A possible structure of the AlB_6H_{13} repeating unit is illustrated in Figure 4. This arrangement is based upon a "3403" structural model for B_7H_{13}, which is favored over other possible geometries because of the maximum use of closed three-center bonding. Further confirmation of this structure must await a complete characterization, which is complicated by difficulties in preparation of sufficient quantities of B_4H_{10} for the preparative reaction. However, the observed physical properties of AlB_6H_{13} indicate a polymeric species similar to AlB_4H_{11}.

As noted previously, the great thermal stability of the aluminoborane compounds is primarily a result of polymerization. Additional stabilization of the aluminoborane framework may be attributed to a greater bonding overlap made possible by the larger aluminum orbitals. Also, polymerization blocks the apex cage position in such a manner that a decomposition mechanism involving the apex could be kinetically inhibited. Detailed studies of B_5H_{11} and B_6H_{12} pyrolyses might provide evidence for this.

Upon an overall examination of the known compounds of aluminum, hydrogen, and boron, it is evident that a polymeric structural configuration such as that found in $(AlH_3)_x$ is most commonly adopted. Forms such as $Al(B_3H_8)_3$ and $Al(B_4H_9)_3$ would be sterically hindered and unstable with respect to decomposition to a polymeric aluminoborane species with one borane group per aluminum. The existence of $Al(BH_4)_3$ as a volatile, monomeric compound is correlated with the lower steric requirements of the BH_4^- group. As such, $Al(BH_4)_3$, the first covalent metalloborane to be isolated,[29] proves an exception to the general structural trend of aluminoborane compounds.

Acknowledgment. F.L.H. sincerely thanks the Colgate-Palmolive Co. for their gift of a fellowship for 1978–1979.

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Metal Atom Syntheses of Metallaboron Clusters. 2. Synthesis of Cobaltathiaborane and Cobaltadithiaborane Complexes. Crystal and Molecular Structures of 2,3,6-$(\eta\text{-}C_5H_5)_2Co_2SB_5H_7$ and 7,6,8-$(\eta\text{-}C_5H_5)CoS_2B_6H_8$

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Abstract: The reactions of cobalt atoms with three different boron hydrides in the presence of cyclopentadiene and various sulfur reagents were examined and found to yield several novel cobaltathiaborane and cobaltadithiaborane complexes. The reaction of pentaborane(9) and cyclopentadiene with cobalt atoms followed by reaction with elemental sulfur yielded 6,8,7,9-$(\eta\text{-}C_5H_5)_2Co_2S_2B_5H_5$ (I), the structure of which was assigned on the basis of the spectroscopic data. If cyclohexene sulfide is used in place of sulfur in the above reaction, improved yields of I are obtained along with a new compound which was identfied as 2,3,6-$(\eta\text{-}C_5H_5)_2Co_2SB_5H_7$ (II). The structure of II was established by a single-crystal X-ray determination and has a cage geometry that can best be described as a tricapped trigonal prism missing one equatorial vertex. Although this structure is predicted by electron-counting rules, this is the first time it has been observed for an eight-vertex, $2n + 4$ skeletal electron system. Crystal data for II: space group $P2_1/c$; $Z = 4$, $a = 8.838$ (4) Å, $b = 22.019$ (19) Å, $c = 7.910$ (4) Å, $\beta = 114.96$ (1)°; $V = 1395$ (3) Å^3. The structure was refined by full-matrix least squares to a final R of 0.051 and R_w of 0.049 for the 1233 reflections which had $F_o^2 > 3\sigma(F_o^2)$. The reaction of hexaborane(10) and cyclopentadiene with cobalt atoms followed by reaction with cyclohexene sulfide yielded 7,6,8-$(\eta\text{-}C_5H_5)CoS_2B_6H_8$ in moderate yields. The structure of II was established by a single-crystal X-ray determination and shown to be consistent with structures observed for other 9-atom, $2n + 6$ skeletal electron systems. Crystal data for III: space group $P2_1/n$; $Z = 4$, $a = 6.862$ (5) Å, $b = 16.703$ (5) Å, $c = 10.037$ (2) Å, $\beta = 100.11$ (1)°; $V = 1132$ (1) Å^3. The structure was refined to a final R of 0.029 and $R_w = 0.034$ for the 1528 reflections which had $F_o^2 > 3\sigma(F_o^2)$. Finally, the reaction of cobalt atoms with cyclopentadiene followed by reaction with decaborane(14) and cyclohexene sulfide was found to yield the previously known compound 1,2-$(\eta\text{-}C_5H_5)CoSB_{10}H_{10}$ in low yield.

Introduction

In 1967 Muetterties[2] was the first to report the synthesis and chemistry of polyhedral boron clusters in which sulfur had been incorporated into the cage system. Since that time several additional thiaboranes and metallathiaboranes have been discovered; however, these have been limited to the larger cage systems which possess sufficient stability to withstand the synthetic conditions normally required for sulfur insertions. Therefore, until the present work, no compounds derived from the smaller boron hydrides have been reported.

We have previously demonstrated the first application of the metal atom technique to the synthesis of metallaborane clusters[3,4] and reported that these unusual reaction conditions have several synthetic advantages. In addition, we have also shown[4,5] that it is possible to use metal atom reactions to incorporate other molecules into these clusters such as the direct insertion of alkynes to form metallacarborane complexes. We have now applied these techniques to the synthesis of various heteroatom metallaboranes complexes and report here our work which has resulted in the synthesis of the first small cage metallathiaborane and metalladithiaborane clusters.

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Table I. ^{11}B NMR Data

compd[a]	δ[b] (*J*, Hz)	rel areas
I 6,8,7,9-(η-(C_5H_5)$_2Co_2S_2B_5H_5$[c]	−11.7 (169)	4
	−15.9 (184)	1
II 2,3,6-(η-C_5H_5)$_2Co_2SB_5H_7$	+100.9 (158)	1
	+6.6 (156)	1
	−4.0 (145)	1
	−22.1 (167)	1
	−32.1 (154)	1
III 7,6,8-(η-C_5H_5)$CoS_2B_6H_8$[c]	+4.8 (156)	2
	−9.8 (166)	2
	−33.7 (153)	1
	−40.2 (143)	1

[a] All complexes were run in CH_2Cl_2 with internal C_6D_6 lock material. [b] Chemical shifts referenced to boron trifluoride etherate, with positive values indicating a shift to lower fields (less shielding). [c] ^{11}B NMR spectrum at 115.5 MHz.

Table II. 100-MHz ^1H NMR Data

compd[a]	δ[b] (rel area)	assignt
I 6,8,7,9-(η-C_5H_5)$_2Co_2S_2B_5H_5$	4.52 (10)	C_5H_5
	2.33 (4)	B-H
II 2,3,6-(η-C_5H_5)$_2Co_2SB_5H_7$	4.69 (5)	C_5H_5
	4.58 (5)	C_5H_5
	11.84 (1)	B-H
	3.79 (1)	B-H
	3.28 (1)	B-H
	0.07 (1)	B-H
	−3.90 (2)[c]	B-H-B
III 7,6,8-(η-C_5H_5)$CoS_2B_6H_8$	5.32 (5)	C_5H_5
	3.19 (4)[c]	B-H
	1.76 (1)	B-H
	0.46 (1)	B-H
	−1.56 (2)	B-H-B

[a] All complexes were run in CS_2 solution with C_6D_6 internal lock material. [b] Parts per million relative to $(CH_3)_4Si$, with positive sign indicating a shift to lower field (less shielding). [c] Overlapping resonance.

Table III. Infrared Data

compd	IR absorptions, cm^{-1}
I 6,8,7,9-(η-C_5H_5)$_2Co_2S_2B_5H_5$[a, b]	2960 (s), 2940 (vs), 2860 (s), 2560 (sh), 2545 (s), 2250 (br), 1750 (m), 1275 (m), 1023 (m), 1005 (sh), 845 (sh), 825 (sh), 815 (s), 720 (w), 580 (br), 505 (br)
II 2,3,6-(η-C_5H_5)$_2Co_2SB_5H_7$[a,c]	2961 (m), 2925 (s), 2858 (m), 2525 (sh), 2501 (s), 2225 (m,br), 1730 (w), 1252 (m), 1090 (w), 1001 (m), 930 (m), 889 (sh), 811 (sh), 800 (m), 540 (br), 440 (br)
III 7,6,8-(η-C_5H_5)$CoS_2B_6H_8$[a,c]	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)

[a] Carbon disulfide solution. [b] Perkin-Elmer 337. [c] Perkin-Elmer 521.

Experimental Section

Materials. Cobalt metal (99.9%, 50 mesh) was obtained from Alfa-Ventron Corp. Cyclopentadiene was freshly distilled from dicyclopentadiene (Aldrich). Pentaborane(9) was obtained from laboratory stock, while Shore's method[6] was used to prepare hexaborane(10) and 1-bromopentaborane(9).[7] Decaborane(14) was obtained from Callery Chemical Co. and sublimed before use. All other reagents were commercially obtained, as indicated, and used as received.

Preparative thin-layer chromatography was conducted on 0.5 mm (20 × 20 cm) silica gel F-254 plates (Merck).

Physical Measurements. Boron-11 and proton Fourier transform NMR spectra at 32.1 and 100 MHz, respectively, were obtained on a JEOL PS-100 spectrometer equipped with the appropriate decoupling accessories. Boron-11 NMR spectra, at 115.5 MHz, were obtained on a Bruker WH-360 Fourier transform spectrometer located in the Mid-Atlantic Regional NMR Facility. All boron-11 chemical shifts were referenced to BF_3–$O(C_2H_5)_2$ = 0.0 ppm with a negative sign indicating an upfield shift and are presented in Table I. All proton chemical shifts (Table II) were measured relative to internal residual benzene from the lock solvent (99.9% C_6D_6) and then referenced to Me_4Si = 0.00 ppm. High- and low-resolution mass spectra were obtained on a Hitachi Perkin-Elmer RMH-2 mass spectrometer which is interfaced to an Kratos DS50S data system. Infrared spectra were obtained on either a Perkin-Elmer 521 or a Perkin-Elmer 337 spectrophotometer. All melting points are uncorrected.

