetectable. Mass measurement (amu): calcd for $^{12}C_{10}{}^{1}H_{32}{}^{32}S_2{}^{11}B_2{}^{59}Co_2$, 476.080; found, 476.067.

**Thermolysis of *nido*-8,10-$(Cp^*)_2Co_2$-7,9-$S_2B_7H_7$ (III).** Approximately 45 mg (0.08 mmol) of III was loaded into a Pyrex tube that was then evacuated, sealed, and heated at 250 °C for 1 day. The tube was then opened, and the contents were extracted with methylene chloride. Analysis by $^{11}B$ NMR and analytical TLC showed conversion to IV (yield 11 mg, 0.02 mmol).

**Thermolysis of *nido*-3,10-$(Cp^*)_2Co_2$-7,9-$S_2B_7H_7$ (IV).** A 15-mg (0.03-mmol) sample of IV was placed in a Pyrex tube that was then evacuated, sealed, and heated at 300 °C for 3 h. The tube was then opened, and the contents were extracted with methylene chloride. Analysis by $^{11}B$ NMR and analytical TLC showed conversion to V (yield 3 mg, 0.006 mmol).

**Reaction of Cobalt Vapor with *arachno*-6,8-$S_2B_7H_9$, $C_5(CH_3)_5H$, and Toluene.** The metal atom apparatus employed in these studies was based on a published design[9] and is described elsewhere.[2] Before metal deposition was begun, 1.3 g (8.7 mmol) of *arachno*-6,8-$S_2B_7H_9$ was placed into the bottom of the metal atom reactor, which was then evacuated. Cobalt vapor (0.3 g), pentamethylcyclopentadiene (10 mL), and toluene (20 mL) were cocondensed over a 1.5-h period onto the walls of the reactor, which were maintained at −196 °C. Upon completion of metal-deposition and ligand cocondensation the matrix was allowed to warm to room temperature and mix with *arachno*-6,8-$S_2B_7H_9$. This mixture was then stirred at room temperature for 30 min. The volatile materials were removed in vacuo, and unreacted *arachno*-6,8-$S_2B_7H_9$ (0.3 g) was sublimed out of the reaction mixture. The residue was extracted with methylene chloride, and the extracts were filtered and evaporated to dryness. The remaining residue was separated by TLC on silica gel using a 50% hexane in benzene solution as the eluant. Final separation gave the following two compounds. *arachno*-7-Cp*Co-6,8-$S_2B_6H_8$ (VIII): $R_f$ 0.60; purple; yield 140 mg (6.3%, based on consumed 6,8-$S_2B_7H_9$); mp 173 °C. Mass measurement (amu): calcd for $^{12}C_{10}{}^{1}H_{23}{}^{32}S_2{}^{11}B_6{}^{59}Co$, 332.113; found, 332.116 and $[(Cp^*)_2Co]^+[(SB_{10}H_{10})_2Co]^-$: $R_f$ 0.30 (20% benzene in methylene chloride), yellow; yield 5 mg (0.1%); identified by comparison of its spectral data with literature values.[1a] Other complexes isolated in trace amounts were *nido*-4,6-$(Cp^*)_2Co_2$-3,5-$S_2B_2H_2$ (I; 3 mg), *nido*-3,5-$(Cp^*)_2Co_2$-7,9-$S_2B_7H_7$ (V; 2 mg), and *nido*-8-Cp*Co-7,9-$S_2B_8H_8$ (VI; <1 mg).

## Results and Discussion

The reaction of *arachno*-$Na^+S_2B_7H_8^-$ and $Li^+C_5(CH_3)_5^-$ with $CoCl_2$ produced a range of dithiacobaltaborane clusters with cage structures containing varying numbers of cobalt and boron atoms. All compounds are air-stable, and their compositions were established by elemental analysis and/or exact mass measurements.

The major product of the reaction was identified as *nido*-4,6-$(Cp^*)_2Co_2$-3,5-$S_2B_2H_2$ (I) on the basis of a comparison of its spectral data with those of the previously characterized compound *nido*-4,6-$(\eta\text{-}C_5H_5)_2Co_2$-3,5-$S_2B_2H_2$.[3] Thus, the compound is proposed to have the open triple-decker structure shown in Figure 2, in which the cobalt atoms adopt apical positions and the sulfur atoms equatorial positions on the open face of a pentagonal-bipyramidal cluster missing one equatorial vertex. Also isolated in trace amounts was a chlorine derivative of I, *nido*-1-Cl-4,6-$(Cp^*)_2Co_2$-3,5-$S_2B_2H$ (II). The formation of chlorinated metallacarborane complexes in reactions involving $CoCl_2$ has previously been observed.[10]

The compound *nido*-4,6-$(\eta\text{-}C_5H_5)_2Co_2$-3,5-$S_2B_2H_2$[3] was originally prepared in only low yields from the reaction of cobalt atoms with pentaborane(9), carbonyl sulfide, and cyclopentadiene. The reaction reported herein thus represents the first viable synthetic route to this unique type of open triple-decker compound. The fact that the cluster still contains one open face, which should be suitable for incorporating an additional transition-metal or main-group atom, suggests that I may be a useful starting material for the generation of a wide range of new types of triple-decker compounds,[11] and we are presently exploring these possibilities.

