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Crystal and Molecular Structure of 5-(η^5-C_5H_5)CoB_9H_{13}, a Cobaltaborane Analogue of $B_{10}H_{14}$

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The structure of 5-(η^5-cyclopentadienyl)-5-cobalta-*nido*-decaborane(14) was determined from a single-crystal x-ray diffraction investigation. The molecule consists of a $B_{10}H_{14}$-like cage in which a (η^5-C_5H_5)Co group replaces a BH unit at the 5 position, in agreement with the structure originally proposed from ^{11}B and ^1H NMR spectra. The compound crystallizes in the monoclinic space group $P2_1/c$, with $a = 8.649$ (3) Å, $b = 12.826$ (6) Å, $c = 11.545$ (5) Å, $\beta = 106.90$ (3)°, $\rho_{obsd} = 1.25$ (2) g cm^{-3}, and $\rho_{calcd} = 1.28$ g cm^{-3} for $Z = 4$. The structure was refined by full-matrix least-squares methods to a final R value of 4.3% and R_w of 5.1% for the 1166 reflections for which $F_o^2 > 3\sigma(F_o^2)$. The molecule has four bridging hydrogens on the open face, of which three are of the B–H–B type and one is B–H–Co, the positions being analogous to those in $B_{10}H_{14}$. The compound is structurally related to other *nido*-metalloboranes containing an MB_9 cage and also to (η^5-C_5H_5)$CoC_2B_7H_{11}$, a *nido*-cobaltacarborane. It can also be viewed as a metal complex consisting of $B_9H_{13}^{2-}$ and η^5-$C_5H_5^-$ ligands sandwiched around a Co^{3+} ion, with the B_4 face of the borane ligand nearly parallel to the $C_5H_5^-$ plane.

Introduction

A recurring theme in metalloborane[1] and metallocarborane[2] chemistry is the formal substitution of heteroatom groups for BH or CH units in borane or carborane cage frameworks, often producing species of higher stability than the parent molecule.[3] A common replacement is that of the cyclopentadienylcobalt [(η^5-C_5H_5)Co] unit for BH; since both groups formally donate two electrons to the skeletal framework,[7] such a substitution leaves unchanged the number of electrons in skeletal bonding molecular orbitals and therefore generates no major structural alterations. An example is red crystalline 2-(η^5-C_5H_5)CoB_4H_8,[8] an analogue of B_5H_9 in which (η^5-C_5H_5)Co replaces a basal BH group. In conformity with the structure originally proposed from NMR data,[8] an x-ray investigation[9] has confirmed that the molecule retains the essential square-pyramidal shape with four basal bridging hydrogens, as in B_5H_9 itself.

The synthesis of 2-(η^5-C_5H_5)CoB_4H_8 from $B_5H_8^-$, $CoCl_2$, and $C_5H_5^-$ also gave a number of other cobaltaboranes having three or four boron atoms, but only one larger species, 5-(η^5-C_5H_5)CoB_9H_{13}, was isolated.[6b,8] This compound was characterized[6b,8] from ^{11}B and ^1H NMR spectra and the geometry proposed was that of a $B_{10}H_{14}$-like basket with the cobalt group replacing the BH in the 5 position on the open face. The present paper describes an x-ray investigation in which this structure was confirmed. Although crystallographic studies of several other cobaltaboranes from the same reaction have been conducted[10] or are in progress, (η^5-C_5H_5)CoB_9H_{13} is structurally distinct from the others and therefore is reported separately.

Experimental Section

Several red crystals of the title compound, prepared from NaB_5H_8, $CoCl_2$, and NaC_5H_5 as described elsewhere,[6b,8] were grown from a hexane solution by slow evaporation. One acicular crystal, ap-

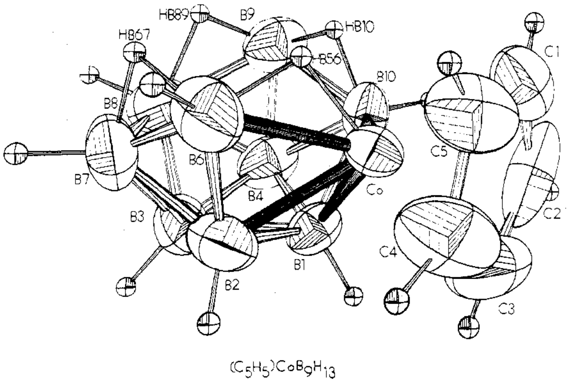

Figure 1. Molecular structure and numbering system for (η^5-C_5H_5)CoB_9H_{13}, with nonhydrogen atoms shown as 50% probability ellipsoids.