General Procedure. The metal atom apparatus employed in these studies was based on a design published by Klabunde[8] and is described elsewhere.[4,9]

In a typical reaction, approximately 0.6 g of cobalt is placed in the evaporation crucible and cobalt vapor is generated by electrical heating (~7.2 V, 60 A). This vapor is then cocondensed over a 1–2-h period with the substrate vapor on the walls of the reactor which are maintained at −196 °C. A large excess of the desired substrates, typically 10 mL of each ligand, is used. In those reactions involving low volatile substrates, a large excess of the ligand (approximately 3 g) is placed in the bottom of the reaction vessel before assembly. After metal deposition is complete, the matrix is allowed to warm gradually to room temperature, followed by removal of the volatiles in vacuo. The reactor is then vented with an inert gas, and the residue remaining in vessel is extracted and filtered. The extract is then separated and purified by normal techniques discussed below. Typically only approximately 50% of the metal contained in the crucible is vaporized. Thus, the yields reported are calculated only on the basis of the metal vaporized and assume only 50% of the vapor reaches the reaction zone.

Reaction of Cobalt Vapor with B_5H_9, C_5H_6, and Sulfur. Cobalt vapor (~0.3 g) was cocondensed with 15 mL of pentaborane(9) and 15 mL of cyclopentadiene at −196 °C. Upon completion of metal evaporation and ligand cocondensation, the reactor was warmed and the condensate allowed to melt and flow to the bottom of the reactor where it was mixed with 3.5 g of powdered sulfur (Baker). This solution was stirred for 30 min. All of the excess volatile reactants were removed in vacuo, and the residue was extracted in methylene chloride. This extract was filtered through a course frit funnel and separated by TLC on silica gel by using a 40% benzene in carbon tetrachloride solution. The resultant separation gave two boron-containing products: I, 6,8,7,9-(η-C_5H_5)$_2Co_2S_2B_5H_5$, R_f = 0.61, red, 25 mg (5.3%), mp 160 °C dec, mass measurement calcd for $^{12}C_{10}{}^{1}H_{15}{}^{32}S_2{}^{11}B_5{}^{59}Co_2$ 371.9745, found 371.9742 (slightly air sensitive); the previously discovered cobaltaborane compound, 1,2-(η-C_5H_5)$_2Co_2B_4H_6$, 2.0 mg (0.5%), which was identified by comparison of its mass spectral and ^{11}B NMR data with literature values.[10]

Reaction of Cobalt Vapor with B_5H_9, C_5H_6, and Cyclohexene Sulfide. Cobalt vapor (0.3 g) was cocondensed with a mixture of 15 mL of pentaborane(9) and 15 mL of cyclopentadiene at −196 °C. Upon completion of metal vaporization and ligand cocondensation, the reactor was warmed to room temperature and the condensate allowed to melt and flow to the bottom of the reactor where it was mixed with 5 mL of cyclohexene sulfide ($C_6H_{10}S$) (Alfa). This mixture was stirred for 30 min at room temperature. Removal of the excess ligands in vacuo left a brown residue which was readily extracted in methylene chloride solution. Filtration of the extract by a course frit funnel and separation of the resultant mother liquor by TLC on silica gel plates using carbon tetrachloride as the eluant gave I (R_f 0.32, red, 26.2 mg (5.5%)) and a new metallathiaborane cluster II (2,3,6-(η-C_5H_5)$_2Co_2SB_5H_7$, R_f = 0.38, green, 30.8 mg (7.1%), mp 175 °C dec, mass measurement calcd for $^{12}C_{10}{}^{1}H_{17}{}^{32}S_1{}^{11}B_5{}^{59}Co_2$ 342.0180, found 342.0148).

Reaction of Cobalt Vapor with B_6H_{10}, C_5H_6, and Cyclohexene Sulfide. In a similar manner, 0.3 g of cobalt vapor was reacted with 7 mL of hexaborane(10) and 15 mL of cyclopentadiene. Upon completion of metal vaporization and ligand cocondensation, the matrix was allowed to melt and flow to the bottom of the reactor where it was mixed with

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5 mL of cyclohexene sulfide. This mixture was stirred at room temperature for 30 min. Removal of the excess ligands in vacuo left a brown residue which was extracted in methylene chloride. This solution was filtered, and the products were separated by TLC on silica gel plates using a 10% benzene in hexanes solution as the elution solvent. This separation gave a single boron-containing product: III, 7,6,8-(η-C_5H_5)-$CoS_2B_6H_8$ R_f = 0.25, violet, 216 mg (32.4%), mp 149 °C dec, mass measurement calcd for $^{12}C_5{}^1H_{13}{}^{32}S_2{}^{11}B_6{}^{59}Co_1$ 262.0350, found 262.0368.

Reaction of Cobalt Vapor with $B_{10}H_{14}$, C_5H_6, and Sulfur. Before metal deposition was begun, decaborane(14) (4 g) and elemental sulfur (4.0 g) were placed in the bottom of the metal atom reactor. Then cobalt vapor (0.3 g) and 20 mL of cyclopentadiene were cocondensed on the walls of the reactor at −196 °C. After metal evaporation was complete, the reactor was allowed to warm to room temperature and the matrix melted into the $B_{10}H_{14}$/sulfur mixture. This mixture was stirred at room temperature for 30 min. The volatile materials were removed in vacuo, the reactor was opened to the air, and the residue was extracted with CH_2Cl_2, filtered, and evaporated to dryness. Excess $B_{10}H_{14}$ was removed by vacuum sublimation and the remaining residue separated by TLC on silica gel using chloroform as the eluant to give one product, 1,2-(η-C_5H_5)$CoSB_{10}H_{10}$[2] (R_f = 0.73, 2.8 mg (0.4%)).

The reaction was repeated except this time $B_{10}H_{14}$ (2.0 g) and elemental sulfur (3.0 g) were dissolved in 25 mL of carbon disulfide and this solution was placed in the bottom of the metal atom reactor. The reaction was then carried out in the manner described. Again, only small amounts of 1,2-(η-C_5H_5)$CoSB_{10}H_{10}$ (2 mg) were formed.

Reaction of Cobalt Vapor with $B_{10}H_{14}$, C_5H_6, and Cyclohexene Sulfide. Before metal deposition was begun, decaborane(14) (3.0 g) was placed into the bottom of the metal atom reactor. Then cobalt vapor (0.3 g), cyclopentadiene (20 mL), and cyclohexene sulfide (4.0 mL) were cocondensed on the walls of the reactor at −196 °C. After metal evaporation was complete, the reactor was allowed to warm to room temperature and the matrix melted into the decaborane(14). This mixture was stirred at room temperature for 30 min. The volatile materials were removed in vacuo, the reactor was opened to the air, and the residue was extracted with methylene chloride, filtered, and evaporated to dryness. Excess decaborane(14) was removed by vacuum sublimation and the remaining residue separated by TLC on silica gel using chloroform as the eluant. Two major boron-containing products were isolated and identified by their mass spectra and ^{11}B NMR data to be the known compounds 1,2-(η-C_5H_5)$CoSB_{10}H_{10}$[2] (R_f = 0.74, 3.3 mg (0.5%)) and 5-(η-C_5H_5)CoB_9H_{13}[10] (R_f = 0.80, 4.1 mg (0.4%)).

Crystallographic Data for 2,3,6-(η-C_5H_5)$_2Co_2SB_5H_7$. Irregularly shaped hexagonal green crystals of 2,3,6-(η-C_5H_5)$_2Co_2SB_5H_7$, prepared in the metal atom reaction of cobalt vapor with pentaborane(9), cyclopentadiene, and cyclohexene sulfide, were grown over a 16-h period by vapor diffusion of heptane into a carbon disulfide solution of the compound. One of these irregularly shaped (0.35 × 0.39 × 0.03 mm) crystals was mounted on a glass fiber and on the basis of good preliminary precession photographs was selected for data collection. Systematic absences for $k = 2n + 1$ on $0k0$ and $l = 2n + 1$ on $h0l$ uniquely establish the space group as $P2_1/c$. The crystal was then mounted on the diffractometer, and the Enraf-Nonius program SEARCH was used to obtain 12 accurately centered reflections which were then used in the program INDEX to obtain an orientation matrix for data collection and also to provide approximate cell dimensions. Refined cell dimensions and their standard deviations were obtained from least-squares refinement of 25 accurately centered reflections. The mosaicity of the crystal was judged acceptable on the basis of several theta scans. Crystal data for $Co_2SC_{10}B_5H_{17}$: mol wt 341.23, space group $P2_1/c$; Z = 4, a = 8.838 (4) Å, b = 22.019 (19) Å, c = 7.910 (4) Å, β = 114.96 (1)°; V = 1395 (3) Å^3; ρ(calcd) = 1.624 g cm^{-3}.

Crystallographic Data for 7,6,8-(η-C_5H_5)$CoS_2B_6H_8$. Several irregular shaped violet crystals of 7,6,8-(η-C_5H_5)$CoS_2B_6H_8$, prepared in the metal atom reaction of cobalt vapor with hexaborane(10), cyclopentadiene, and cyclohexene sulfide, were grown over a 24-h period by vapor diffusion of pentane in a carbon disulfide solution of the compound. One of these crystals was cut to a suitable size (0.23 × 0.23 × 0.05 mm), mounted on a glass fiber, and on the basis of good preliminary precession photographs was selected for data collection. Systematic absences for $k = 2n + 1$ on $0k0$ and $h + l = 2n + 1$ on $h0l$ uniquely establish the space group as $P2_1/n$. Refined cell dimensions and their standard deviations were again obtained from the least-squares refinement of 25 accurately centered reflections. The mosaicity of the crystal was judged acceptable on the basis of several theta scans. Crystal data for $CoS_2C_5B_6H_{13}$: mol wt 261.09, space group $P2_1/n$; Z = 4, a = 6.862 (5) Å, b = 16.703 (5) Å, c = 10.037 (2) Å, β = 100.11 (1)°; V = 1132 (1) Å^3; ρ(calcd) = 1.531 g cm^{-3}.

