VI (44 mg, 1.6%), with 10-15 mg of each of the other species. Exact mass determinations: calcd for $^{12}C_{20}{}^{11}B_5{}^{59}Co_2{}^{1}H_{37}{}^{+}$ (VIII) 450.2024, found 450.2013.

Isomerization of 2-[$C_5(CH_3)_5$]CoB_4H_8 (V). A 21.9-mg sample of V dissolved in pentane was placed in a 1-L Pyrex bulb and attached to the vacuum line. After removal of the pentane under vacuum, the bulb was sealed (via a vacuum stopcock fitted with Viton or Buna-N O-rings) and heated in an oven to 180 °C for 5.5 h and then at 200 °C overnight. When the contents cooled, both red and yellow crystals were visible. As the two isomers are less volatile than their (C_5H_5)CoB_4H_8 counterparts, they were removed from the bulb with pentane and transferred to an evacuated 0.5 × 20 cm Pyrex tube. Separation of pale yellow 1-[$C_5(CH_3)_5$]CoB_4H_8 (XI) from the red V that remained was accomplished by slow sublimation in the Pyrex tube at ~37 °C, which caused crystals of the more volatile XI (5.5 mg, 25%) to collect at the opposite (room-temperature) end. Some decomposition also occurred, as evidenced by the formation of nonvolatile dark solids.

Thermolysis of 1,2-[$C_5(CH_3)_5$]$_2Co_2B_5H_7$ (VIII). A 15-mg sample of VIII dissolved in dichloromethane was placed in a Pyrex reactor, the reactor was attached to the vacuum line, and the solvent was removed under vacuum, after which the bulb was sealed under vacuum and placed in an oven at 225 °C for 17 h. The contents were removed with CH_2Cl_2 in air and filtered to remove decomposed material. The filtrate was developed on TLC plates to give three bands. The first band (R_f = 0.51) contained a trace of a green compound formulated from mass spectra as [$C_5(CH_3)_5$]$_2Co_2B_6H_6$ (mol wt 460) but was not further characterized. The second band (R_f = 0.46) was yellow-red 1,2-[$C_5(CH_3)_5$]$_2Co_2B_5H_5$ (XII) (8.4 mg, 56%), and the third band (R_f = 0.32) was a trace of violet VI, identical with the complex isolated in the $CoCl_2$/$Li^+[C_5(CH_3)_5]^-$/$Na^+B_5H_8^-$ reaction.

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Cobaltaborane Analogues of $B_{10}H_{14}$. Crystal and Molecular Structures of 6-[η^5-$C_5(CH_3)_5$]CoB_9H_{13}, 6,9-[η^5-$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$, 5,7-[η^5-$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$, and 6-Cl-5,7-[η^5-$C_5(CH_3)_5$]$_2Co_2B_8H_{11}$[1]

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Crystal and molecular structures have been determined for the title compounds, which were obtained from the reaction in THF of $Li^+C_5(CH_3)_5^-$, $CoCl_2$, and $Na^+B_9H_{14}^-$ (generated during the deprotonation of B_5H_9 with NaH) followed by workup in air, as described in the preceding paper. All four compounds exhibit 10-vertex nido cage structures analogous to $B_{10}H_{14}$ with one or two BH units replaced by Co[η^5-$C_5(CH_3)_5$], and the observed solid-state geometries are compatible with ^{11}B and ^1H FT NMR spectra in solution. In each case the four bridging hydrogens, present as B-H-B and Co-H-B groups, occupy locations equivalent to those in $B_{10}H_{14}$ itself; the Co-H-B bridges are unsymmetrical, with the hydrogen closer to boron than cobalt. The dicobalt complexes are the first structurally characterized metallaborane analogues of $B_{10}H_{14}$ having more than one metal atom in the cage. The molecular parameters are compared with those of the previously reported compounds 5-(η^5-C_5H_5)CoB_9H_{13}, 5-THF-6-$(CO)_3MnB_9H_{12}$, and $B_{10}H_{14}$. Crystal data: 6-[$C_5(CH_3)_5$]CoB_9H_{13}, mol wt 305, space group $P2_12_12_1$, $Z = 4$, $a = 10.535$ (3) Å, $b = 12.830$ (3) Å, $c = 13.037$ (3) Å, $V = 1762$ Å^3, $R = 0.028$ for 1427 reflections having $F_o^2 > 3\sigma(F_o^2)$; 6,9-[$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$, mol wt 487, space group $P2_1/n$, $Z = 4$, $a = 8.543$ (2) Å, $b = 14.636$ (8) Å, $c = 20.88$ (2) Å, $\beta = 90.38$ (4)°, $V = 2611$ Å^3, $R = 0.059$ for 1418 reflections having $F_o^2 > 3\sigma(F_o^2)$; 5,7-[$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$, mol wt 487, space group $P2_1/n$, $Z = 4$, $a = 9.236$ (4) Å, $b = 20.229$ (9) Å, $c = 13.681$ (6) Å, $\beta = 98.05$ (4)°, $V = 2531$ Å^3, $R = 0.076$ for 2501 reflections having $F_o^2 > 3\sigma(F_o^2)$; 6-Cl-5,7-[$C_5(CH_3)_5$]$_2Co_2B_8H_{11}$, mol wt 521, space group $P\bar{1}$, $Z = 2$, $a = 9.842$ (8) Å, $b = 11.693$ (6) Å, $c = 12.154$ (8) Å, $\alpha = 68.93$ (6)°, $\beta = 84.95$ (4)°, $\gamma = 86.85$ (4)°, $V = 1300$ Å^3, $R = 0.063$ for 3870 reflections having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

The preceding article[2] describes the reaction of $CoCl_2$, $Li^+[C_5(CH_3)_5]^-$, and $Na^+B_5H_8^-$ in cold tetrahydrofuran (THF), in which it was shown that $B_5H_8^-$, under surprisingly mild reaction conditions, forms $B_9H_{14}^-$ ion in significant concentration. Under these conditions the major isolable product following workup in air was 6-[η^5-$C_5(CH_3)_5$]CoB_9H_{13}, a burgundy crystalline solid obtained in 25% yield. Isolated in much smaller quantities were dark green 6,9-[η^5-$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$, dark brown 5,7-[η^5-$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$, the 6-chloro derivative of the latter complex, and several other (pentamethylcyclopentadienyl)cobalt metallaboranes having one to three metal atoms in the cage.

The CoB_9 and Co_2B_8 products were characterized from high-resolution ^{11}B and ^1H pulse Fourier transform NMR spectra and assigned $B_{10}H_{14}$-like nido cage structures in which the cobalt atoms occupy verticles on the open face and participate in Co-H-B bridging groups. In order to rigorously establish the proposed structures of these compounds (which are the first known metallaboranes containing the $C_5(CH_3)_5$ ligand[3]) and also to obtain molecular parameters of interest,

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(1) Taken in part from the Ph.D. dissertation of T.L.V., University of Virginia, 1982.

(2) Venable, T. L.; Grimes, R. N. *Inorg. Chem.* preceding paper in this issue.

(3) Metalla*carboranes* utilizing the pentamethylcyclopentadienyl ligand have been reported from this laboratory: (a) Finster, D. C.; Grimes, R. N. *Inorg. Chem.* **1981**, *20*, 863. (b) Finster, D. C.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1981**, *103*, 1399.

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X-ray crystallographic studies were conducted on each of the four complexes.

Experimental Section

Burgundy crystals of 6-[η^5-$C_5(CH_3)_5$]CoB_9H_{13} were grown by vapor diffusion of pentane into a CH_2Cl_2 solution. A rectangular crystal was selected and mounted on a glass fiber for data collection. Crystal data: $CoC_{10}B_9H_{28}$, mol wt 305; space group $P2_12_12_1$; $Z = 4$; $a = 10.535$ (3), $b = 12.830$ (3), $c = 13.037$ (3) Å; $V = 1762$ Å^3; $\rho_{calcd} = 1.15$ g cm^{-3}; μ(Mo Kα) = 9.9 cm^{-1}; crystal dimensions (distance in mm of faces from centroid) (100) 0.20, ($\bar{1}$00) 0.20, (010) 0.17, (0$\bar{1}$0) 0.17, (001) 0.11, (00$\bar{1}$) 0.11; maximum and minimum transmission coefficients 0.89 and 0.83. The Enraf-Nonius program SEARCH was used to obtain 25 accurately centered reflections, which were then used in the program INDEX to obtain approximate cell dimensions and an orientation matrix for data collection. Refined cell dimensions and their estimated standard deviations were obtained from least-squares refinement of 28 accurately centered reflections. The mosaicity of the crystal was examined by the ω-scan technique and judged to be satisfactory.

The orthorhombic space group $P2_12_12_1$ was identified from systematic absences at $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd.

Dark green crystals of 6,9-[η^5-$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$, dark brown crystals of 5,7-[η^5-$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$, and dark brown crystals of 6-Cl-5,7-[η^5-$C_5(CH_3)_5$]$_2Co_2B_8H_{11}$ were each grown by slow evaporation of a CH_2Cl_2 solution, and a high-quality crystal of each was mounted on a glass fiber. Crystal data for 6,9-[$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$: $Co_2B_8C_{20}H_{42}$, mol wt 486.9; space group $P2_1/n$; $Z = 4$; $a = 8.543$ (2), $b = 14.636$ (8), $c = 20.88$ (2) Å; $\beta = 90.38$ (4)°; $V = 2611$ Å^3; $\rho_{calcd} = 1.23$ g cm^{-3}; μ(Mo Kα) = 13.3 cm^{-1}; crystal dimensions (see above) (100) 0.42, ($\bar{1}$00) 0.42, (010) 0.09, (0$\bar{1}$0) 0.09, (001) 0.05, (00$\bar{1}$) 0.05; maximum and minimum transmission coefficients 0.96 and 0.89.