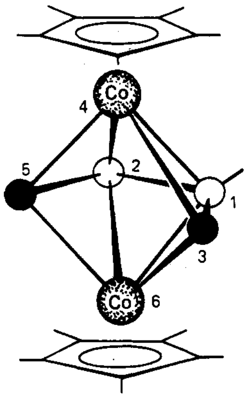

**Figure 2.** Proposed structures for *nido*-4,6-$(\eta\text{-}C_5(CH_3)_5)_2Co_2$-3,5-$S_2B_2H_2$ (I) and *nido*-1-Cl-4,6-$(\eta\text{-}C_5(CH_3)_5)_2Co_2$-3,5-$S_2B_2H$ (II).

Three different isomers, III, IV, and V, having chemical compositions that correspond to the formula $(Cp^*)_2Co_2S_2B_7H_7$ were found. According to electron-counting rules, compounds of this formula are 11-vertex nido cage systems (26 skeletal electrons) and would be expected to adopt structures based on an icosahedron missing one vertex. The gross geometries and relative placement of the metal atoms were confirmed by preliminary single-crystal X-ray studies[12] of each of the isomers, but because of extensive disorder observed between the sulfur and boron cage atoms in each of the compounds, it was not possible to satisfactorily refine their structures or to establish the sulfur atom positions. However, the NMR and rearrangement data, discussed below, in combination with the partial X-ray data strongly support the structures proposed in Figure 3.

Consistent with the X-ray results, the $^{11}B$ NMR spectrum of each compound consists of seven doublets and their $^{1}H$ NMR spectra show two inequivalent pentamethylcyclopentadienyl resonances, indicating a lack of symmetry. The 2D $^{11}B$–$^{11}B$ COSY NMR spectra of the isomers are summarized in Table I and support the structures shown in Figure 3. All cross peaks consistent with these structures were observed, except between B5 and B6 in III and between borons in all three isomers that are bridged by a sulfur atom. We have previously observed that cross peaks are generally not observed between two borons that are bridged by a sulfur.[1j,13] In one case, B4–B8 in IV, a cross peak was observed; however, in this case the two borons are bridged by both sulfur and cobalt atoms.

The fact that isomer III was formed in higher yields than either IV or V and that it was the only isomer to contain both cobalt atoms on the open face suggested that this isomer may have been formed initially in the reaction and that IV and V may have resulted from subsequent rearrangement reactions. This possibility is further supported by the observations that when III was heated at 250 °C in vacuo it slowly converted to IV and when IV was heated at 300 °C V was obtained. Reactions at higher temperatures gave complete decomposition. These rearrangements are in agreement with established tendencies in polyhedral metallacarboranes.[14] Thus, as observed here, metal cage atoms tend to migrate to the highest coordination vertices, while sulfur atoms prefer lower coordinate positions.

Surprisingly, the formation of an eight-boron cluster, *nido*-8-Cp*Co-7,9-$S_2B_8H_8$ (VI), was also observed. The compound is

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(9) Klabunde, K. J.; Timms, P.; Skell, P. S.; Ittel, S. D. *Inorg. Synth.* **1979**, *19*, 59–86.

(10) Venable, T. L.; Sinn, E.; Grimes, R. N. *Inorg. Chem.* **1982**, *21*, 895–904.

(11) For a general discussion of triple-decker compounds see: Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 943–958 and references therein.

(12) Crystal data: III, space group $P2_1/n$, $Z = 4$, $a = 8.284$ (1) Å, $b = 26.719$ (5) Å, $c = 11.766$ (2) Å, $\beta = 101.87$ (2)°; IV space group $P2_1/n$, $Z = 4$, $a = 8.330$ (1) Å, $b = 14.738$ (3) Å, $c = 21.294$ (2) Å, $\beta = 100.10$ (1)°; V, space group $P2_1/c$, $Z = 4$, $a = 15.737$ (2) Å, $b = 9.912$ (2) Å, $c = 16.901$ (4), $\beta = 100.53$ (2)°.