Collection and Reduction of the Data. Diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP 8/A computer, using Mo Kα radiation from a highly oriented graphite crystal monochrometer. A combined θ–2θ and ω scan technique was used to record the intensities for all reflections for which $1.0 < 2\theta < 50°$. Scan widths (SW) were calculated from the formula SW = $A + B \tan \theta$, where A is estimated from thee mosaicity of the crystal and B allows for the increase in peak width due to Kα_1 and Kα_2 splitting. The values for A and B for 2,3,6-(η-C_5H_5)$_2Co_2SB_5H_7$ were 0.5 and 0.35, respectively. The values for A and B for 7,6,8-(η-C_5H_5)-$CoS_2B_6H_8$ were 0.6 and 0.35, respectively. This calculated scan angle was extended at each side by 25% for background determination (BG1 and BG2). The net count (NC) was then calculated as NC = TOT − 2(BG1 + BG2) where TOT is the estimated peak intensity. Reflection data were considered insignificant if intensities registered less than 30 counts above background on a rapid prescan; such reflections were rejected automatically by the computer. The intensities of three standard reflections measured at intervals of 100 reflections showed no systematic change during data collection. The raw intensities were then corrected for Lorentz and polarization effects using the Enraf-Nonius program DATARED. Of the 2638 measured intensities for 2,3,6-(η-C_5H_5)$_2Co_2SB_5H_7$, 1233 had $F_o^2 > 3\sigma(F_o^2)$ and were used in analysis. Of the 2103 measured intensities for 7,6,8-(η-C_5H_5)$_2CoS_2B_6H_8$, 1528 had $F_o^2 > 3\sigma(F_o^2)$.

Solution and Refinement of the Structure. All calculations were performed on a PDP 11/60 computer using the Enraf-Nonius structure package.[11] The full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights (w) were taken as $(4F_o/\sigma(F_o)^2)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber[12] and those for hydrogen from Stewart.[13] The effects of anomalous dispersion were included in E_c by using Cromer and Ibers' values[14] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

2,3,6-(η-C_5H_5)$_2Co_2SB_5H_7$. Normalized structure factors were calculated by using a K curve. The intensity distribution statistics support a centrosymmetric space group. The coordinates of the two cobalt atoms were located from a three-dimensional Patterson synthesis. The sharpened Patterson map gave a large peak at (0.304, 0.0, 0.158), indicating that the y coordinates of the two cobalt atoms must be equal. The y coordinates for the two cobalt atoms were then obtained from the large Patterson peak (0.0, 0.241, 0.5) corresponding to the Harker line $(0, {}^1/_2 - 2y_{1\text{ or }2}, {}^1/_2)$. Following Donohue and Trueblood's method[15] of interpreting multimetal Patterson maps, the location of the respective x and z coordinates from the relationships $(0.0, 0.5, 0.0) \rightarrow (2x_1, {}^1/_2, {}^1/_2 - 2z_1)$ and $(0.652, 0.5, 0.368) \rightarrow (2x_2, {}^1/_2, {}^1/_2 + 2z_2)$ were obtained.

Full-matrix least-squares refinement of these cobalt coordinates, using preliminary scale and thermal parameters obtained from a Wilson plot, showed minimal shifting. An electron density map phased on the two refined cobalt atoms yielded the sulfur atom and ten carbon atoms from the two cyclopentadienyl rings. Several cycles of isotropic refinement on these new atom positions and a Fourier map phased on all of these refined positions led to the location of all of the cage boron atoms. Several cycles of anisotropic refinement on all of these parameters followed by a difference Fourier synthesis located four of the cyclopentadienyl hydrogen atoms as well as three terminal hydrogens on the cage boron atoms. Subsequent anisotropic refinement on all of the nonhydrogen atoms and isotropic refinement on all of the hydrogen atoms followed by another difference Fourier synthesis led to the location of the remaining two terminal hydrogens on the cage boron atoms as well as the two boron–boron bridging hydrogen positions. The remaining cyclopentadienyl hydrogen (HC25) could not be isolated, so its position was calculated and included (but not refined) in the structure factor calculations. Final refinement with an absorption correction (transmission coefficient: maximum 92.96, minimum 58.64) including anisotropic thermal parameters for nonhydrogen atoms and fixed isotropic thermal parameters for the hydrogen atoms led to the final residual factors R = 0.051 and R_w = 0.049.

The final positional and thermal parameters for 2,3,6-(η-C_5H_5)$_2Co_2SB_5H_7$ are given in Table IV. Intramolecular bond distances, selected bond angles, and molecular planes are presented in Tables V, VI, and VII, respectively.

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Table IV. Final Positional and Thermal Parameters for 2,3,6-$(\eta\text{-}C_5H_5)_2Co_2SB_5H_7$[a]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Co3	−0.3269 (1)	0.62693 (6)	−0.3911 (1)	0.0155 (2)	0.00247 (3)	0.0191 (2)	−0.0019 (2)	0.0100 (3)	−0.0007 (2)
Co2	−0.0152 (1)	0.62189 (7)	−0.2413 (1)	0.0150 (2)	0.00266 (3)	0.0167 (2)	−0.0003 (1)	0.0140 (3)	0.0003 (2)
S6	−0.1800 (3)	0.5435 (1)	−0.3284 (4)	0.0259 (4)	0.00238 (6)	0.0267 (5)	−0.0007 (4)	0.0277 (6)	−0.0019 (4)
C31	−0.393 (1)	0.6662 (5)	−0.650 (1)	0.018 (2)	0.0049 (3)	0.020 (2)	−0.001 (1)	0.009 (3)	0.008 (1)
C32	−0.549 (1)	0.6707 (5)	−0.499 (1)	0.024 (2)	0.0049 (4)	0.041 (3)	0.010 (1)	0.036 (3)	0.008 (2)
C33	−0.469 (1)	0.6116 (5)	−0.672 (1)	0.026 (2)	0.0039 (3)	0.020 (2)	−0.000 (2)	0.007 (3)	−0.001 (2)
C34	−0.436 (1)	0.7030 (4)	−0.538 (2)	0.026 (2)	0.0024 (3)	0.040 (3)	−0.002 (1)	0.013 (4)	−0.000 (2)
C35	−0.567 (1)	0.6136 (5)	−0.577 (2)	0.011 (1)	0.0049 (4)	0.041 (3)	−0.004 (1)	0.011 (3)	0.005 (2)
C21	0.116 (1)	0.6906 (5)	−0.291 (1)	0.019 (2)	0.0037 (3)	0.051 (3)	0.000 (1)	0.035 (3)	0.010 (2)
C22	0.211 (1)	0.6610 (6)	−0.137 (1)	0.019 (2)	0.0069 (4)	0.024 (2)	−0.012 (1)	0.016 (3)	−0.002 (2)
C23	0.137 (1)	0.5975 (6)	−0.368 (2)	0.031 (2)	0.0045 (3)	0.070 (3)	−0.006 (1)	0.072 (3)	−0.008 (2)
C24	0.071 (1)	0.6512 (6)	−0.430 (1)	0.020 (2)	0.0089 (5)	0.018 (2)	−0.007 (2)	0.016 (3)	0.003 (2)
C25	0.230 (1)	0.6033 (5)	−0.176 (2)	0.019 (1)	0.0042 (3)	0.073 (3)	0.011 (1)	0.045 (3)	0.019 (2)
B1	−0.169 (1)	0.6790 (5)	−0.181 (1)	0.013 (1)	0.0025 (3)	0.012 (2)	−0.004 (1)	0.008 (2)	−0.001 (1)
B4	−0.278 (1)	0.6295 (6)	−0.099 (1)	0.029 (2)	0.0031 (3)	0.025 (2)	0.003 (2)	0.029 (3)	−0.001 (2)
B5	−0.054 (1)	0.6339 (6)	0.014 (1)	0.026 (2)	0.0035 (4)	0.017 (2)	−0.002 (2)	0.015 (3)	−0.002 (2)
B8	−0.163 (2)	0.5719 (7)	0.059 (2)	0.032 (2)	0.0050 (5)	0.019 (2)	−0.003 (2)	0.025 (4)	0.001 (2)
B7	−0.296 (1)	0.5531 (6)	−0.183 (2)	0.027 (2)	0.0035 (4)	0.026 (3)	−0.005 (2)	0.025 (4)	0.001 (2)

atom[b]	*x*	*y*	*z*	atom[b]	*x*	*y*	*z*
HB4	−0.389 (7)	0.647 (3)	−0.096 (9)	HC35	−0.628 (7)	0.593 (3)	−0.578 (8)
HB5	0.024 (7)	0.663 (3)	0.129 (8)	HC21	0.064 (7)	0.723 (3)	−0.304 (8)
HB8	−0.189 (7)	0.572 (3)	0.203 (9)	HC22	0.244 (7)	0.671 (3)	−0.021 (9)
HB7	−0.416 (7)	0.523 (3)	−0.235 (9)	HC23	0.109 (7)	0.552 (3)	−0.379 (9)
HB5-8	−0.017 (7)	0.576 (3)	0.055 (9)	HC24	−0.004 (7)	0.654 (3)	−0.555 (9)
HC31	−0.321 (7)	0.677 (3)	−0.705 (9)	HC25	0.295 (0)	0.573 (0)	−0.099 (0)
HC32	−0.599 (7)	0.681 (3)	−0.437 (9)	HB1	−0.166 (7)	0.718 (3)	−0.168 (8)
HC33	−0.455 (7)	0.574 (3)	−0.715 (9)	HB7-8	−0.250 (7)	0.550 (3)	−0.028 (9)
HC34	−0.392 (6)	0.741 (3)	−0.506 (9)				

[a] The form of the anisotropic thermal parameter is $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$. [b] B = 4.1000 (0) Å^2.