Crystal data for 5,7-[$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$: $Co_2B_8C_{20}H_{42}$, mol wt 486.9; space group $P2_1/n$; $Z = 4$; $a = 9.236$ (4), $b = 20.229$ (9), $c = 13.681$ (6) Å; $\beta = 98.05$ (4)°; $V = 2531$ Å^3; $\rho_{calcd} = 1.28$ g cm^{-3}; μ(Mo Kα) = 13.7 cm^{-1}; crystal dimensions (110) 0.28, ($\bar{1}\bar{1}$0) 0.28, (1$\bar{1}$0) 0.28, ($\bar{1}$10) 0.28, (010) 0.30, (0$\bar{1}$0) 0.30, (001) 0.10, (00$\bar{1}$) 0.10; maximum and minimum transmission coefficients 0.87 and 0.70.

Crystal data for 6-Cl-5,7-[$C_5(CH_3)_5$]$_2Co_2B_8H_{11}$: $Co_2B_8C_{20}ClH_{41}$, mol wt 521.4; space group $P\bar{1}$; $Z = 2$; $a = 9.842$ (8), $b = 11.693$ (6), $c = 12.154$ (8) Å; $\alpha = 68.93$ (6)°; $\beta = 84.95$ (4)°; $\gamma = 86.85$ (4)°; $V = 1300$ Å^3; $\rho_{calcd} = 1.40$ g cm^{-3}; μ(Mo Kα) = 14.4 cm^{-1}; crystal dimensions (110) 0.10, ($\bar{1}\bar{1}$0) 0.10, (101) 0.15, ($\bar{1}$0$\bar{1}$) 0.15, (011) 0.03, (0$\bar{1}\bar{1}$) 0.03; maximum and minimum transmission coefficients 0.95 and 0.78.

For each of the latter three compounds, the same procedures as described above for the first compound were employed to produce orientation matrices and refined cell constants. The mosaicity of each crystal was examined by the ω-scan technique and judged satisfactory.

Identification of the space group $P2_1/n$ for the two Co_2B_8 isomers was based on systematic absences for $k = 2n + 1$ on $0k0$ and $h + l = 2n + 1$ on $h0l$. This is a nonstandard setting of $P2_1/c$ but can be converted to it by the transformation $a' = a$, $b' = b$, and $c' = -a + c$, where a, b, and c are axes in $P2_1/n$ and a', b', and c' are axes in $P2_1/c$. All data collection and refinement were conducted in the $P2_1/n$ setting.

For the 6-chloro derivative, the space group was determined as $P\bar{1}$ by the absence of higher symmetry.

Collection and Reduction of the Data. For all four compounds, diffraction data were collected at 292 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer, with Mo Kα radiation from a highly oriented graphite-crystal monochromator. The θ–2θ scan technique was used to record the intensities for all nonequivalent reflections for which $1° < 2\theta < 46°$ for the 6-CoB_9 species; for the 6,9-Co_2B_8, 5,7-Co_2B_8, and 6-Cl-5,7-Co_2B_8 complexes the corresponding ranges were $1° < 2\theta < 44°$, $1° < 2\theta < 50°$, and $1.7° < 2\theta < 50°$, respectively. Scan widths (SW) were calculated from the formula SW = $(A + B \tan \theta)°$, where A is estimated from the mosaicity of the crystal and B allows for the increase in width of peak due to Kα_1–Kα_2 splitting. For the four compounds (same order as above), the values of A and B were 0.6 and 0.35, 0.6 and 0.35, 0.8 and 0.35, and 0.60 and 0.35, respectively. The calculated scan angle was extended at each side by 25% for background determination (BG1 and BG2). The net count was then calculated as NC = TOT − 2(BG1 + BG2) where TOT is the integrated peak intensity.

The intensities of four standard reflections, monitored at periodic intervals, showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects (including the polarization effect of the crystal monochromator) and then for absorption. After the intensities of equivalent reflections were averaged, the data for 6-[$C_5(CH_3)_5$]CoB_9H_{13} were reduced to 1575 independent intensities of which 1427 had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics ($\rho = 0.03$).[4] For the 6,9-Co_2B_8, 5,7-Co_2B_8, and 6-Cl-5,7-Co_2B_8 species the corresponding numbers were respectively 2930 and 1418, 3432 and 2501, and 4433 and 3870. In each case, only the 3σ data were used in the refinement of structural parameters.

Solution and Refinement of the Structures. 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 then taken as $[2F_o/\sigma(F_o^2)]^2$, 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[5] and those for hydrogen from Stewart et al.[6] The effects of anomalous dispersion for all nonhydrogen atoms were included in F_c with use of the values of Cromer and Ibers[7] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum w|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

For each compound, the position(s) of the cobalt atom(s) was (were) determined from a three-dimensional Patterson function calculated from all intensity data. The intensity data were phased sufficiently well by these positional coordinates to permit location of the remaining nonhydrogen atoms from Fourier difference functions. Anisotropic temperature factors were introduced for all nonhydrogen atoms.

In the case of 6-[$C_5(CH_3)_5$]CoB_9H_{13}, all of the hydrogen atoms, including those on the $C_5(CH_3)_5$ ligand, were located from difference maps; the coordinates of the hydrogens were included for two cycles of least-squares refinement and thereafter held fixed. The correct absolute configuration was chosen by refinement of the atomic parameters for both possible configurations using all data. Following absorption corrections (see above for transmission coefficients), refinement was continued to convergence with final values of $R = 0.028$ and $R_w = 0.036$. The error in an observation of unit weight was 1.01. Tables of the observed and calculated structure factors for the four structures reported herein are available (see paragraph on Supplementary Material). The principal programs used have been described elsewhere.[8]

For 6,9-[$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$, Fourier difference maps revealed the locations of all nonmethyl hydrogen atoms and several of the methyl hydrogens; positions of some remaining methyl hydrogens were calculated. The hydrogen positions were included for two cycles of refinement and subsequently held fixed. Following absorption corrections, refinement was continued to final values of $R = 0.059$ and $R_w = 0.064$. The error in an observation of unit weight was 2.53, and the largest parameter shift in the final cycle of refinement was 0.09 times its estimated standard deviation.

For 5,7-[$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$, Fourier syntheses were used to locate several of the hydrogen atoms associated with the cage framework, and the remaining cage hydrogen positions were calculated. A few of the methyl hydrogens were also located or calculated. The refinement was conducted as in the structures described above, leading to final R and R_w values of 0.076 and 0.086, respectively. The error in an observation of unit weight was 3.50, and the largest parameter shift/esd was 0.02.

For 6-Cl-5,7-[$C_5(CH_3)_5$]$_2Co_2B_8H_{11}$, Fourier maps revealed some cage hydrogen locations and the remainder were calculated; no methyl hydrogens were located or calculated. Following refinement as described above, final R and R_w values of 0.063 and 0.078 were obtained. The error in an observation of unit weight was 3.1, and the largest parameter shift/esd was 0.06.

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Table I. Positional Parameters and Their Estimated Standard Deviations for 6-$(C_5Me_5)CoB_9H_{13}$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Co	0.80470 (6)	0.76509 (4)	0.80626 (5)	H(5)	0.752 (6)	0.932 (4)	0.647 (5)
C(P1)	0.6103 (4)	0.7634 (4)	0.8212 (3)	H(56)	0.796 (4)	0.770 (3)	0.690 (3)
C(P2)	0.6627 (5)	0.6679 (4)	0.8609 (4)	H(67)	0.924 (5)	0.682 (4)	0.799 (4)
C(P3)	0.7466 (5)	0.6956 (4)	0.9418 (4)	H(7)	1.052 (5)	0.746 (5)	0.891 (4)
C(P4)	0.7483 (5)	0.8071 (4)	0.9515 (4)	H(8)	1.191 (6)	0.653 (4)	0.722 (4)
C(P5)	0.6635 (5)	0.8489 (4)	0.8763 (4)	H(89)	1.033 (5)	0.642 (4)	0.668 (4)
C(M1)	0.5149 (5)	0.7728 (7)	0.7357 (4)	H(9)	1.054 (6)	0.601 (5)	0.522 (5)
C(M2)	0.6322 (6)	0.5586 (4)	0.8267 (6)	H(910)	0.927 (5)	0.712 (4)	0.572 (4)
C(M3)	0.8168 (7)	0.6200 (5)	1.0086 (5)	H(10)	0.915 (5)	0.833 (4)	0.485 (4)
C(M4)	0.8192 (7)	0.8683 (5)	1.0299 (4)	H(11)	0.533 (5)	0.730 (4)	0.689 (4)
C(M5)	0.6317 (6)	0.9623 (4)	0.8638 (5)	H(12)	0.444 (5)	0.785 (4)	0.755 (4)
				H(13)	0.524 (6)	0.857 (5)	0.698 (5)
B(1)	0.9810 (7)	0.9005 (5)	0.6452 (6)	H(21)	0.551 (6)	0.535 (4)	0.846 (5)
B(2)	0.9372 (7)	0.8825 (5)	0.7746 (5)	H(22)	0.692 (6)	0.505 (4)	0.819 (5)
B(3)	1.0895 (7)	0.8441 (6)	0.7333 (6)	H(23)	0.630 (6)	0.551 (4)	0.752 (5)
B(4)	1.0991 (7)	0.8099 (6)	0.6013 (5)	H(31)	0.773 (6)	0.599 (5)	1.072 (5)
B(5)	0.8285 (6)	0.8552 (5)	0.6709 (5)	H(32)	0.832 (5)	0.550 (4)	0.972 (4)
B(7)	1.0052 (5)	0.7608 (6)	0.8172 (5)	H(33)	0.889 (5)	0.645 (4)	1.026 (4)
B(8)	1.1119 (6)	0.7110 (5)	0.6979 (6)	H(41)	0.909 (6)	0.866 (5)	1.026 (5)
B(9)	1.0333 (7)	0.6882 (6)	0.5796 (5)	H(42)	0.783 (5)	0.864 (4)	1.090 (4)
B(10)	0.9376 (7)	0.8039 (6)	0.5577 (5)	H(43)	0.820 (6)	0.945 (4)	1.018 (5)
H(1)	0.976 (5)	0.986 (4)	0.609 (4)	H(51)	0.696 (6)	1.001 (4)	0.888 (4)
H(2)	0.934 (4)	0.960 (3)	0.823 (4)	H(52)	0.559 (5)	0.981 (4)	0.911 (4)
H(3)	1.168 (6)	0.896 (4)	0.773 (4)	H(53)	0.590 (6)	0.978 (4)	0.802 (5)
H(4)	1.179 (6)	0.845 (4)	0.553 (4)				