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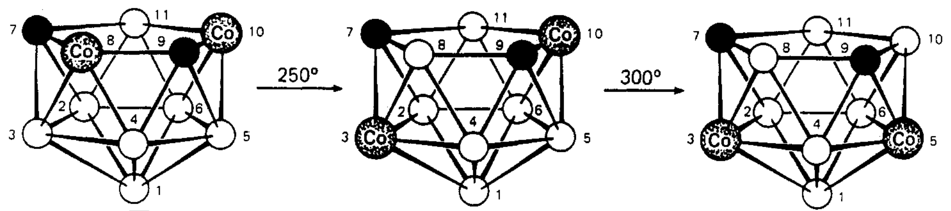

III IV V

**Figure 3.** Proposed structures and observed rearrangements of *nido*-8,10-($\eta$-$C_5(CH_3)_5)_2Co_2$-7,9-$S_2B_7H_7$ (III), *nido*-3,10-($\eta$-$C_5(CH_3)_5)_2Co_2$-7,9-$S_2B_7H_7$ (IV), and *nido*-3,5-($\eta$-$C_5(CH_3)_5)_2Co_2$-7,9-$S_2B_7H_7$ (V). The Cp* ligands are not shown.

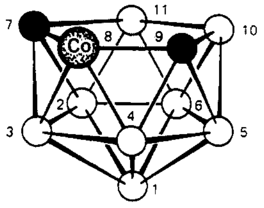

**Figure 4.** Proposed structure for *nido*-8-($\eta$-$C_5(CH_3)_5$)Co-7,9-$S_2B_8H_8$ (VI). The Cp* ligand is not shown.

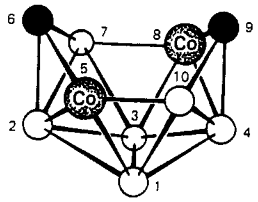

**Figure 5.** Proposed structure for *nido*-5,8-($\eta$-$C_5(CH_3)_5)_2Co_2$-6,9-$S_2B_6H_6$ (VII). The Cp* ligands are not shown.

isoelectronic (in a cluster sense) with compounds III, IV, and V and is proposed to have a similar gross geometry. The $^{11}B$ NMR spectrum shows evidence for a molecular mirror plane, and the 2D $^{11}B$–$^{11}B$ NMR spectra show connectivities supporting the structure shown in Figure 4.

Two compounds containing six borons were isolated in trace amounts. VIII is the Cp* analogue of the previously characterized[2] cluster *arachno*-7-($\eta$-$C_5H_5$)Co-6,8-$S_2B_6H_8$ and is the only compound isolated in the above reaction that retained two bridging hydrogens. The compound thus adopts the arachno structure shown in Figure 5, which is based on an octadecahedron missing two adjacent vertices. Also found was *nido*-5,8-$(Cp^*)_2Co_2$-6,9-$S_2B_6H_6$ (VII), which is a dithiaborane analogue of metallacarborane clusters such as 6-($\eta^6$-$MeC_6H_5$)Fe-9,10-$C_2B_7H_{11}$[15] and 2,5-($\eta$-$C_5H_5)_2Co_2$-6,7-$Me_2C_2B_6H_8$[16] and, like these compounds, is proposed to adopt a structure derived from an octadecahedron by removal of one vertex. The $^{11}B$ NMR spectrum, which contains three doublets of equal intensity, and the $^1H$ NMR spectrum, which has only one Cp* resonance, strongly support a skeletal arrangement, such as shown in Figure 6, having a 2-fold rotation axis.

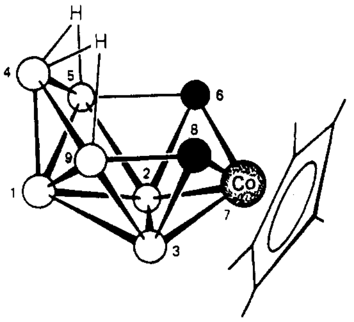

**Figure 6.** Proposed structure for *arachno*-7-($\eta$-$C_5(CH_3)_5$)Co-6,8-$S_2B_6H_8$ (VIII).

It is surprising that I is the major product of the $CoCl_2$ reaction since its formation requires extensive degradation ($-B_5H_7$) of the starting *arachno*-6,8-$S_2B_7H_9$ cage framework. It is possible that if the reaction were carried out under different conditions, less extensive fragmentation would occur, resulting in a different product distribution. Indeed, the reaction of cobalt atoms with *arachno*-6,8-$S_2B_7H_9$ and pentamethylcyclopentadiene in a toluene matrix also resulted in cage degradation but gave the six-boron cluster *arachno*-7-Cp*Co-6,8-$S_2B_6H_8$ (VIII) as the major product ($-B_2H$). However, VIII was the only product in the metal vapor reaction found in more than trace amounts. The other isolated complexes included I, V, VI, and $[(Cp^*)_2Co]^+[(SB_{10}H_{10})_2Co]^-$ and obviously arise from recombination or degradation reactions.

The work presented here has resulted in the production of a variety of new cobaltadithiaborane clusters with cage framework compositions including $S_2B_2$ and the $S_2B_5$–$S_2B_8$ series. These results also suggest that an even wider range of both dithia or higher sulfur-containing clusters are possible and that the cage structures exhibited by these new hybrid clusters may well provide the structural bridges between electron-deficient and electron-precise cluster systems.

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