Table V. Intramolecular Bond Distances (Å) for 2,3,6-$(\eta\text{-}C_5H_5)_2Co_2SB_5H_7$

Co3–C31	2.067 (8)	HB1–B1	0.85 (6)
Co3–C32	2.024 (9)	HB4–B4	1.06 (5)
Co3–C33	2.070 (9)	HB5–B5	1.09 (6)
Co3–C34	2.033 (9)	HB8–B8	1.25 (6)
Co3–C35	2.032 (9)	HB7–B7	1.17 (5)
Co3–S6	2.182 (2)	HB5-8–B5	1.32 (6)
Co3–Co2	2.500 (1)	HB5-8–B8	1.31 (6)
Co3–B1	2.019 (8)	HB7-8–B8	0.93 (7)
Co3–B4	2.168 (9)	HB7-8–B7	1.12 (8)
Co3–B7	2.25 (1)	C31–C34	1.37 (1)
Co2–C21	2.043 (9)	C31–C33	1.35 (1)
Co2–C22	2.005 (9)	C33–C35	1.37 (1)
Co2–C23	2.06 (1)	C35–C32	1.38 (1)
Co2–C24	2.05 (1)	C32–C34	1.37 (1)
Co2–C25	2.047 (9)	C21–C22	1.33 (1)
Co2–S6	2.174 (2)	C21–C24	1.32 (1)
Co2–B1	2.049 (9)	C22–C25	1.34 (2)
Co2–B5	2.20 (1)	C25–C23	1.39 (2)
B1–B5	1.75 (1)	C23–C24	1.32 (2)
B1–B4	1.76 (1)	HC31–C31	0.94 (6)
B4–B7	1.79 (1)	HC32–C32	0.82 (6)
B4–B8	1.77 (1)	HC33–C33	0.92 (6)
B4–B5	1.80 (1)	HC34–C34	0.91 (6)
B5–B8	1.79 (2)	HC35–C35	0.71 (6)
B8–B7	1.83 (2)	HC21–C21	0.82 (6)
B7–S6	1.85 (1)	HC22–C22	0.86 (6)
HC23–C23	1.03 (6)	HC24–C24	0.93 (6)
HC25–C25	0.93 (1)		

Table VI. Selected Bond Angles (Deg) for 2,3,6-$(\eta\text{-}C_5H_5)_2Co_2SB_5H_7$

Co3–S6–B7	67.2 (4)	C21–Co2–C22	38.2 (4)
Co3–S6–Co2	70.04 (7)	B8–B7–Co3	63.7 (5)
Co2–Co3–B1	52.6 (2)	Co3–B7–S6	63.5 (4)
B1–Co3–B4	49.4 (4)	S6–B7–B8	113.5 (6)
B4–Co3–B7	47.9 (4)	C33–C31–C34	110.6 (9)
B7–Co3–S6	49.3 (3)	C31–C34–C32	105.7 (9)
S6–Co2–Co3	55.13 (7)	C34–C32–C35	109 (1)
Co3–Co2–B1	51.5 (2)	C32–C35–C33	107.2 (9)
B1–Co2–B5	48.5 (4)	C35–C33–C31	107.2 (9)
Co3–B1–Co2	75.9 (3)	C24–C21–C22	107 (1)
Co2–B1–B5	70.2 (5)	C21–C22–C25	110 (1)
B5–B1–B4	61.8 (5)	C22–C25–C23	105 (1)
Co3–B4–B1	60.9 (4)	C25–C23–C24	106 (1)
B1–B4–B5	59.0 (5)	C23–C24–C21	110 (1)
B5–B4–B8	60.3 (6)	B8–B7–HB8-7	24 (3)
B8–B4–B7	61.6 (6)	B7–HB8-7–B8	126 (7)
B7–B4–Co3	68.4 (5)	HB8-7(5)–B8–B7	30 (5)
Co2–B5–B1	61.3 (4)	B5–B8–HB5-8	47 (2)
B1–B5–B4	59.2 (5)	B8–HB5-8–B5	86 (3)
B4–B5–B8	59.0 (6)	HB5-8–B5–B8	46 (2)
B8–B5–Co2	113.5 (6)	C31–Co3–C34	39.0 (4)
B7–S6–Co2	100.7 (4)	C34–Co3–C32	39.3 (4)
B5–B8–B4	60.7 (6)	C32–Co3–C35	39.8 (4)
B4–B8–B7	59.8 (6)	C35–Co3–C33	39.0 (4)
B5–B8–B7	97.1 (7)	C33–Co3–C31	38.2 (4)
B5–Co2–S6	92.5 (3)	C22–Co2–C25	38.5 (5)
C25–Co2–C23	39.7 (5)	C23–Co2–C24	37.5 (4)
C24–Co2–C21	37.8 (5)	Co3–B1–B4	69.7 (4)

7,6,8-$(\eta\text{-}C_5H_5)CoS_2B_6H_8$. Normalized structure factors were calculated by using a K curve, and the intensity distribution statistics support a centrosymmetric space group. The coordinates of the cobalt atom were determined from a three-dimensional Patterson synthesis. Full-matrix least-squares refinement of these cobalt coordinates showed minimal shifting. An electron density map phased on the refined cobalt position yielded the two cage sulfur atoms and the five carbon atoms in the cyclopentadienyl ring. Several cycles of isotropic refinement, using preliminary scale and thermal parameters obtained from a Wilson plot, and a Fourier map phased on all of these refined positions led to the location of all of the cage boron atoms. Several cycles of anisotropic refinement on all of these parameters followed by a difference Fourier synthesis located all of the terminal hydrogens on the boron atoms as well as the five cyclopentadienyl hydrogens. Subsequent anisotropic refinements on all of the nonhydrogen atoms and isotropic refinement on all of the hydrogen atoms followed by another difference Fourier synthesis led to the locations of the two boron–boron bridging hydrogens. Final refinement with an absorption correction (transmission coefficient: maximum 0.91, minimum 0.69) including anisotropic thermal parameters on nonhydrogen atoms and fixed isotropic thermal parameters for the hydrogen atoms led to the final residual factors R = 0.029 and R_w = 0.034.

The final positional and thermal parameters for 7,6,8-$(\eta\text{-}C_5H_5)CoS_2B_6H_8$ are given in Table VIII. Intramolecular bond distances, selected bond angles, and molecular planes are presented in Tables IX, X, and XI, respectively.

Table VII. Selected Molecular Planes for $2,3,6\text{-}(\eta\text{-}C_5H_5)_2Co_2SB_5H_7$

atom	dev, Å	atom	dev, Å
Plane 1. Cyclopentadienyl Ring on Cobalt 3			
$-0.4535x + 0.3508y - 0.8193z = 9.5398$			
Atoms in Plane			
C31	0.014 (9)	C34	−0.018 (11)
C32	0.016 (11)	C35	−0.008 (11)
C33	−0.003 (10)		
Other Atoms			
HC31	0.051 (64)	HC34	−0.040 (62)
HC32	0.032 (63)	HC35	0.079 (62)
HC33	−0.166 (63)	Co3	−1.682 (1)
Plane 2. Cyclopentadienyl Ring on Cobalt 2			
$0.9575x + 0.2492y - 0.1450z = 5.9969$			
Atoms in Plane			
C21	0.006 (10)	C24	−0.001 (11)
C22	−0.008 (11)	C25	0.007 (11)
C23	−0.003 (11)		
Other Atoms			
HC21	−0.205 (66)	HC24	−0.086 (70)
HC22	−0.167 (66)	HC25	0.064 (0)
HC23	−0.440 (67)	Co2	−1.691 (1)

planes	dihedral angle, deg
1,2	103.2

Results

The reactions of cobalt atoms with three different boron hydrides in the presence of cyclopentadiene and either elemental sulfur or cyclohexene sulfide were studied. In all cases, structures of the new cobaltathiaborane products were deduced from ^{11}B and ^1H NMR data and infrared data (Tables I–III) as well as exact mass measurements. In two cases the structures were also confirmed by single-crystal X-ray structure determinations.

The reaction of cobalt atoms with pentaborane(9) and cyclopentadiene followed by reaction with elemental sulfur gave only one boron-containing product which was found to have a formula, $S_2B_5H_5Co_2(\eta\text{-}C_5H_5)_2$, based on exact mass determinations. The mass spectrum also showed peaks at *m/e* 189 ($CoCp_2^+$), *m/e* 124 ($CoCp^+$), *m/e* 64 (S_2^+), and *m/e* 32 (S^+), all of which support the proposed formulation. The ^{11}B NMR at 115.5 MHz (Figure 1) shows two overlapping doublets which upon proton decoupling gives two singlets in a 4:1 ratio, suggesting that the basic pentaborane(9) framework has been left intact. The 100-MHz ^1H NMR spectrum shows only one cyclopentadienyl resonance, indicating that the cobalt atoms must be in equivalent positions in the cage. A compound of this formula would be a $2n + 4$ electron system (9 cage atoms, 22 skeletal electrons) and according to simple electron counting rules[16] would be predicted to adopt an open-cage nine-vertex nido structure. The nine-vertex nido fragment which has previously been observed for compounds, such as $(CH_3)_2C_2B_7H_9$[17] is a bicapped square antiprism missing one equatorial position. All possible structures for $S_2B_5H_5Co_2(\eta\text{-}C_5H_2)_2$ which are based on this geometry would, however, be inconsistent with the spectroscopic data, since for each of these structures at least three different boron resonances would be expected. A second nido structure which has been observed for three other multimetal nine-atom, $2n + 4$ cluster systems, $CB_5H_5Ni_3(\eta\text{-}C_5H_5)_3$,[18] $(\eta\text{-}C_5H_5)_4Ni_4B_5H_5$,[19] and $(\eta\text{-}C_5H_5)_2Ni_2(CH_3)_2C_2B_5H_5$,[19] consists of a monocapped square antiprism. A nido structure for I based on this geometry, which is consistent with the spectroscopic data, is shown in Figure 1. Thus this structure leaves the basic pentaborane boron framework intact and has a $(\eta\text{-}C_5H_5)_2Co_2S_2$ unit substituted on the open face.

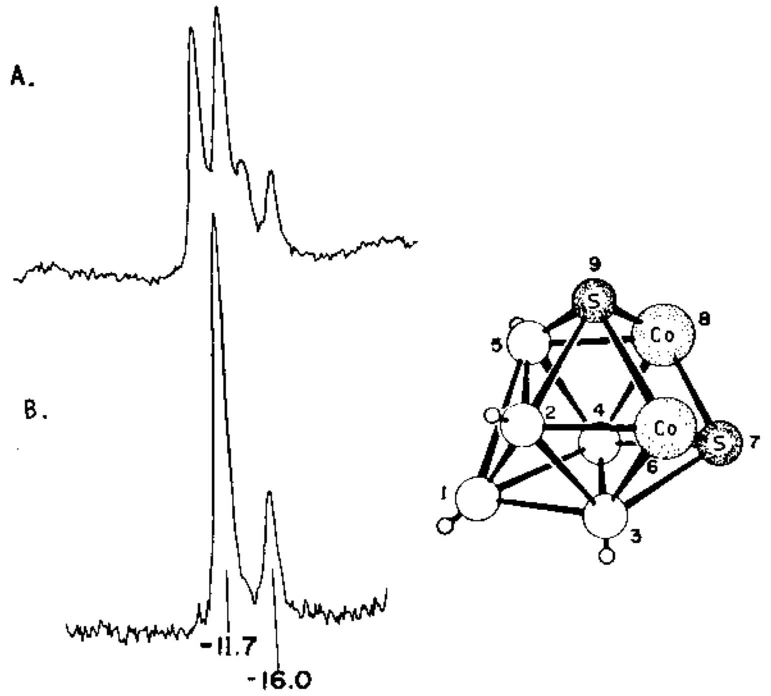

Figure 1. Proposed cage structure and 115.5-MHz ^{11}B NMR of $6,8,7,9\text{-}(\eta\text{-}C_5H_5)_2Co_2S_2B_5H_5$ (1) (bottom spectrum is proton spin decoupled).