Table II. Positional Parameters and Their Estimated Standard Deviations for 6,9-$(C_5Me_5)_2Co_2B_8H_{12}$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Co(6)	0.1710 (2)	0.8102 (1)	0.61270 (7)	H(1)	−0.098 (13)	1.033 (1)	0.660 (5)
Co(9)	−0.0533 (2)	0.8193 (1)	0.79231 (7)	H(2)	0.185 (11)	1.006 (6)	0.606 (5)
C(1)	0.213 (1)	0.6827 (9)	0.5747 (6)	H(3)	0.206 (12)	1.042 (2)	0.728 (5)
C(2)	0.109 (2)	0.7309 (10)	0.5348 (6)	H(4)	−0.069 (13)	1.006 (2)	0.806 (5)
C(3)	0.201 (2)	0.8124 (10)	0.5175 (5)	H(5)	−0.139 (13)	0.894 (6)	0.581 (5)
C(4)	0.350 (2)	0.8129 (9)	0.5492 (6)	H(65)	0.006 (14)	0.803 (1)	0.649 (6)
C(5)	0.355 (2)	0.7298 (9)	0.5815 (6)	H(67)	0.223 (11)	0.802 (2)	0.676 (5)
C(6)	−0.112 (1)	0.6935 (8)	0.8308 (5)	H(7)	0.100 (14)	0.405 (6)	0.804 (6)
C(7)	−0.005 (1)	0.7411 (9)	0.8699 (6)	H(8)	0.265 (12)	0.905 (1)	0.824 (5)
C(8)	−0.067 (2)	0.8274 (8)	0.8903 (5)	H(89)	0.115 (15)	0.802 (2)	0.763 (6)
C(9)	−0.220 (1)	0.8333 (7)	0.8592 (6)	H(10)	−0.255 (15)	0.921 (1)	0.713 (6)
C(10)	−0.247 (1)	0.7525 (7)	0.8247 (5)	H(910)	−0.134 (8)	0.800 (5)	0.740 (3)
C(M1)	0.182 (2)	0.5869 (10)	0.6090 (9)	H(31)	0.211 (10)	0.932 (5)	0.472 (4)
C(M2)	−0.044 (2)	0.6984 (14)	0.5138 (8)	H(32)	0.052 (12)	0.917 (7)	0.489 (5)
C(M3)	0.134 (4)	0.8840 (16)	0.4726 (10)	H(33)	0.108 (12)	0.872 (7)	0.434 (5)
C(M4)	0.475 (2)	0.8865 (13)	0.5415 (9)	H(61)	−0.016 (9)	0.584 (6)	0.775 (4)
C(M5)	0.504 (2)	0.6993 (13)	0.6214 (8)	H(62)	−0.101 (10)	0.555 (6)	0.812 (4)
C(M6)	−0.090 (1)	0.6023 (8)	0.7997 (7)	H(71)	0.234 (11)	0.723 (6)	0.886 (5)
C(M7)	0.153 (2)	0.7052 (11)	0.8907 (7)	H(72)	0.164 (12)	0.644 (7)	0.874 (5)
C(M8)	0.000 (2)	0.8956 (11)	0.9338 (6)	H(73)	0.157 (12)	0.694 (7)	0.933 (5)
C(M9)	−0.334 (2)	0.9085 (10)	0.8691 (7)	H(81)	−0.034 (12)	0.952 (7)	0.957 (5)
C(M10)	−0.393 (1)	0.7265 (9)	0.7887 (6)	H(82)	0.076 (12)	0.915 (7)	0.910 (5)
B(1)	−0.034 (2)	0.9748 (9)	0.6788 (7)	H(83)	0.032 (11)	0.865 (7)	0.968 (5)
B(2)	0.138 (2)	0.9471 (10)	0.6362 (7)	H(91)	−0.276 (10)	0.973 (6)	0.871 (4)
B(3)	0.152 (2)	0.9754 (9)	0.7161 (7)	H(92)	−0.407 (12)	0.906 (7)	0.903 (5)
B(4)	−0.022 (2)	0.9521 (10)	0.7625 (7)	H(93)	−0.398 (14)	0.917 (8)	0.820 (6)
B(5)	−0.036 (2)	0.8822 (9)	0.6261 (6)	H(101)	−0.473 (11)	0.670 (6)	0.800 (4)
B(7)	0.263 (2)	0.8865 (10)	0.6885 (7)	H(102)	−0.365 (14)	0.685 (9)	0.744 (6)
B(8)	0.160 (2)	0.8908 (9)	0.7758 (8)	H(103)	−0.437 (13)	0.773 (8)	0.773 (5)
B(10)	−0.146 (2)	0.8874 (8)	0.7112 (7)				

Results and Discussion

Final positional parameters for the four compounds are given in Tables I–IV, Tables V and VI list bond distances, and Tables VII and VIII contain selected bond angles. For comparative purposes, bond lengths from the structurally related species 5-THF-6-$(CO)_3MnB_9H_{12}$[9] and $B_{10}D_{14}$[10] are included in Table V and those from 5-$(\eta^5\text{-}C_5H_5)CoB_9H_{13}$[12] in Table VI (in each table, the digits in parentheses are the estimated standard deviations in the least significant figures quoted). Tables of selected mean planes are available as supplementary data.

The cage structures and numbering system for the complexes are depicted in Figure 1, Figures 2–4 present stereoviews of the molecular structures, and Figures 5–8 show the unit cell packing.

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(9) Lott, J. W.; Gaines, D. F. *Inorg. Chem.* **1974**, *13*, 2261.

(10) Tippe, A.; Hamilton, W. C. *Inorg. Chem.* **1969**, *8*, 464. The data quoted were obtained by neutron diffraction and are the most accurate presently available on decaborane(14). Since hydrogen (deuterium) positions as determined by neutron diffraction are not directly comparable with those found from X-ray data, we note that the B(5)–H(56) and B(6)–H(56) distances (our numbering) determined from the best X-ray data[11] are 1.34 and 1.42 Å, respectively.

(11) (a) Kasper, J. S.; Lucht, C. M.; Harker, D. *Acta Crystallogr.* **1950**, *3*, 436. (b) Moore, E. B.; Dickerson, R. E.; Lipscomb, W. N. *J. Chem. Phys.* **1957**, *27*, 209.

(12) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1977**, *16*, 3251.

Table III. Positional Parameters and Their Estimated Standard Deviations for 5,7-$(C_5Me_5)_2Co_2B_8H_{12}$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Co(5)	−0.0670 (2)	0.28198 (7)	0.2739 (1)	B(3)	0.037 (2)	0.4155 (7)	0.1639 (11)
Co(7)	−0.0784 (2)	0.46280 (7)	0.2645 (1)	B(4)	0.206 (2)	0.3731 (9)	0.2001 (11)
C(P1)	−0.056 (1)	0.1844 (6)	0.2219 (10)	B(6)	−0.136 (2)	0.3736 (7)	0.3248 (10)
C(P2)	−0.051 (2)	0.1834 (6)	0.3268 (11)	B(8)	0.156 (2)	0.4476 (7)	0.2635 (11)
C(P3)	−0.185 (1)	0.2151 (6)	0.3497 (10)	B(9)	0.252 (2)	0.3762 (8)	0.3248 (12)
C(P4)	−0.267 (1)	0.2325 (6)	0.2610 (10)	B(10)	0.164 (2)	0.3012 (7)	0.2686 (11)
C(P5)	−0.186 (1)	0.2142 (6)	0.1812 (10)	H(1)	0.027 (16)	0.290 (7)	0.126 (10)
C(M1)	0.059 (2)	0.1536 (7)	0.1680 (11)	H(2)	−0.178 (13)	0.368 (6)	0.131 (9)
C(M2)	0.067 (2)	0.1514 (7)	0.4024 (12)	H(3)	0.018 (18)	0.451 (8)	0.119 (11)
C(M3)	−0.225 (2)	0.2237 (8)	0.4519 (12)	H(4)	0.292 (10)	0.372 (5)	0.156 (7)
C(M4)	−0.418 (1)	0.2645 (6)	0.2479 (12)	H(56)	−0.052 (9)	0.322 (4)	0.357 (6)
C(M5)	−0.242 (2)	0.2220 (7)	0.0725 (11)	H(67)	−0.048 (9)	0.425 (4)	0.348 (6)
C(P6)	−0.075 (1)	0.5601 (6)	0.2064 (9)	H(6)	−0.263 (10)	0.375 (5)	0.353 (7)
C(P7)	−0.074 (2)	0.5627 (6)	0.3097 (10)	H(8)	0.224 (16)	0.475 (8)	0.239 (10)
C(P8)	−0.208 (2)	0.5299 (6)	0.3325 (10)	H(89)	0.200 (14)	0.432 (7)	0.353 (9)
C(P9)	−0.282 (1)	0.5076 (6)	0.2437 (9)	H(9)	0.358 (20)	0.379 (8)	0.375 (12)
C(P10)	−0.203 (1)	0.5256 (6)	0.1651 (9)	H(910)	0.213 (14)	0.319 (6)	0.355 (9)
C(M6)	0.034 (2)	0.5911 (7)	0.1483 (11)	H(10)	0.230 (15)	0.270 (7)	0.250 (10)
C(M7)	0.044 (2)	0.5958 (7)	0.3821 (11)	H(M41)	−0.442 (14)	0.290 (6)	0.201 (10)
C(M8)	−0.251 (2)	0.5242 (7)	0.4326 (11)	H(M42)	−0.467 (11)	0.233 (5)	0.254 (7)
C(M9)	−0.431 (1)	0.4734 (7)	0.2322 (11)	H(M43)	−0.428 (13)	0.287 (6)	0.308 (9)
C(M10)	−0.255 (2)	0.5142 (7)	0.0552 (11)	H(M91)	−0.482 (17)	0.494 (8)	0.238 (10)
B(1)	0.040 (2)	0.3275 (7)	0.1684 (11)	H(M92)	−0.448 (14)	0.452 (6)	0.177 (9)
B(2)	−0.119 (1)	0.3691 (7)	0.1903 (9)	H(M93)	−0.438 (12)	0.437 (6)	0.270 (8)