An alternate closo structure for I must also be considered since previous work has shown that the addition of extra electrons in multimetal sulfur clusters does not always lead to an open-cage structure. In particular, studies[20] of $S_2Co_3(\eta\text{-}C_5H_5)_3$, which is also a $2n + 4$ electron system, have suggested that these electrons may be accommodated in metal–metal antibonding molecular orbitals resulting in the selective lengthening of metal–metal bonds rather than an opening of the cage. If this is the case for $S_2B_5H_5Co_2(\eta\text{-}C_5H_5)_2$, then the structure could be that of a closo tricapped trigonal prism, with an elongated cobalt–cobalt bond. This structure would also retain the pentaborane framework but, in addition, would allow the cobalt atoms to assume five-coordinate positions. In the limit where cobalt–cobalt bond lengthening is considerable, the structure shown in Figure 1 is reached. Unfortunately, due to the relative instability of this compound in air, we have been unable to grow suitable single crystals for a definitive crystallographic structural investigation.

The initial reactions employed elemental sulfur as a reactant and normally gave only 1–2% yields; however, a more efficient source of sulfur atoms was obtained, utilizing cyclohexene sulfide in place of elemental sulfur. A single metal atom reaction between pentaborane(9), cyclopentadiene, cyclohexene sulfide, and cobalt atoms not only gave improved yields of the red dimetallaborane cluster $6,8,7,9\text{-}(\eta\text{-}C_5H_5)_2Co_2S_2B_5H_5$ but also gave equal yields of a new green metallathiaborane cluster II.

$$\text{cobalt (atoms)} + C_5H_6 + B_5H_9 + \text{cyclohexene sulfide} \rightarrow \underset{\text{I}}{6,8,7,9\text{-}(\eta\text{-}C_5H_5)_2Co_2S_2B_5H_5} + \underset{\text{II}}{2,3,6\text{-}(\eta\text{-}C_5H_5)_2Co_2SB_5H_7}$$

In contrast to compound I, compound II was air stable for extended periods of time. Exact mass measurements on the parent ion supported a formula of $SB_5H_7Co_2(\eta\text{-}C_5H_5)_2$. This cluster is another 2n + 4 electron system (8 framework atoms, 20 skeletal electrons), and electron counting rules[16] would, therefore, predict an open-cage nido structure. The ^{11}B NMR data at 32.1 MHz (Figure 2) show five nonequivalent resonances all of equal intensity, indicating that the structure lacks a plane of symmetry. In addition, the resonance at low field may be assigned to a four-coordinate boron adjacent to two cobalt atoms.[21] The 100-MHz ^1H NMR spectrum shows two nonequivalent cyclopentadienyl resonances and, upon boron decoupling, the appropriate terminal B–H resonances as well as two nonequivalent

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Table VIII. Final Positional and Thermal Parameters for 7,6,8-(η-C_5H_5)$CoS_2B_6H_8$[a]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Co7	0.06358 (5)	0.23961 (2)	0.24657 (4)	0.01317 (8)	0.00222 (1)	0.00687 (4)	0.00026 (6)	0.00405 (9)	0.00048 (4)
S8	−0.2280 (1)	0.29407 (5)	0.26537 (9)	0.0128 (2)	0.00279 (3)	0.01349 (10)	−0.0003 (1)	0.0074 (2)	0.00087 (10)
S6	0.1974 (1)	0.32330 (5)	0.11460 (8)	0.0233 (2)	0.00315 (3)	0.00913 (8)	0.0001 (1)	0.0144 (2)	0.00123 (9)
C1	0.0046 (7)	0.1366 (3)	0.3398 (3)	0.037 (1)	0.0022 (2)	0.0165 (4)	0.0040 (7)	0.0300 (9)	0.0041 (4)
C2	0.1528 (8)	0.1374 (3)	0.1598 (3)	0.033 (1)	0.0029 (2)	0.0126 (4)	0.0034 (8)	0.0162 (11)	0.0000 (4)
C3	−0.0224 (8)	0.1237 (3)	0.2018 (4)	0.021 (1)	0.0022 (2)	0.0160 (5)	−0.0010 (8)	−0.0091 (12)	−0.0004 (4)
C4	0.2060 (9)	0.1597 (3)	0.3831 (4)	0.052 (2)	0.0027 (2)	0.0091 (4)	0.0056 (10)	−0.0100 (13)	0.0016 (4)
C5	0.2935 (7)	0.1611 (3)	0.2699 (5)	0.009 (1)	0.0027 (2)	0.0288 (6)	0.0027 (9)	0.0063 (13)	0.0044 (5)
B1	0.0692 (6)	0.4295 (2)	0.3298 (4)	0.0210 (9)	0.0028 (1)	0.0099 (4)	−0.0012 (6)	0.0064 (10)	−0.0028 (4)
B9	−0.1882 (6)	0.4048 (2)	0.2930 (4)	0.0198 (8)	0.0028 (2)	0.0120 (5)	0.0021 (6)	0.0099 (10)	−0.0003 (4)
B5	0.1568 (6)	0.4281 (2)	0.1717 (4)	0.0223 (9)	0.0027 (1)	0.0130 (5)	−0.0017 (7)	0.0110 (11)	0.0019 (5)
B2	0.2234 (5)	0.3458 (2)	0.3045 (3)	0.0127 (7)	0.0032 (2)	0.0084 (4)	−0.0016 (8)	0.0031 (9)	−0.0006 (4)
B3	0.0066 (7)	0.3305 (3)	0.3805 (3)	0.0167 (10)	0.0030 (2)	0.0072 (3)	−0.0004 (7)	0.0071 (9)	−0.0012 (4)
B4	−0.0775 (9)	0.4719 (3)	0.1869 (5)	0.0237 (13)	0.0018 (2)	0.0149 (5)	0.0004 (9)	0.0081 (12)	0.0008 (5)

atom[b]	*x*	*y*	*z*	atom[b]	*x*	*y*	*z*
HB3	0.025 (5)	0.316 (2)	0.489 (2)	HC2	0.160 (5)	0.133 (2)	0.066 (3)
HB1	0.134 (5)	0.473 (2)	0.408 (2)	HC1	−0.078 (5)	0.135 (2)	0.391 (2)
HB9	−0.281 (5)	0.433 (2)	0.354 (2)	HB4	−0.093 (5)	0.531 (2)	0.198 (3)
HC3	−0.110 (5)	0.112 (2)	0.148 (2)	HB4-5	−0.012 (5)	0.450 (2)	0.091 (3)
HB2	0.370 (5)	0.345 (2)	0.367 (2)	HB4-9	−0.232 (5)	0.440 (2)	0.168 (2)
HB5	0.274 (5)	0.473 (2)	0.149 (2)	HC5	0.401 (5)	0.173 (2)	0.272 (2)
HC4	0.268 (5)	0.171 (2)	0.467 (2)				

[a] The form of the anisotropic thermal parameter is $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$. [b] B = 2.6000 (0) Å.

Table IX. Intramolecular Bond Distances (Å) for 7,6,8-(η-C_5H_5)$CoS_2B_6H_8$

Co–S8	2.235 (1)	B1–HB1	1.10 (4)
Co–S6	2.231 (1)	B9–HB9	1.07 (4)
Co–B2	2.112 (4)	B9–HB9-4	1.38 (3)
Co–B3	2.109 (4)	B5–HB5-4	1.15 (4)
Co–C1	2.033 (4)	B5–HB5-4	1.34 (4)
Co–C2	2.058 (4)	B2–HB2	1.09 (4)
Co–C3	2.052 (6)	B3–HB3	1.11 (3)
Co–C4	2.036 (5)	B4–HB4	1.01 (3)
Co–C5	2.034 (6)	B4–HB9-4	1.17 (4)
S8–B9	1.883 (4)	B4–HB5-4	1.19 (3)
S8–B3	1.908 (5)	C1–C3	1.383 (8)
S6–B5	1.878 (4)	C1–C4	1.427 (9)
S6–B2	1.920 (4)	C2–C3	1.362 (11)
S6–B2	1.920 (4)	C2–C3	1.362 (11)
B1–B9	1.788 (6)	C2–C5	1.392 (12)
B1–B5	1.792 (5)	C4–C5	1.375 (8)
B1–B2	1.799 (5)	C1–HC1	0.83 (4)
B1–B3	1.805 (6)	C2–HC2	0.95 (3)
B1–B4	1.751 (7)	C3–HC3	0.76 (4)
B9–B3	1.920 (6)	C4–HC4	0.89 (4)
B9–B4	1.803 (6)	C5–HC5	0.76 (4)
B5–B2	1.913 (5)	B2–B3	1.805 (5)
B5–B4	1.797 (7)		

Table X. Selected Bond Angles (Deg) for 7,6,8-(η-C_5H_5)$CoS_2B_6H_8$

S8–Co–B2	93.7 (1)	B2–B3–Co	64.8 (2)
S8–Co–B3	52.0 (1)	Co–B3–S8	67.4 (1)
S6–Co–B2	52.37 (9)	S8–B3–B9	58.9 (2)
S6–Co–B3	93.9 (1)	B9–B3–B1	57.3 (2)
B2–Co–B3	50.6 (1)	B1–B3–B2	59.8 (2)
Co–S8–B3	60.6 (1)	B9–B4–B1	60.4 (2)
B3–S8–B9	60.9 (2)	B1–B4–B5	60.7 (3)
Co–S6–B2	60.6 (1)	HB9-4–B9–B4	40 (1)
B2–S6–B5	60.5 (2)	B9–B4–HB9-4	49 (1)
B3–B1–B2	60.1 (2)	B9–HB9-4–B4	90 (2)
B2–B1–B5	64.4 (2)	HB5-4–B5–B4	41 (1)
B5–B1–B4	60.9 (2)	B5–B4–HB5-4	48 (2)
B4–B1–B9	61.3 (2)	B5–HB5-4–B4	90 (2)
B9–B1–B3	64.6 (2)	C3–C1–C4	107.5 (4)
S8–B9–B3	60.2 (2)	C3–C2–C5	109.2 (4)
B3–B9–B1	58.1 (2)	C1–C3–C2	108.3 (8)
B1–B9–B4	58.3 (3)	C1–C4–C5	107.0 (4)
S6–B5–B2	60.8 (2)	C2–C5–C4	108.0 (8)
B2–B5–B1	58.0 (2)	C1–Co–C3	39.5 (2)
B1–B5–B4	58.4 (2)	C1–Co–C4	41.1 (2)
Co–B2–S6	67.0 (1)	C2–Co–C3	38.7 (3)
Co–B2–B3	64.6 (2)	C2–Co–C5	39.8 (3)
B3–B2–B1	60.1 (2)	C4–Co–C5	39.5 (2)
B1–B2–B5	57.6 (2)	B5–B2–S6	58.7 (2)
B3–B9–B4	109.9 (3)	B2–B5–B4	110.0 (3)
B5–B2–B3	106.4 (3)	B9–B3–B2	105.9 (3)
B9–B4–B5	105.8 (3)		

boron–boron bridging hydrogen resonances above Me_4Si. Thus, these data also suggest a lack of symmetry within the structure. An arrangement of atoms with the predicted nido framework which is consistent with the spectroscopic data is shown in Figure 2 along with its 32.1-MHz ^{11}B NMR spectrum. This structure can be described as a tricapped trigonal prism missing one noncapping position.