Table IV. Positional Parameters and Their Estimated Standard Deviations for 6-Cl-5,7-$(C_5Me_5)_2Co_2B_8H_{11}$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Co(5)	0.30360 (8)	0.31056 (7)	0.35260 (6)	C(M9)	−0.1481 (9)	0.2036 (10)	0.0482 (7)
Co(7)	0.13178 (8)	0.16233 (7)	0.18777 (6)	C(M10)	−0.0616 (9)	−0.0685 (8)	0.2173 (7)
Cl	0.4572 (2)	0.1033 (2)	0.2504 (2)	B(1)	0.1208 (8)	0.3938 (7)	0.2813 (7)
C(1)	0.5036 (6)	0.3740 (6)	0.3013 (6)	B(2)	0.2219 (7)	0.3230 (6)	0.1908 (6)
C(2)	0.4082 (7)	0.4752 (6)	0.2934 (6)	B(3)	0.0396 (8)	0.3215 (7)	0.2019 (6)
C(3)	0.3473 (7)	0.4517 (6)	0.4097 (6)	B(4)	−0.0400 (8)	0.3246 (8)	0.3388 (7)
C(4)	0.3996 (7)	0.3393 (6)	0.4855 (5)	B(6)	0.2959 (7)	0.1787 (6)	0.2775 (6)
C(5)	0.4967 (6)	0.2921 (6)	0.4200 (6)	B(8)	−0.0371 (8)	0.1857 (7)	0.3035 (7)
C(6)	0.1778 (7)	0.0182 (5)	0.1272 (5)	B(9)	−0.0192 (8)	0.1823 (8)	0.4520 (6)
C(7)	0.2284 (7)	0.1289 (5)	0.0397 (5)	B(10)	0.0968 (8)	0.3031 (7)	0.4350 (6)
C(8)	0.1178 (8)	0.2127 (6)	0.0056 (5)	H(1)	0.116 (7)	0.491 (6)	0.247 (6)
C(9)	−0.0050 (7)	0.1519 (6)	0.0687 (5)	H(2)	0.284 (7)	0.384 (6)	0.091 (6)
C(10)	0.0335 (8)	0.0339 (6)	0.1440 (5)	H(3)	−0.026 (7)	0.392 (6)	0.130 (6)
C(M1)	0.6020 (8)	0.3705 (7)	0.1969 (6)	H(4)	−0.146 (7)	0.374 (6)	0.356 (6)
C(M2)	0.3897 (10)	0.5873 (7)	0.1841 (8)	H(8)	−0.122 (7)	0.150 (6)	0.276 (6)
C(M3)	0.2545 (9)	0.5429 (7)	0.4456 (7)	H(9)	−0.086 (7)	0.142 (6)	0.527 (6)
C(M4)	0.3667 (9)	0.2836 (9)	0.6189 (6)	H(10)	0.088 (7)	0.328 (6)	0.489 (6)
C(M5)	0.5862 (7)	0.1777 (7)	0.4655 (7)	H(56)	0.296 (7)	0.177 (6)	0.382 (6)
C(M6)	0.2612 (10)	−0.0975 (7)	0.1852 (7)	H(67)	0.223 (8)	0.100 (6)	0.271 (6)
C(M7)	0.3763 (9)	0.1510 (8)	−0.0161 (7)	H(89)	−0.010 (7)	0.090 (6)	0.394 (6)
C(M8)	0.1279 (11)	0.3392 (7)	−0.0896 (7)	H(910)	0.104 (7)	0.178 (6)	0.509 (6)

Cage Frameworks. Each of the complexes contains an open 10-vertex CoB_9 or Co_2B_8 framework and can be described as a $B_{10}H_{14}$ derivative in which one or two BH units have been formally replaced[13] by $Co[\eta^5-C_5(CH_3)_5]$ groups. The $B_{10}H_{14}$ analogy includes the hydrogen atoms, in that each cobaltaborane has four Co–H–B and/or B–H–B bridges whose locations on the open face are the same as in $B_{10}H_{14}$ itself. Several other metallaborane analogues of $B_{10}H_{14}$ have previously been reported, as discussed below.

The structure of 6-$[\eta^5-C_5(CH_3)_5]CoB_9H_{13}$ has virtual (not crystallographic) mirror symmetry with respect to the plane formed by Co, B(2), B(4), and B(9). Although it is conveniently viewed as a $B_{10}H_{14}$ derivative, the molecule can also be regarded as a sandwich complex of formal Co^{3+} with $[\eta^5-C_5(CH_3)_5]^-$ and $[\eta^3-B_9H_{13}]^{2-}$ ligands.;[14] thus, the plane of the borons bonded to cobalt [B(2), B(5), B(7)] is nearly parallel to that of the $C_5(CH_3)_5^-$ ligand (dihedral angle 3.2°).

The dimetallic species 6,9-$[\eta^5-C_5(CH_3)_5]_2Co_2B_8H_{12}$ has idealized C_{2v} symmetry, with a pseudo mirror plane through Co(6), Co(9), B(2), and B(4), and a second plane containing B(1) and B(3), which is perpendicular to the first. As is evident from Table V, the molecular parameters in the 6-CoB_9 and 6,9-Co_2B_8 cage systems are closely similar. Again, one can view the dicobalt species as formally derived from $B_{10}H_{14}$, or alternatively as a $B_8H_{12}^{4-}$ ligand face-coordinated to two $[\eta^5-C_5(CH_3)_5]Co^{2+}$ moieties. In the latter model, the coordinating boron faces consist respectively of B(2), B(5), B(7) and B(4), B(8), B(10); each of these planes is nearly parallel to its neighboring $C_5(CH_3)_5^-$ ligand and is about 0.2 Å closer to the metal than is the $C_5(CH_3)_5^-$ plane (~1.45 vs. 1.65 Å).

As expected, the Co–H–B bridges in both compounds are unsymmetrical, with the hydrogen closer to boron than to cobalt [the apparent location of H(910) nearer to Co(9) than B(10) in the 6,9-Co_2B_8 species is anomalous and not statistically significant].

The 5,7-$[\eta^5-C_5(CH_3)_5]_2Co_2B_8H_{12}$ isomer is bisected by a virtual mirror plane through B(2), B(4), B(6), and B(9) and can also be regarded as a complex of formal $B_8H_{12}^{4-}$ (obviously different from that in the 6,9-isomer) coordinated to two

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[13] Replacement of BH by $Co(\eta^5-C_5H_5)$ has been discussed: Miller, V. R.; Weiss, R.; Grimes, R. N. *J. Am. Chem. Soc.* **1977**, *99*, 5646.

[14] The "η^3" designation for the coordination of $B_9H_{13}^{2-}$ to cobalt ignores the bridging hydrogens.

Table V. Bond Distances (Å) in 6-[η^5-$C_5(CH_3)_5$]CoB_9H_{13} and 6,9-[η^5-$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$

	6-(C_5Me_5)-CoB_9H_{13}	6,9-(C_5Me_5)$_2$-$Co_2B_8H_{12}$	5-THF-6-(CO)$_3$-MnB_9H_{12}[a]	$B_{10}D_{14}$[b]
B(1)-B(2)	1.763 (10)	1.779 (12)	1.774 (6)	1.774 (5)
B(1)-B(3)	1.775 (12)	1.777 (12)	1.775 (6)	1.772 (6)
B(1)-B(4)	1.797 (11)	1.782 (12)	1.784 (7)	1.782 (5)
B(1)-B(5)	1.741 (11)	1.747 (11)	1.733 (6)	1.754 (4)
B(1)-B(10)	1.746 (12)	1.732 (11)	1.750 (7)	1.758 (4)
B(2)-B(3)	1.763 (11)	1.723 (12)	1.774 (6)	1.782 (5)
B(2)-B(5)	1.806 (10)	1.782 (12)	1.764 (6)	1.785 (5)
B(2)-B(6)				1.715 (4)
B(2)-Co(6)	2.095 (7)	2.082 (8)		
B(2)-Mn(6)			2.226 (4)	
B(2)-B(7)	1.806 (11)	1.757 (12)	1.897 (6)	1.787 (5)
B(3)-B(4)	1.780 (12)	1.813 (12)	1.803 (7)	1.774 (5)
B(3)-B(7)	1.768 (10)	1.706 (12)	1.770 (7)	1.758 (4)
B(3)-B(8)	1.758 (11)	1.753 (13)	1.758 (7)	1.754 (4)
B(4)-B(8)	1.793 (11)	1.819 (12)	1.779 (7)	1.785 (5)
B(4)-B(9)	1.731 (11)		1.711 (8)	1.715 (4)
B(4)-Co(9)		2.061 (9)		
B(4)-B(10)	1.795 (13)	1.779 (12)	1.782 (7)	1.787 (5)
B(5)-B(6)				1.788 (5)
B(5)-Co(6)	2.125 (7)	2.081 (8)		
B(5)-Mn(6)			2.232 (4)	
B(5)-B(10)	1.983 (11)	2.022 (11)	1.993 (6)	1.973 (4)
B(6)-B(7)				1.762 (5)
Co(6)-B(7)	2.118 (6)	2.088 (10)		
Mn(6)-B(7)			2.206 (5)	
B(7)-B(8)	2.023 (11)	2.023 (13)	2.037 (7)	1.973 (4)
B(8)-B(9)	1.774 (13)		1.774 (7)	1.788 (5)
B(8)-Co(9)		2.139 (9)		
B(9)-B(10)	1.817 (12)		1.781 (7)	1.762 (5)
Co(9)-B(10)		2.126 (9)		
⟨B-B⟩	1.808 (3)	1.800 (3)	1.806 (2)	1.800 (2)
B(5)-H(56)	1.17 (5)	1.30 (5)	1.26	1.298 (5)[c]
B(6)-H(56)				1.355 (7)[c]
Co(6)-H(56)	1.52 (5)	1.60 (5)		
Mn(6)-H(56)			1.67	
B(6)-H(67)				1.339 (7)[c]
Co(6)-H(67)	1.65 (6)	1.41 (5)		
Mn(6)-H(67)			1.83	
B(7)-H(67)	1.34 (6)	1.31 (5)	1.27	1.297 (5)[c]
B(8)-H(89)	1.28 (6)	1.38 (5)	1.19	1.298 (5)[c]
B(9)-H(89)	1.30 (7)		1.19	1.355 (7)[c]
Co(9)-H(89)		1.59 (5)		
B(9)-H(910)	1.17 (7)		1.36	1.339 (7)[c]
Co(9)-H(910)		1.32 (5)		
B(10)-H(910)	1.20 (6)	1.42 (5)	1.17	1.297 (5)[c]
⟨B-$H_{terminal}$⟩	1.18 (2)	1.19 (3)	1.13	1.180 (3)
⟨B-H_{bridge}⟩	1.24 (3)	1.35 (3)	1.24	1.322 (3)
⟨metal-H_{bridge}⟩	1.59 (4)	1.48 (3)	1.75	
⟨C-C⟩ (ring)	1.431 (4)	1.425 (4)		
⟨C-H⟩ (methyl)	0.950 (7)	0.940 (3)		

[a] Taken from ref 9. [b] Taken from ref 10. [c] B-D distances.

Table VI. Bond Distances (Å) in 5,7-[η^5-$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$ and 6-Cl-5,7-[η^5-$C_5(CH_3)_5$]$_2Co_2B_8H_{11}$

	5,7-(C_5Me_5)$_2$-$Co_2B_8H_{12}$	6-Cl-5,7-(C_5Me_5)$_2$-$Co_2B_8H_{11}$	5-CpCo-B_9H_{13}[a]
B(1)-B(2)	1.752 (10)	1.805 (5)	1.768 (7)
B(1)-B(3)	1.781 (9)	1.756 (5)	1.746 (7)
B(1)-B(4)	1.786 (11)	1.786 (6)	1.765 (7)
B(1)-Co(5)	2.077 (8)	2.100 (4)	2.082 (5)
B(1)-B(10)	1.743 (10)	1.788 (6)	1.767 (7)
B(2)-B(3)	1.793 (9)	1.788 (5)	1.754 (8)
B(2)-Co(5)	2.119 (7)	2.143 (3)	2.091 (5)
B(2)-B(6)	1.859 (9)	1.792 (5)	1.749 (8)
B(2)-B(7)			1.777 (9)
B(2)-Co(7)	2.158 (7)	2.135 (3)	
B(3)-B(4)	1.788 (10)	1.787 (5)	1.743 (8)
B(3)-B(7)			1.734 (8)
B(3)-Co(7)	2.086 (8)	2.082 (4)	
B(3)-B(8)	1.757 (11)	1.782 (6)	1.743 (8)
B(4)-B(8)	1.827 (11)	1.821 (6)	1.763 (8)
B(4)-B(9)	1.702 (11)	1.752 (7)	1.712 (8)
B(4)-B(10)	1.801 (11)	1.809 (5)	1.776 (7)
Co(5)-B(6)	2.104 (7)	2.062 (3)	2.072 (6)
Co(5)-B(10)	2.182 (8)	2.180 (4)	2.183 (5)
B(6)-B(7)			1.771 (10)
B(6)-Co(7)	2.078 (8)	2.081 (3)	
B(6)-Cl		1.835 (3)	
B(7)-B(8)			1.949 (11)
Co(7)-B(8)	2.192 (8)	2.152 (4)	
B(8)-B(9)	1.835 (11)	1.814 (5)	1.784 (9)
B(9)-B(10)	1.838 (11)	1.808 (6)	1.779 (7)
⟨B-B⟩	1.789 (3)	1.791 (2)	1.757 (2)
Co(5)-H(56)	1.38 (1)	1.48 (1)	1.49 (1)
B(6)-H(56)	1.33 (1)	1.27 (1)	1.26 (1)
B(6)-H(67)	1.33 (1)	1.23 (1)	1.36 (1)
B(7)-H(67)			1.33 (1)
Co(7)-H(67)	1.37 (1)	1.38 (1)	
B(8)-H(89)	1.26 (1)	1.29 (1)	1.40 (1)
B(9)-H(89)	1.32 (1)	1.48 (1)	1.28 (1)
B(9)-H(910)	1.32 (1)	1.44 (1)	1.28 (1)
B(10)-H(910)	1.26 (1)	1.42 (1)	1.28 (1)
⟨B-$H_{terminal}$⟩	1.02 (3)	1.10 (3)	1.10 (1)
⟨B-H_{bridge}⟩	1.30 (1)	1.36 (1)	1.32 (1)
⟨Co-H_{bridge}⟩	1.38 (1)	1.43 (1)	1.49 (1)
C-C (ring)	1.424 (3)	1.422 (2)	1.376 (4)

[a] Taken from ref 12.

[η^5-$C_5(CH_3)_5$]Co^{2+} units. The η^4-coordinating faces B(6), B(2), B(1), B(10) and B(6), B(2), B(3), B(8) are virtually parallel to their respective $C_5(CH_3)_5^-$ ligands. The Co–H–B bridges are again unsymmetrical (Table VI).

Comparison of the structural parameters in the 5,7-Co_2B_8 system and its 6-chloro derivative reveals no marked differences in the cobaltaborane skeletal framework; there is, however, a clear indication of steric interaction between the chlorine substituent and the pentamethylcyclopentadienyl ligands. The chlorine atom lies on the molecular mirror plane (deviation only 0.02 Å) and forces the $C_5(CH_3)_5$ rings slightly further apart, in comparison to the positions in the unsubstituted molecule. Thus, the dihedral angle subtended by the planes of the C(1)–C(5) and C(6)–C(10) rings decreases from 56.7° in the parent complex to 45.1° in the 6-chloro derivative. Another consequence of the Cl–$C_5(CH_3)_5$ interaction is that the rings are no longer parallel to the borane faces coordinated to cobalt; in the chloro compound these dihedral angles are

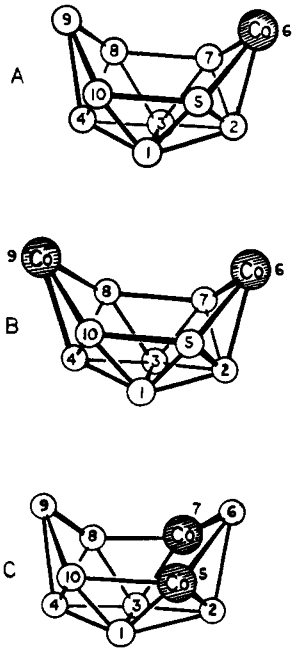

Figure 1. Cage structures and numbering system: A, 6-[η^5-$C_5(CH_3)_5$]CoB_9H_{13}; B, 6,9-[η^5-$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$; C, 5,7-[η^5-$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$.

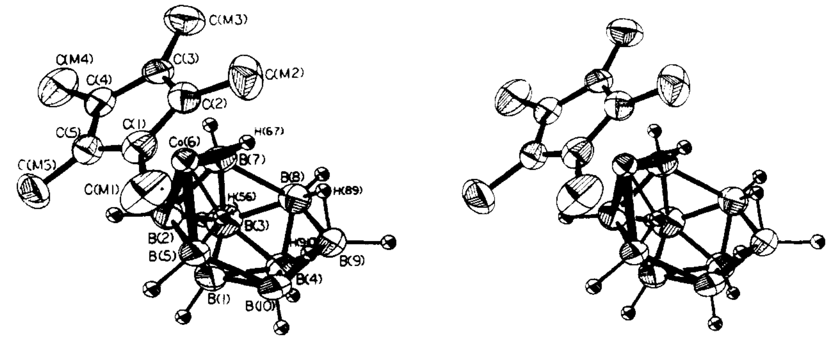

Figure 2. Stereoview of 6-[η^5-$C_5(CH_3)_5$]CoB_9H_{13}. Methyl hydrogen atoms are omitted for clarity.

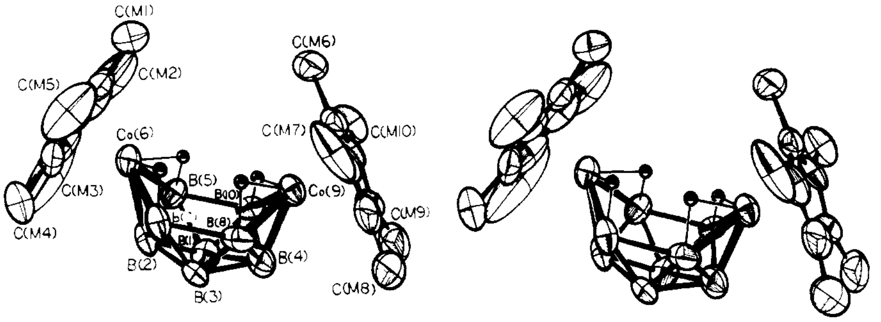

Figure 3. Stereoview of 6,9-[η^5-$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$. Hydrogens other than those in bridging positions are not shown. Numbering of the cyclopentadienyl carbon atoms C(1)–C(10) corresponds to that of the methyl carbons C(M1)–C(M10).

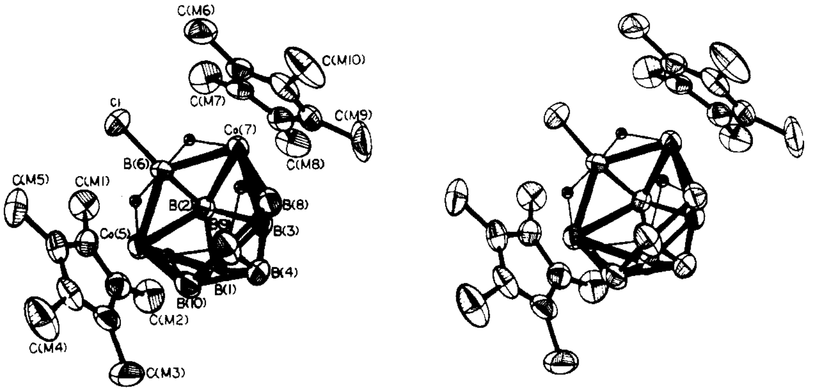

Figure 4. Stereoview of 6-Cl-5,7-[η^5-$C_5(CH_3)_5$]$_2Co_2B_8H_{11}$, showing bridging hydrogens only. The structure of the unsubstituted molecule is virtually identical.