Although the structure shown in Figure 2 is in agreement with both electron counting rules and the spectroscopic data, it should be noted that such a geometry has not been previously confirmed for an eight-atom, $2n + 4$ cage system. All such boron cage systems previously reported have adopted either closo dodecahedral structures (predicted for $2n + 2$ systems) or open-cage arachno structures (predicted for $2n + 6$ systems). Thus, a closo dodecahedral structure has been confirmed for (η-C_5H_5)$_4Ni_4B_4H_4$[19] and has been proposed, on the basis of the NMR data, for (η-C_5H_5)$_2Ni_2(CH_3)_2C_2B_4H_4$.[19] Likewise, arachno structures have been confirmed for B_8H_{12}[22] and (η-C_5H_5)$Co(C_6H_5)_4C_4B_3H_3$,[23] and are proposed, again on the basis of the NMR data, for $C_2B_6H_{10}$[24] and $(CH_3)_4C_4B_4H_4$.[25a] Only in the case of the compound $(C_2H_5)_4C_4B_4(CH_3)_4$, which has the same cage skeleton as $(CH_3)_4C_4B_4H_4$, has evidence (NMR data) been obtained[25b] which suggests a nido structure.

In the case of (η-C_5H_5)$_2Co_2SB_5H_7$, it is also possible to propose closo or arachno structures which would be consistent with the spectroscopic data; therefore a crystallographic investigation was undertaken in order to clarify the cage geometry. The results of this determination are depicted in Figure 3 which gives a stere-

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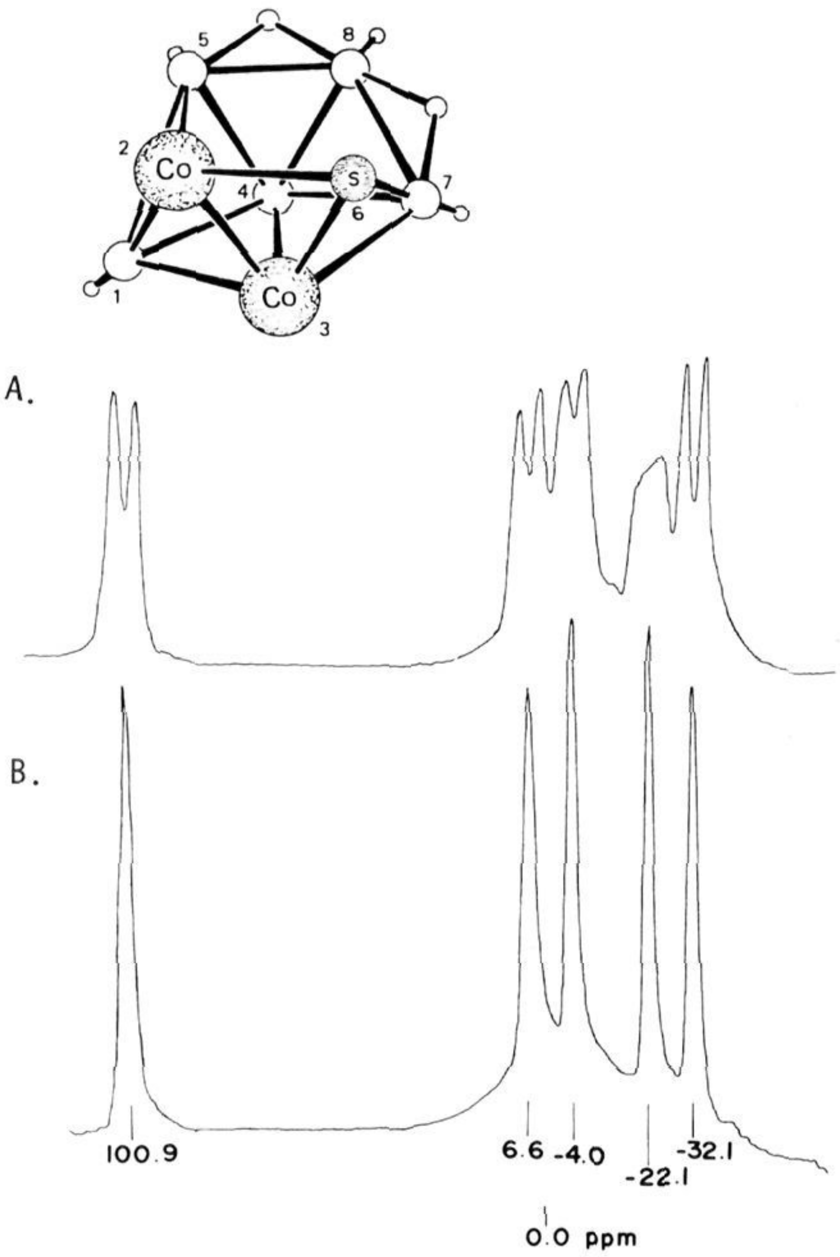

Figure 2. Cage structure and 32.1-MHz ^{11}B NMR of 2,3,6-(η-$C_5H_5)_2Co_2SB_5H_7$ (II) (bottom spectrum is proton spin decoupled).

Table XI. Selected Molecular Planes for 7,6,8-(η-$C_5H_5)CoS_2B_6H_8$

atom	dev, Å	atom	dev, Å
Plane 1. Cyclopentadienyl Ring			
$-0.2358x + 0.9579y - 0.1639z = 1.7676$			
Atoms in Plane			
C1	0.002 (4)	C4	−0.007 (5)
C2	−0.009 (4)	C5	0.009 (5)
C3	0.004 (5)		
Other Atoms			
Co	1.666 (0)	HC3	0.020 (34)
HC1	0.041 (34)	HC4	−0.030 (34)
HC2	0.021 (33)	HC5	0.026 (36)
Plane 2. Base of the Hexaborane(10) Unit			
$-0.2383x - 0.6447y - 0.7263z = -6.1124$			
Atoms in Plane			
B9	0.082 (4)	B3	−0.028 (4)
B5	0.085 (4)	B4	−0.106 (5)
B2	−0.034 (4)		

oscopic view of the molecule. The structure can be seen to be consistent with that expected on the basis of a nido electron count; that is, the cage framework is obtained from a tricapped trigonal prism by removal of one noncapping position. Thus, the atoms B1, B8, and S each occupy positions derived from the capping positions in the parent polyhedron, while atoms Co3, Co2, B4, B5, and B7 constitute the remainder of the trigonal prism (missing one vertex). The atoms Co2–S–B7–B8–B5 define an open pentagonal face with hydrogens bridging boron positions B5–B8 and B7–B8. The two cobalt atoms are adjacent (2.500 (1) Å) with Co3 being in a five-coordinate position. The sulfur atom bridges the two cobalt atoms and is also bound to B7 (1.85 (1) Å). If this compound had an arachno structure, then it would be expected that the Co3–B5 distance would be long; however, the observed distance of 2.20 (1) Å is consistent with a bonding interaction between these atoms (for example, compare Co3–B7 = 2.25 (1) Å and Co3–B4 = 2.168 (9) Å), and a nido structural classification is justified. The remaining distances and angles are all in the normal ranges expected.

The fact that three different geometries have now been observed for eight-atom, $2n + 4$ electron cage systems apparently indicates that these three geometries are energetically similar and other factors may dictate cage structure. We have previously noted[23] that among the few presently known examples, arachno structures appear to be favored for those clusters containing either one or no metal atoms, whereas those systems containing more than one metal appear to adopt more closed geometries. This observation suggests that metal–metal interactions within the cage systems may be a dominant factor in determining cage geometry in multimetal systems.

The reaction of cobalt atoms with cyclopentadiene, cyclohexene sulfide, and hexaborane(10) was found to give in good yields the second example of a small cage dithiametallaborane complex.

$$\text{cobalt (atoms)} + C_5H_6 + B_6H_{10} + \text{cyclohexene sulfide} \rightarrow 7,6,8\text{-}(\eta\text{-}C_5H_5)CoS_2B_6H_8$$

The compound was obtained as an air-stable violet crystalline material which was assigned the formula indicated above on the basis of exact mass measurements. The ^{11}B NMR of this complex at 115.5 MHz (Figure 5) shows four distinct boron resonances of intensity 2:2:1:1. In addition the doublet of intensity one at −33.7 ppm shows fine structure, indicating coupling with bridging hydrogens. The 100-MHz ^1H NMR spectrum indicated a cyclopentadienyl resonance of intensity 5 and upon boron decoupling showed three resonances attributable to terminal B–H protons of relative intensity 4:1:1 along with one resonance of intensity 2, appearing above Me_4Si, which can be assigned to boron–boron bridging hydrogens.