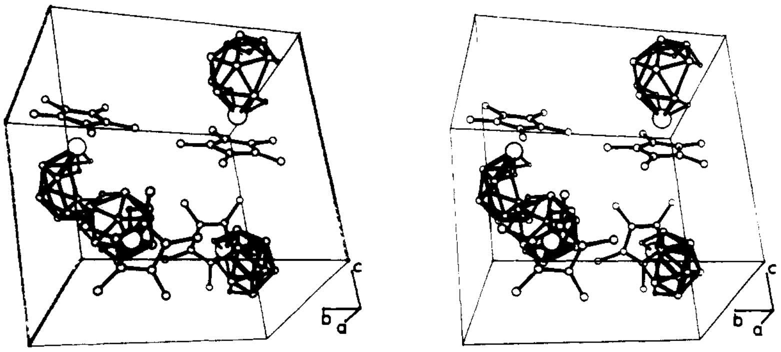

Figure 5. Packing of the unit cell in 6-[η^5-$C_5(CH_3)_5$]CoB_9H_{13}.

6–7° as compared to 1.6° in the unsubstituted molecule.

Not surprisingly, the gross structures of 5,7-[η^5-C_5-$(CH_3)_5$]$_2Co_2B_8H_{12}$ and 5-(η^5-C_5H_5)CoB_9H_{13}[12] are similar (Table VI), although the mean boron–boron distance in the latter species is notably shorter [1.757 (2) vs. 1.789 (3) Å]. This effect is not huge but may be significant, since the average B–B value in the chloro derivative of the dicobalt complex is the same [1.791 (2) Å] as that of the parent compound; moreover, it is noteworthy that the average B–B distances in the four molecules in Table V (~1.80 Å) are statistically indistinguishable. Whether the apparent anomaly in the 5-CoB_9 system signals a real (perhaps electronic) effect cannot be resolved from present evidence.

Comparison with Other Metallaborane Analogues of $B_{10}H_{14}$. Several 10-vertex *nido*-cobaltaboranes having a decaborane-like cage structure have been reported previously, but of these,

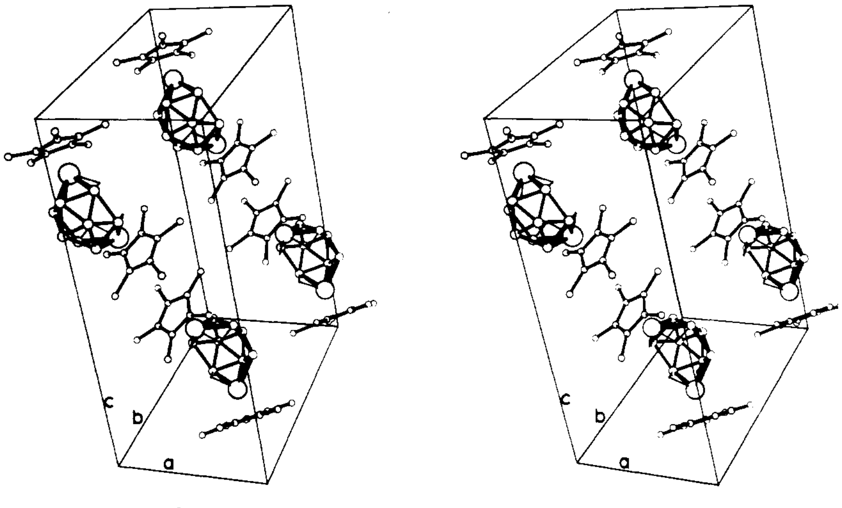

Figure 6. Packing of the unit cell in 6,9-$[\eta^5\text{-}C_5(CH_3)_5]_2Co_2B_8H_{12}$.

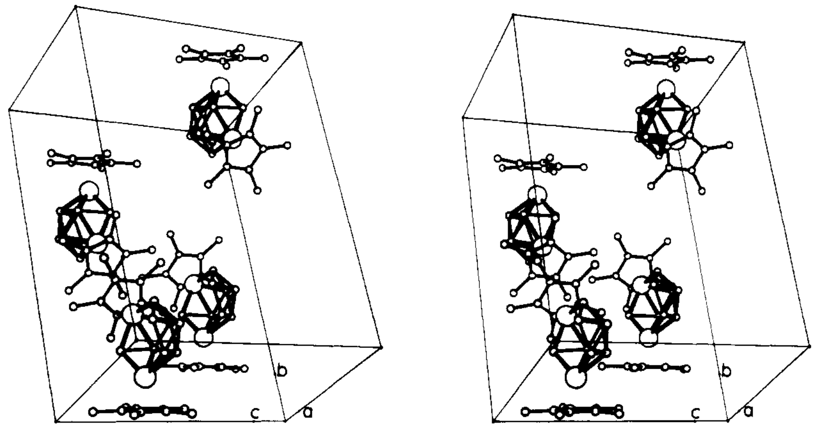

Figure 7. Packing of the unit cell in 5,7-$[\eta^5\text{-}C_5(CH_3)_5]_2Co_2B_8H_{12}$.

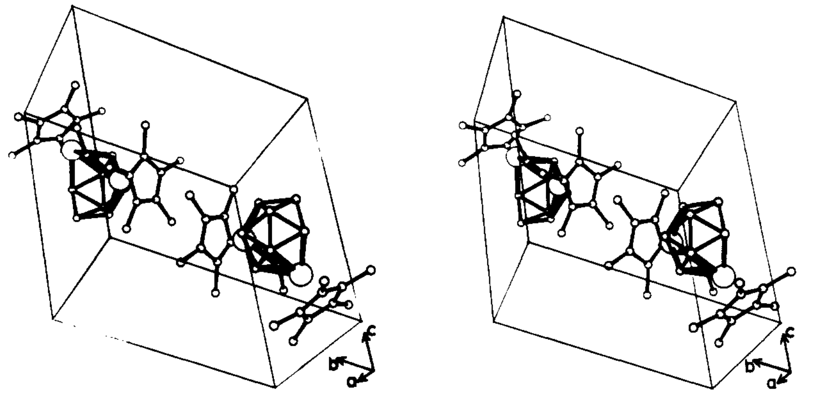

Figure 8. Packing of the unit cell in 6-Cl-5,7-$[\eta^5\text{-}C_5(CH_3)_5]_2Co_2B_8H_{11}$.

only 5-$(\eta^5\text{-}C_5H_5)CoB_9H_{13}$,[13] mentioned above, has been characterized by X-ray diffraction.[12] However, in our laboratory the crystal structures of several borane–metal–carborane sandwich complexes, in which the borane ligand is $(B_9H_{12}\cdot THF)^-$, have been determined and will be reported subsequently.[15]

Sneddon and co-workers[16,17] have reported 2- and 6-$(\eta^5\text{-}C_5H_5)CoB_9H_{13}$, whose structures were proposed from NMR data; since the ^{11}B and ^1H NMR spectra of the latter species[17] closely conform to those of the crystallographically established complex 6-$[\eta^5\text{-}C_5(CH_3)_5]CoB_9H_{13}$ reported here, the structure of 6-$(\eta^5\text{-}C_5H_5)CoB_9H_{13}$ is confirmed. From this it follows that the assignment of the 2-isomer[16] must also be correct, since it is the only remaining structural possibility (based on a $B_{10}H_{14}$-type framework) that is consistent with the NMR evidence.[16b]

One cobaltacarborane analogue, 8,6,7-$(\eta^5\text{-}C_5H_5)CoC_2B_7H_{11}$, has been characterized from X-ray data;[18] this molecule is isoelectronic with the CoB_9 and Co_2B_8 systems, and hence has

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Table VII. Selected Bond Angles (Deg) in 6-[η^5-$C_5(CH_3)_5$]CoB_9H_{13} and 6,9-[η^5-$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$

	6-(C_5Me_5)-CoB_9H_{13}	6,9-(C_5Me_5)$_2$-$Co_2B_8H_{12}$		6-(C_5Me_5)-CoB_9H_{13}	6,9-(C_5Me_5)$_2$-$Co_2B_8H_{12}$
		Cobaltaborane Cage			
B(5)–Co(6)–B(8)	87.3 (3)	86.8 (3)	B(4)–B(8)–B(7)	105.9 (5)	104.8 (6)
B(5)–Co(6)–B(2)	50.7 (3)	50.6 (3)	B(4)–B(8)–B(9)	58.1 (5)	
B(7)–Co(6)–B(2)	50.8 (3)	50.0 (3)	B(4)–B(8)–Co(9)		62.3 (4)
B(2)–Co(6)–H(56)	79 (3)	80 (3)	B(7)–B(8)–B(9)	117.5 (5)	
B(2)–Co(6)–H(67)	87 (3)	85 (3)	B(7)–B(8)–Co(9)		120.4 (5)
B(5)–Co(6)–H(56)	32 (3)	39 (3)	B(7)–B(8)–H(89)	95 (3)	85 (3)
B(7)–Co(6)–H(67)	39 (3)	38 (3)	B(4)–B(9)–H(910)	100 (3)	
H(56)–Co(6)–H(67)	91 (3)	80 (3)	B(4)–Co(9)–H(910)		91 (3)
B(2)–B(1)–B(4)	113.7 (6)	114.0 (6)	B(4)–B(9)–H(89)	106 (3)	
B(5)–B(1)–B(10)	69.3 (5)	70.8 (5)	B(4)–Co(9)–H(89)		85 (3)
B(5)–B(2)–Co(6)	65.5 (3)	64.7 (4)	B(4)–B(9)–B(8)	61.5 (5)	
Co(6)–B(2)–B(7)	65.3 (3)	65.2 (4)	B(4)–Co(9)–B(8)		51.2 (3)
B(1)–B(2)–B(3)	60.5 (5)	60.7 (5)	B(4)–B(9)–B(10)	60.7 (5)	
B(5)–B(2)–B(7)	108.3 (5)	108.0 (6)	B(4)–Co(9)–B(10)		50.4 (3)
B(2)–B(3)–B(4)	114.6 (6)	114.9 (7)	B(8)–B(9)–B(10)	105.2 (6)	
B(7)–B(3)–B(8)	69.4 (5)	71.6 (6)	B(8)–Co(9)–B(10)		87.5 (4)
B(1)–B(4)–B(3)	59.5 (5)	58.9 (5)	B(8)–B(9)–H(89)	46 (3)	
B(8)–B(4)–B(9)	60.4 (5)		B(8)–Co(9)–H(89)		40 (3)
B(8)–B(4)–Co(9)		66.4 (4)	B(4)–B(9)–H(9)	140 (3)	
B(8)–B(4)–B(10)	105.3 (6)	109.7 (6)	B(10)–B(9)–H(910)	41 (3)	
B(9)–B(4)–B(10)	62.0 (5)		B(10)–Co(9)–H(910)		41 (3)
Co(9)–B(4)–B(10)		66.4 (4)	H(89)–B(9)–H(910)	101 (4)	
B(1)–B(5)–Co(5)	116.7 (5)	118.2 (5)	H(89)–Co(9)–H(910)		97 (3)
B(2)–B(5)–Co(6)	63.8 (3)	64.7 (4)	H(89)–B(9)–H(9)	97 (4)	
B(2)–B(5)–B(10)	104.7 (5)	105.7 (5)	H(910)–B(9)–H(9)	109 (4)	
Co(6)–B(5)–B(10)	120.4 (4)	122.7 (4)	B(1)–B(10)–B(9)	109.4 (6)	
B(10)–B(5)–H(56)	91 (3)	81 (3)	B(1)–B(10)–Co(9)		116.9 (6)
B(2)–B(7)–Co(6)	64.0 (3)	64.8 (4)	B(4)–B(10)–B(9)	57.3 (5)	
B(2)–B(7)–B(8)	104.9 (5)	106.0 (6)	B(4)–B(10)–Co(9)		63.2 (4)
B(3)–B(7)–Co(6)	116.3 (5)	117.0 (6)	B(4)–B(10)–B(5)	107.5 (5)	105.6 (6)
Co(6)–B(7)–B(8)	120.7 (4)	122.2 (5)	B(9)–B(10)–B(5)	118.4 (5)	
B(8)–B(7)–H(67)	89 (3)	95 (3)	Co(9)–B(10)–B(5)		120.8 (4)
B(3)–B(8)–B(9)	108.7 (6)		B(5)–B(10)–H(910)	99 (3)	108 (3)
B(3)–B(8)–Co(9)		115.6 (6)			
		B–H–B and Co–H–B Bridges			
B(5)–H(56)–Co(6)	104 (4)	91 (3)	B(8)–H(89)–Co(9)		91 (3)
B(7)–H(67)–Co(6)	90 (3)	100 (3)	B(10)–H(910)–B(9)	100 (5)	
B(8)–H(89)–B(9)	87 (4)		B(10)–H(910)–Co(9)		101 (3)
		$C_5(CH_3)_5$ Rings			
⟨C_{ring}–C_{ring}–C_{ring}⟩	108.0	108.0	⟨C_{ring}–C_{ring}–C_{Me}⟩	126.0	126.0

only two bridging hydrogens (Co–H–B and B–H–B) to compensate for the presence of two CH units.

The 6-[η^5-$C_5(CH_3)_5$]CoB_9H_{13} complex and its C_5H_5 counterpart are structural analogues of the 6-$(CO)_3MB_9H_{12}R$ family (M = Mn, Re; R = H, THF, $(C_2H_5)_2O$, $(C_2H_5)_3N$-$(CH_2)_4O$) reported earlier by Gaines and co-workers.[19] In all of those species the metal tricarbonyl group occupies the 6-position in a $B_{10}H_{14}$-type framework and, again, the four bridging hydrogens adopt locations analogous to those in the parent borane. As the data in Table V show, there are no large or systematic discrepancies between corresponding bond distances in 6-[η^5-$C_5(CH_3)_5$]CoB_9H_{13}, 5-THF-6-$(CO)_3MnB_9H_{12}$ (or the 2-THF derivative),[19] and $B_{10}H_{14}$. As expected from the larger covalent radius of Mn(I) compared to that of Co(III), the Mn–B distances exceed those of their Co–B counterparts by ~0.09–0.14 Å.

The Pentamethylcyclopentadienyl Rings. In each of the four compounds examined in this study, the $C_5(CH_3)_5$ groups exhibit a feature previously noted[3,20] in other compounds containing this ligand: in general, the methyl carbon atoms are bent significantly out of the C_5 ring plane in a direction away from the metal. The magnitude of the deflection is as much as 0.19 Å but in most instances falls between 0.05 and 0.10 Å. Although both electronic[21] and steric[20] arguments have been advanced to account for this phenomenon in various species, in the present instance it appears more likely an electronic effect produced by optimization of orbital overlap[21] between the ring carbons and the coordinated metal atom. There is, however, an unusual aspect to the out-of-plane deformations in 6,9-[η^5-$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$: two of the methyl carbons C(M1) and C(M6), are bent *toward* their respective cobalt atoms, opposite to the trend just noted. These particular methyl groups happen to be the ones located above the open face of the cluster, suggesting some kind of weak CH_3···Co interaction.

Also notable is the orientation of the methyl hydrogen atoms in 6-[$C_5(CH_3)_5$]CoB_9H_{13} (the only one of the four structures in which all of the methyl hydrogens were located and refined). While one might expect the methyl orientations to be nearly random or badly disordered, such is not the case; as shown in Figure 9, each CH_3 unit places two of its hydrogens at equal proximity to cobalt, with the third directed away from the metal. This arrangement has been noted in other η^5-$C_5(CH_3)_5$ transition-metal complexes[22,23] and is curious in that it appears to produce greater than minimal steric interaction between methyl groups. Nearest-neighbor H–H interactions for the

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Table VIII. Selected Bond Angles (Deg) in 5,7-$[\eta^5\text{-}C_5(CH_3)_5]_2Co_2B_8H_{12}$ and 6-Cl-5,7-$[\eta^5\text{-}C_5(CH_3)_5]_2Co_2B_8H_{11}$

	5,7-$(C_5Me_5)_2$-$Co_2B_8H_{12}$	6-Cl-5,7-$(C_5Me_5)_2$-$Co_2B_8H_{11}$		5,7-$(C_5Me_5)_2$-$Co_2B_8H_{12}$	6-Cl-5,7-$(C_5Me_5)_2$-$Co_2B_8H_{11}$
		Cobaltaborane Cage			
B(2)-B(1)-B(4)	114.7 (4)	114.1 (3)	H(56)-B(6)-Cl		106 (2)
Co(5)-B(1)-B(10)	69.0 (4)	67.7 (2)	H(67)-B(6)-Cl		95 (2)
Co(5)-B(2)-B(6)	63.5 (3)	62.4 (1)	B(2)-Co(7)-B(6)	52.0 (2)	50.3 (1)
Co(7)-B(2)-B(6)	61.8 (3)	63.3 (2)	B(2)-Co(7)-B(8)	88.8 (3)	90.1 (1)
B(1)-B(2)-B(3)	60.3 (4)	58.5 (2)	B(3)-Co(7)-B(6)	92.4 (3)	91.2 (1)
Co(5)-B(2)-Co(7)	117.8 (5)	116.9 (2)	B(6)-Co(7)-B(8)	100.8 (3)	100.9 (1)
B(2)-B(3)-B(4)	112.6 (5)	114.9 (2)	B(8)-Co(7)-H(67)	81 (3)	100 (2)
Co(7)-B(3)-B(8)	69.0 (4)	67.2 (2)	B(3)-B(8)-B(9)	106.0 (5)	108.0 (3)
B(1)-B(4)-B(3)	59.8 (4)	58.9 (2)	Co(7)-B(8)-B(4)	115.5 (5)	116.4 (3)
B(8)-B(4)-B(9)	62.6 (4)	61.0 (2)	B(4)-B(8)-B(9)	55.4 (4)	57.6 (2)
B(8)-B(4)-B(10)	109.5 (5)	105.3 (3)	Co(7)-B(8)-B(9)	121.5 (5)	123.5 (2)
B(9)-B(4)-B(10)	63.2 (4)	61.0 (2)	Co(7)-B(8)-H(89)	102 (3)	97 (2)
B(1)-Co(5)-B(6)	91.7 (3)	91.5 (1)	B(4)-B(9)-H(910)	104 (3)	111 (2)
B(2)-Co(5)-B(6)	52.2 (2)	50.4 (1)	B(4)-B(9)-H(89)	106 (3)	106 (2)
B(2)-Co(5)-B(10)	88.9 (3)	89.5 (1)	B(4)-B(9)-B(8)	62.1 (4)	61.4 (2)
B(6)-Co(5)-B(10)	101.3 (3)	100.5 (1)	B(4)-B(9)-B(10)	61.0 (4)	61.1 (2)
B(10)-Co(5)-H(56)	86 (3)	87 (2)	B(8)-B(9)-B(10)	107.6 (5)	105.6 (3)
Co(5)-B(6)-Co(7)	122.2 (3)	123.3 (2)	B(8)-B(9)-H(89)	44 (2)	45 (1)
Co(5)-B(6)-B(2)	64.3 (3)	67.2 (2)	B(4)-B(9)-H(9)	134.0 (5)	127.5 (4)
Co(7)-B(6)-B(2)	66.2 (3)	66.4 (2)	B(10)-B(9)-H(910)	43 (2)	50 (1)
B(2)-B(6)-H(56)	100 (3)	107 (2)	H(89)-B(9)-H(910)	123 (4)	110 (2)
B(2)-B(6)-H(67)	99 (3)	106 (2)	H(89)-B(9)-H(9)	96 (3)	103 (2)
Co(5)-B(6)-H(56)	41 (2)	45 (1)	H(910)-B(9)-H(9)	97 (3)	99 (2)
Co(7)-B(6)-H(67)	40 (2)	40 (1)	B(1)-B(10)-B(9)	106.3 (5)	108.4 (3)
H(56)-B(6)-H(67)	103 (3)	112 (2)	B(4)-B(10)-B(9)	55.8 (4)	58.0 (2)
B(2)-B(6)-H(6)	120.9 (5)		B(4)-B(10)-Co(5)	116.2 (5)	116.3 (2)
H(56)-B(6)-H(6)	115 (3)		B(9)-B(10)-Co(5)	120.7 (5)	123.3 (2)
H(67)-B(6)-H(6)	117 (3)		Co(5)-B(10)-H(910)	104 (3)	96 (2)
B(2)-B(6)-Cl		129.8 (2)			
		B-H-B and Co-H-B Bridges			
Co(5)-H(56)-B(6)	101 (3)	98 (2)	B(8)-H(89)-B(9)	91 (3)	82 (2)
Co(7)-H(67)-B(6)	100 (3)	106 (2)	B(9)-H(910)-B(10)	92 (3)	79 (2)
		$C_5(CH_3)_5$ Rings			
$\langle C_{ring}-C_{ring}-C_{ring}\rangle$	108.0	108.0	$\langle C_{ring}-C_{ring}-C_{Me}\rangle$	126.0	126.0