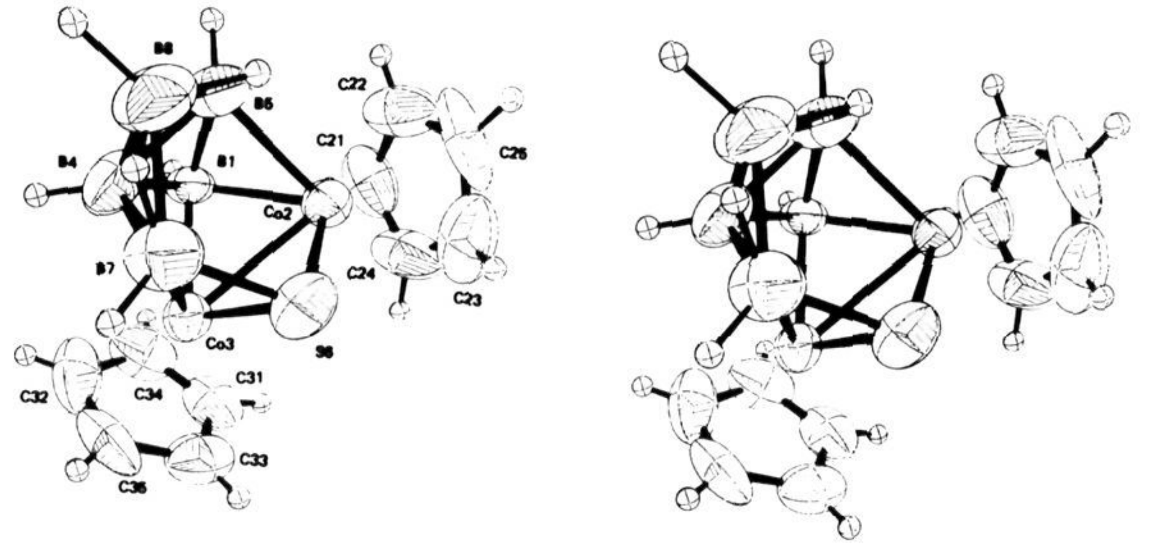

Figure 3. Stereo ORTEP drawing of 2,3,6-(η-$C_5H_5)_2Co_2SB_5H_7$ (II).

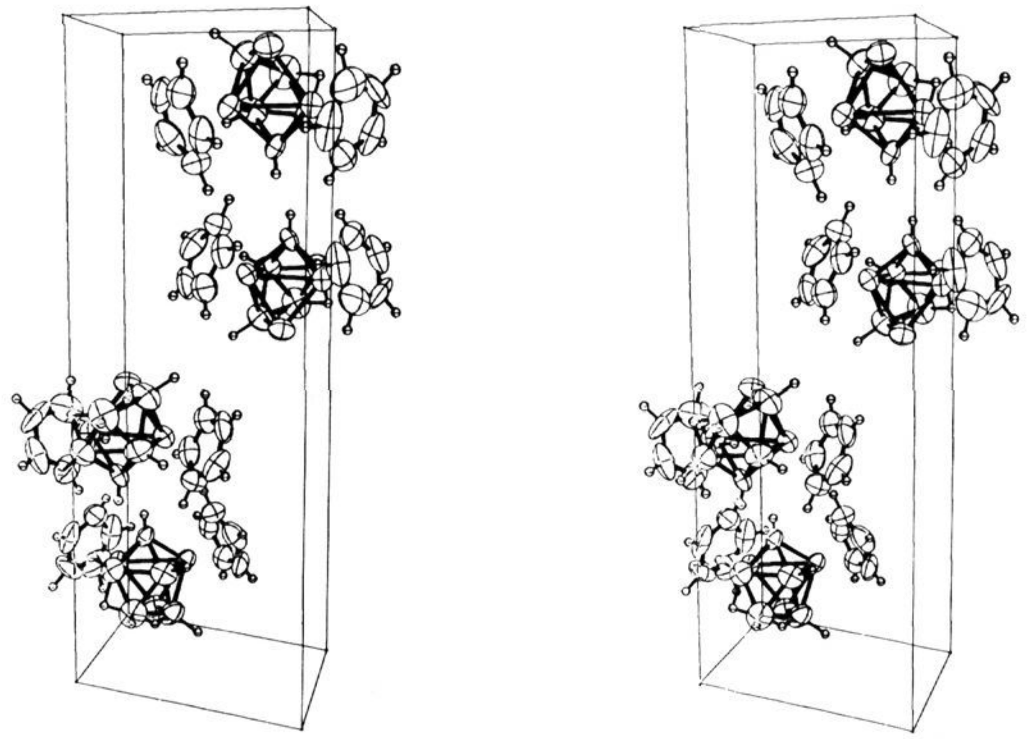

Figure 4. Molecular packing diagram for 2,3,6-(η-C_5H_5)$_2$$Co_2SB_5H_7$ (II). The contents of one unit cell are shown as viewed down the *a* axis, the *c* axis being horizontal.

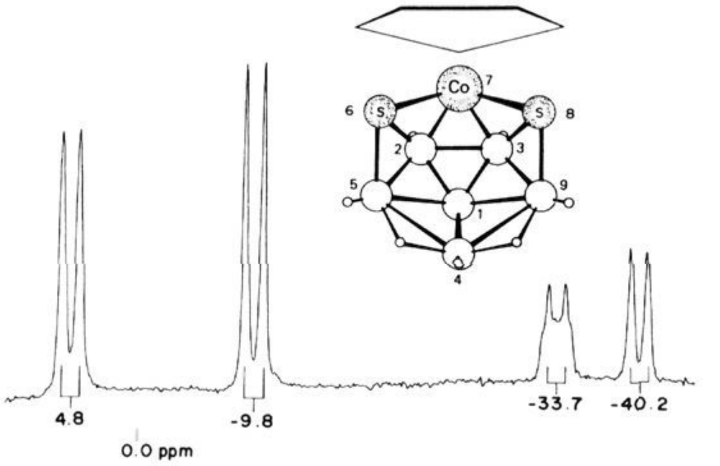

Figure 5. Structure and 115.5-MHz ^{11}B NMR of 7,6,8-(η-C_5H_5)-$CoS_2B_6H_8$ (III).

Compound III is a $2n + 6$ electron system (9 framework atoms, 24 skeletal electrons), and an arachno cage structure, based on an octadecahedron missing two vertices, would be predicted. A structure for III which is derived from this geometry and which is consistent with the spectroscopic data is shown in Figure 5. A similar cage framework has been confirmed for $B_9H_{14}^-$[26] and $B_9H_{13}(NCCH_3)$[27] and proposed, on the basis of NMR data, for $C_2B_7H_{13}$,[28] $S_2B_7H_9$,[29] and CSB_7H_{11}.[29]

The prosposed structure for III was subsequently confirmed by a crystallographic study. The results of this study are depicted in Figure 6, which gives two different stereographic views of the molecule. As can be seen in this figure, the basic hexaborane boron framework has remained intact, but two bridge hydrogens have been removed and a (η-C_5H_5)CoS_2 unit substituted on the open face. Each of these heteroatoms (Co, S6, S8) occupies a bridging position between two borons and, as a result, each of the corresponding boron–boron distances (B5–B2 = 1.913 (5) Å, B2–B3 = 1.803 (5) Å, and B9–B3 = 1.920 (6) Å) are lengthened compared to the basal boron–boron distances in hexaborane(10),[30] and there is no evidence for the short boron–boron single bond observed in B_6H_{10}. Atoms Co, S8, B9, B4, B5, and S6 define an open face, and the observed Co–S and B–S distances are normal and similar to those found for compound II. Bridging hydrogens are attached across B5–B4 and B9–B4, and the boron–boron and boron–hydrogen distances are similar to those observed in hexaborane(10). Similarly the apex (B1) to basal boron distances seem largely unperturbed although atom B6 lies out of the plane of the four remaining basal borons (B9, B5, B2, B3).

The reactions of cobalt atoms cyclopentadiene and decaborane(14) with either elemental sulfur or cyclohexene sulfide were also explored, but, in contrast to the results obtained with pentaborane(9) and hexaborane(10), low yields were obtained and only one metallathiaborane complex was produced, 1,2-(η-C_5H_5)$CoSB_{10}H_{10}$. This compound had been previously[2] prepared by Muetterties and was identified by comparison of its ^{11}B and ^1H NMR spectra with literature values.

Discussion

The development of small cage metallathiaborane chemistry has been hampered by the lack of suitable synthetic pathways for sulfur insertions into small cage systems. For example, the synthetic routes which had been proven successful for larger cage systems such as the reaction of a borane anion and sulfur reagent in aqueous solution are clearly inappropriate for the more reactive small cage systems. On the basis of the results of our previous work[4,5] which showed that metal atom reactions could be used for the direct synthesis of metallacarborane clusters, it was felt that these techniques could be used to incorporate other heteroatoms into metallaborane systems. Furthermore, it appeared that the unique metal atom reaction conditions, which employ high metal reactivity in a low-temperature environment, could be used to advantage for the reaction with the small cage boranes, in particular. That this is indeed the case was clearly demonstrated in the results section presented above. Thus compounds I, II, and III are the first three examples of metallathiaboranes to be derived from the small cage boron hydrides.

It is significant that each of the new metallathiaborane complexes obtained contain the same number of boron atoms as the starting boron hydride. Furthermore compounds I and III, 6,8,7,9-(η-C_5H_5)$_2$$Co_2S_2B_5H_5$ and 7,6,8-(η-C_5H_5)$CoS_2B_6H_8$, have retained the basic pentaborane(9) and hexaborane(10) boron frameworks, respectively. Although the exact mechanism of formation is unknown, both of these compounds appear to have resulted from the abstraction of bridge hydrogens from the face of the parent borane accompanied by a substitution of either a (η-C_5H_5)$_2$$Co_2S_2$ or a (η-C_5H_5)CoS_2 unit on the open face. At first glance, the formation of compound II, 2,3,6-(η-C_5H_5)$_2$$Co_2SB_5H_7$, seems more complicated since the pentaborane(9) boron framework is distorted. However, as can be seen in Figure 8, the same