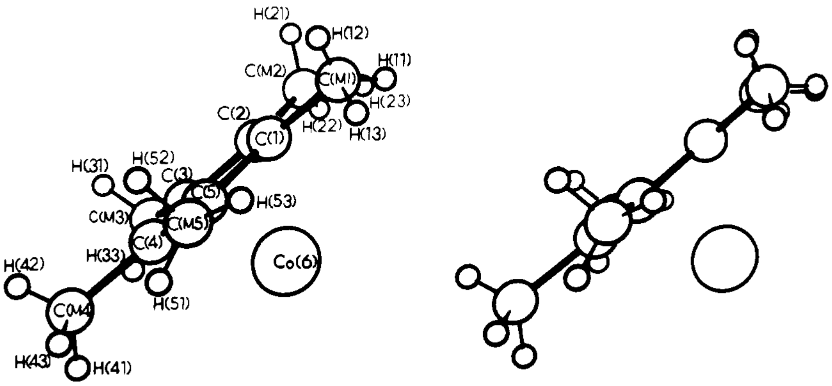

Figure 9. Detailed view of the pentamethylcyclopentadienyl ligand coordinated to Co(6), showing the orientation of the methyl hydrogen atoms.

10 hydrogen atoms on the cobalt side of the ring range from 2.49 to 2.84 Å, which fall within the values (2.40[24] to 2.90[25] Å) typically cited for van der Waals interactions between hydrogen atoms.

Conclusions

The 6,9- and 5,7-$[\eta^5\text{-}C_5(CH_3)_5]_2Co_2B_8H_{12}$ isomers, and the 6-Cl derivative of the latter, are the first structurally characterized metallaborane analogues of $B_{10}H_{14}$ containing more than one metal atom in the framework. The observed structures are remarkably similar to that of $B_{10}H_{14}$ itself. It is intriguing, however, to speculate as to what further extent it might be possible to replace BH with $Co(\eta^5\text{-}C_5R_5)$ units in the B_{10} cage and on what the structural consequences of such replacement might be. All of the cobaltaboranes described here, as well as their analogues discussed above, are 24-electron, 10-vertex $(2n + 4)$ cage systems, which adopt nido structures and thus obey the skeletal electron-counting rules for clusters.[26] However, there is evidence that as the metal content increases, local metal–metal interactions become more important in determining cage geometry; this is seen, for example, in $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$[27] and $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$,[28] both of which are closo 8-vertex polyhedra in violation of Wade's

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rules. Molecular orbital treatments[29] strongly suggest that localized Co–Co and Ni–Ni bonding plays an important role in these systems. In the family of cobaltaboranes under consideration here, in which the general formula is $[(C_5R_5)Co]_{10-n}B_nH_{n+4}$, only the members for which $n = 8$, 9, or 10 are presently known. Stable species with quite high metal content may well exist, but major structural deviation from the $B_{10}H_{14}$ geometry can be expected.

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Registry No. 6-$[C_5Me_5]CoB_9H_{13}$, 80145-64-8; 6,9-$[C_5Me_5]_2Co_2B_8H_{12}$, 80160-31-2; 5,7-$[C_5Me_5]_2Co_2B_8H_{12}$, 80145-65-9; 6-Cl-5,7-$[C_5Me_5]_2CoB_8H_{11}$, 80145-66-0.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, anisotropic thermal parameters, C–C distances in $C_5(CH_3)_5$ rings, and selected mean planes (60 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of $[\eta^5\text{-}C_5(CH_3)_5]_3Co_3B_4H_4$, an Electron-Hyperdeficient Cluster with Severe Intramolecular Ligand–Ligand Crowding[1]

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An X-ray diffraction study of the title compound confirmed its structure as a *closo*-Co_3B_3 octahedron whose tricobalt face is capped by BH, analogous to the previously described complex $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$. The three $C_5(CH_3)_5$ ligands are η^5-coordinated to cobalt and are in close proximity to each other, with interligand C_{methyl}–C_{methyl} contacts as short as 3.33 Å. This molecule is the first structurally characterized complex in which three mutually bonded metal atoms are each η^5-coordinated to a $C_5(CH_3)_5$ ligand. The methyl groups are bent out of the C_5 ring planes by 0.08–0.19 Å (average deflection 0.14 Å), and the three Co–Co bond distances are increased to a mean value of 2.497 (5) Å compared to 2.441 (1) Å for the $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$ analogue; both effects are ascribed to relief of steric crowding of the $C_5(CH_3)_5$ ligands. The observed structure is in conformity with the ^1H and ^{11}B NMR data and with the electron-counting rules for polyhedral cluster systems. Crystal data: mol wt 630; space group $P\bar{1}$; $Z = 2$; $a = 8.480$ (9), $b = 10.747$ (8), $c = 17.585$ (15) Å; $\alpha = 89.55$ (7), $\beta = 85.76$ (6), $\gamma = 71.59$ (8)°; $V = 1516$ Å^3; $R = 0.069$ for 2699 reflections for which $F_o^2 > 3\sigma(F_o^2)$.

Introduction

In the two accompanying articles we describe the synthesis[2] of a series of (pentamethylcyclopentadienyl)cobaltaboranes from the $B_5H_8^-$ ion, $CoCl_2$, and $C_5(CH_3)_5^-$ ion in THF solution and the structural characterization[3] of several 10-vertex complexes containing CoB_9 or Co_2B_8 nido cage systems. These 10-vertex species, which are structural and electronic analogues of $B_{10}H_{14}$, have been shown[2] to originate from the $B_9H_{14}^-$ ion, which under certain conditions is formed in large concentration during the deprotonation of B_5H_9 with NaH. However, under other conditions the predominant borane species is $B_5H_8^-$, and its reaction with $CoCl_2$ and $C_5(CH_3)_5^-$ ion generates primarily *small* cobaltaboranes having 5- to 7-vertex cages.[2] Several of these products are counterparts of cyclopentadienylcobaltaboranes obtained previously[4] from $B_5H_8^-$, $CoCl_2$, and $C_5H_5^-$. One such complex, formulated as $[C_5(CH_3)_5]_3Co_3B_4H_4$, appeared to be analogous to the known species $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$, which was earlier shown from NMR[4] and X-ray[5] studies to have a capped-octahedral cage geometry in which a BH unit is coordinated to a Co_3 face of a *closo*-Co_3B_3 polyhedron.

The apparent analogy between these $(C_5R_5)_3Co_3B_4H_4$ complexes was reinforced by the ^1H and ^{11}B FT NMR data,[2,4] which are closely similar and support a C_{3v} capped-octahedral geometry for $[C_5(CH_3)_5]_3Co_3B_4H_4$. This structure, however, requires a triangular, bonded Co_3 array with each cobalt η^5-coordinated to a $C_5(CH_3)_5$ ligand; a priori, such an arrangement seemed incompatible with the large steric requirements of the bulky pentamethylcyclopentadienyl groups. Hence an X-ray crystallographic study was undertaken to establish the solid-state geometry.

Experimental Section

Yellow crystals of the title compound, prepared as described elsewhere,[2] were grown by slow evaporation of a pentane solution at 0 °C. A small platelet was selected for data collection after preliminary precession photographs indicated satisfactory crystal quality. Crystal data: $Co_3C_{30}B_4H_{49}$, mol wt 630; space group $P\bar{1}$; $Z = 2$; $a = 8.480$ (9), $b = 10.747$ (8), $c = 17.585$ (15) Å; $\alpha = 89.55$ (7), $\beta = 85.76$ (6), $\gamma = 71.59$ (8)°; $V = 1516$ Å^3; $\rho_{calcd} = 1.34$ g cm^{-3}; μ(Mo Kα) = 17.0 cm^{-1}; crystal dimensions (distances in mm of faces from centroid) (100) 0.21, ($\bar{1}00$) 0.21, (010) 0.11, ($0\bar{1}0$) 0.11, (001) 0.09, ($00\bar{1}$) 0.09; maximum and minimum transmission coefficients 0.88 and 0.79.

The Enraf-Nonius program SEARCH was used to obtain 25 accurately centered reflections which were then used in the program INDEX to obtain approximate cell dimensions and an orientation matrix for data collection. Refined cell dimensions and their estimated standard deviations were obtained from least-squares refinement of 28 accurately centered reflections. The mosaicity of the crystal was examined by the ω-scan technique and judged to be satisfactory.

Collection and Reduction of the Data. Diffraction data were collected at 292 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer, with Mo Kα radiation from a highly oriented graphite-crystal monochromator. The θ–2θ scan technique was used to record the intensities for all nonequivalent reflections for which $1° < 2\theta < 46°$. Scan widths (SW) were calculated from SW = $(A + B \tan \theta)°$, where A is estimated from the mosaicity of the crystal and B allows for the increase in width of peak due to Kα_1–Kα_2 splitting. The values of A and B were 0.6 and 0.35,

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