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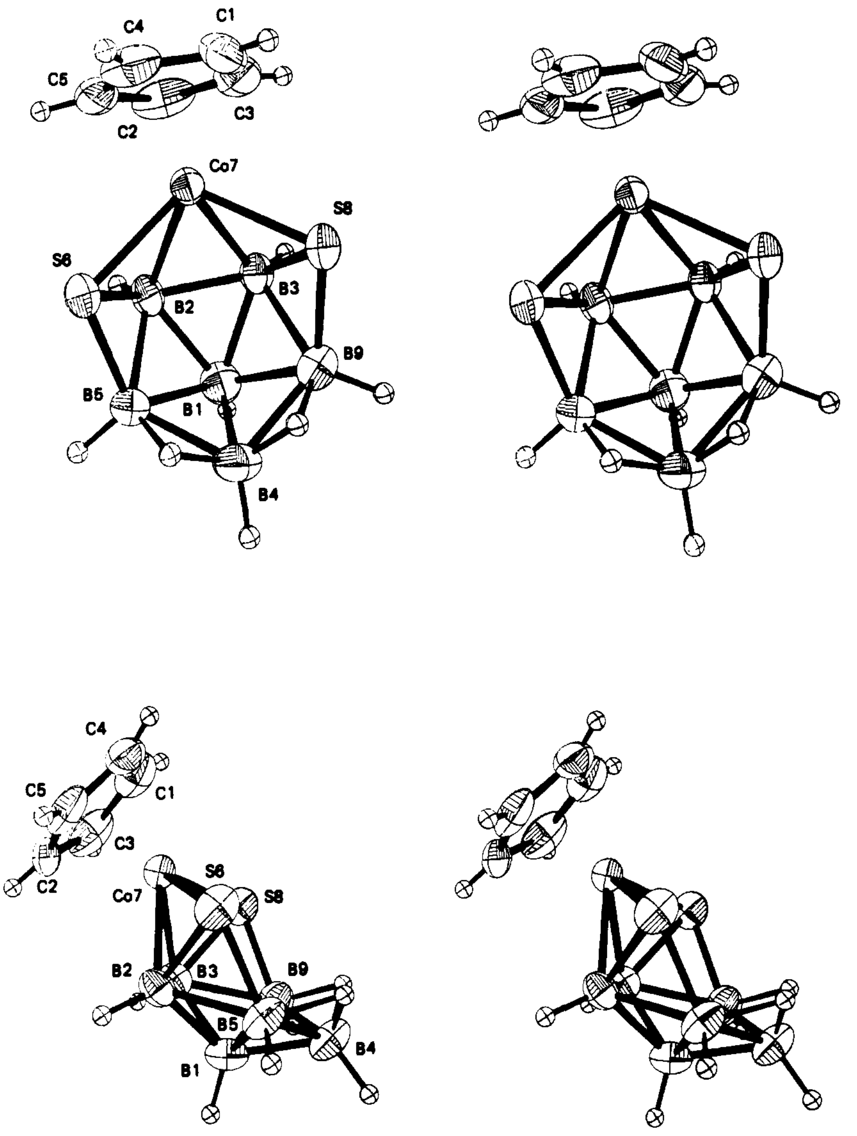

Figure 6. Stereo ORTEP drawings of 7,6,8-(η-C_5H_5)$CoS_2B_6H_8$ (III).

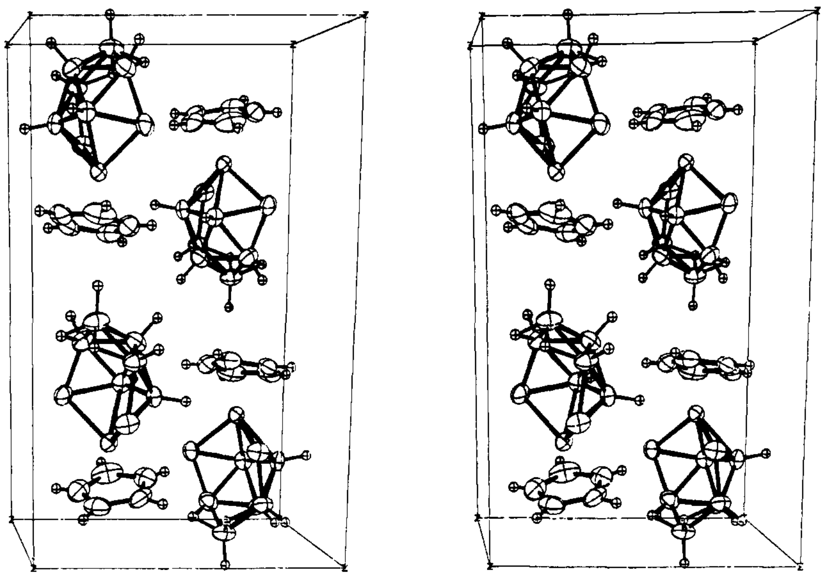

Figure 7. Molecular packing diagram for 7,6,8-(η-C_5H_5)$CoS_2B_6H_8$ (III). The contents of one unit cell are shown as viewed down the *a* axis, the *c* axis being horizontal.

basic process envisioned for the formation of I and III can account for the formation of II; that is, the abstraction of two bridge hydrogens and substitution of a (η-C_5H_5)$_2Co_2S$ unit on the open face, followed by the formation of new bonds as indicated in the

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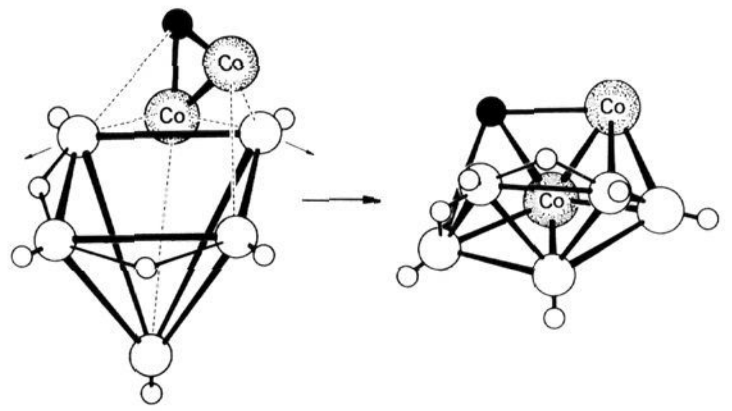

Figure 8. Scheme for the formation of 2,3,6-(η-C_5H_5)$_2$$Co_2SB_5H_7$.

figure, leads directly to the structure observed for II.

The absence of boron cage degradation products along with the production of few, if any, other side products in the reactions used to obtain compounds I, II, and III, illustrates the significant synthetic advantages of the mild conditions employed in metal atom reactions. In addition, each of these compounds could be produced in reasonable quantities when cyclohexene sulfide was employed as a reactant, thus enabling future chemical investigations of their properties.

In contrast to the results obtained with pentaborane(9) and hexaborane(10) the reactions with decaborane(14) produced only the previously[2] known metallathiaborane 1,2-(η-C_5H_5)$CoSB_{10}H_{10}$ in low yield. This lower reactivity of decaborane(14) as well as the production of a nine-boron rather than a ten-boron species is consistent with our previous[4] investigations of the metal atom reactions of decaborane(14) and is probably linked to its greater stability compared to that of the smaller boranes.

Finally, it should also be noted that compounds I and III are two of the relatively few examples of dithiametallaboranes. In fact until recently[29,31] neither dithiaboranes or dithiametallaboranes had been isolated, even for large cage systems. The isolation of I and III illustrates that the metal atom technique may be used in the future to incorporate even larger numbers and types of heteroatoms into boron cage systems resulting in the production of new classes of hybrid clusters.

Acknowledgment. We thank the National Science Foundation and the Army Research Office for support of this work.

Supplementary Material Available: Listings of structure factor amplitudes for compounds II and III (20 pages). Ordering information is given on any current masthead page.

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Unusual Platinum Complexes of Deprotonated 1-Methylcytosine: Bis(μ-1-methylcytosinato-N^3,N^4)-bis(*cis*-diammineplatinum(II)) Dinitrate Dihydrate, $[(NH_3)_2Pt(C_5H_6N_3O)_2Pt(NH_3)_2](NO_3)_2{\cdot}2H_2O$, and [Diaquahydrogen(1+)] [Bis(μ-1-methylcytosinato-N^3,N^4)-bis(*cis*-nitrodiammine-platinum)(*Pt-Pt*)] Dinitrate, $(H_5O_2)[(NH_3)_2(NO_2)Pt(C_5H_6N_3O)_2Pt(NH_3)_2(NO_2)](NO_3)_2$

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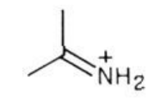
Abstract: The reaction of aqueous *cis*-$Pt(NH_3)_2(NO_3)_2$ with 1-methylcytosine yields a variety of products including the novel compounds bis(μ-1-methylcytosinato-N^3,N^4)-bis(*cis*-diammineplatinum(II)) dinitrate dihydrate, $[(NH_3)_2Pt(C_5H_6N_3O)_2Pt(NH_3)_2](NO_3)_2{\cdot}2H_2O$ (A) and [diaquahydrogen(1+)] [bis(μ-1-methylcytosinato-N^3,N^4)-bis(*cis*-nitrodiammineplatinum)] dinitrate, $(H_5O_2)[(O_2N)(NH_3)_2Pt(C_5H_6N_3O_2)_2Pt(NH_3)_2(NO_2)](NO_3)_2$ (B), both of which contain the cytosine ligand deprotonated at the 4-NH_2 group. The crystal structures of both have been determined by X-ray diffraction. A has the space group $P2_1/c$ with cell dimensions a = 9.887 (3) Å, b = 17.191 (5) Å, c = 15.532 (4) Å, and β = 116.40 (2)° and has four formula units in the unit cell. Data for both compounds were collected by using Mo Kα radiation and a Syntex P2_1 diffractometer. Both crystal structures were determined by standard methods, and A was refined to R_1 = 0.0739 and R_2 = 0.0953 on the basis of 3248 independent reflections. B has space group $P\bar{1}$ with a = 8.676 (4) Å, b = 10.877 (4) Å, c = 15.462 (6) Å, α = 90.24 (3)°, β = 117.98 (3)°, and γ = 95.09 (4)° and has two formula units in the unit cell. The final R_1 = 0.0618 and R_2 = 0.0779 was based on 2780 independent reflections. Both compounds contain a dimeric cation in which two square-planar arrays about each platinum atom lie very roughly parallel and these are bridged in the cis positions by the 1-methylcytosinato ligands through N^3 and N^4. The bridging ligands are arranged head to tail. In addition B has two axially bonded nitro groups (Pt–N = 2.12 (3), 2.13 (2) Å). The Pt–Pt distances are markedly different (Pt–Pt (A) = 2.981 (2) Å, (B) = 2.584 (1) Å), but the Pt–N distances (ammonia and 1-methylcytosine range 2.00 (2)–2.11 (3) Å) are normal.

Introduction

It has been generally accepted that the exocyclic group of cytosine is no site for metal coordination unless the NH_2 group is deprotonated.[2-5] This is because a good representation of the group is



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