proximately 0.62 × 0.12 × 0.06 mm, was found to be suitable for x-ray analysis. Crystal data: $CoC_5B_9H_{18}$, mol wt = 234.4; space group $P2_1/c$; $Z = 4$; $a = 8.649$ (3), $b = 12.826$ (6), $c = 11.545$ (5) Å; $\beta = 106.90$ (3)°; $V = 1225$ (1) Å^3; μ(Mo Kα) = 14.12 cm^{-1}; $\rho_{\text{calcd}} = 1.279$, $\rho_{\text{obsd}} = 1.25$ (2) g cm^{-3}; $F(000) = 480$. The Enraf-Nonius program SEARCH was used to obtain 15 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 28 accurately centered reflections. The mosaicity of the crystal was judged marginally acceptable. Systematic absences for $k = 2n + 1$ on $0k0$ and $l = 2n + 1$ on $h0l$ uniquely establish the space group as $P2_1/c$.

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 PDP8/M computer, using Mo Kα radiation from a highly oriented graphite crystal monochrometer. The θ–2θ scan technique was used to record the intensities for all reflections for which $1.0 < 2\theta < 44°$. 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 peak width due to Kα_1 and Kα_2 splitting. The values of A and B were 0.9 and 0.3°, 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 5 counts above background on a rapid prescan, such reflections being 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. Of the 1352 measured intensities, 1166 had $F_o^2 > 3\sigma(F_o^2)$ where $\sigma(F_o^2)$ was estimated from counting statistics.[11]

Solution and Refinement. The coordinates of the cobalt atom were determined virtually by inspection from a three-dimensional Patterson synthesis. 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 $[2F_o/\sigma(F_o)^2]^2$ 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[12] and those for hydrogen from Stewart.[13] The effects of anomalous dispersion were included in F_c using Cromer and Ibers'[14] values for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. The computing system and programs used are described elsewhere.[15]

An electron density map phased on the refined cobalt position yielded 12 (5 carbon, 7 boron) of the remaining 14 nonhydrogen atoms. Further isotropic refinement with 13 atoms followed by another map resulted in the location of another boron. More refinement with the cobalt and the cyclopentadienyl carbons anisotropic, inclusion of cyclopentadienyl hydrogens at calculated positions (not refined), and an absorption correction (transition coefficient: maximum 0.94, minimum 0.88) resulted in the location of the remaining boron. Further refinement with all nonhydrogen atoms anisotropic reduced R to 5.8%. At this point another electron density map yielded the location of 11 of the 13 cage hydrogen atoms, including all four bridging hydrogens. The remaining two hydrogen positions had to be calculated. Several more cycles of least-squares refinement resulted in the model converging at $R = 4.3$ and $R_w = 5.1$%. The error in an observation of unit weight was 2.1. The largest final parameter shift for a nonhydrogen atom was 0.02 times its esd. Hydrogens were refined isotropically except for the thermal parameters of H1CP–H5CP which were held fixed at 5.00 Å^2. The value of R including unobserved reflections [$F_o^2 \leq 3\sigma(F_o^2)$] was 5.3%, indicating that nothing would be gained by careful measurement of reflections automatically rejected during data collection. A table of observed structure factors is available.[16]

Discussion

Final positional and thermal parameters are given in Table I while Tables II and III contain the bond lengths and angles, respectively. Standard deviations were derived from the inverse matrix in the course of least-squares refinement calculations and are given in parentheses. The molecular structure and numbering are given in Figure 1 while Figure 2 is a stereoscopic pair view of the molecule as seen from above the open face. The closest intermolecular contacts and mean planes are given in Tables IV and V, respectively.

The structure is in full agreement with that proposed originally[8] from ^{11}B and ^{1}H NMR data and electron-counting rules and may be regarded as a $B_{10}H_{14}$ cage with a (η^5-C_5H_5)Co group replacing the BH group at position 5 (equivalent to 7, 8, and 10). The close analogy between this molecule and $B_{10}H_{14}$ is demonstrated by a comparison of crystallographic bond distances[17a] in the two species, which reveals that the individual B–B bonds in the cobaltaborane differ from their counterparts in $B_{10}H_{14}$ by an average of 0.019 Å, corresponding to less than three standard deviations. The largest variations occur at B3–B4 and B2–B6 where the cobaltaborane distances are respectively 0.039 and 0.034 Å

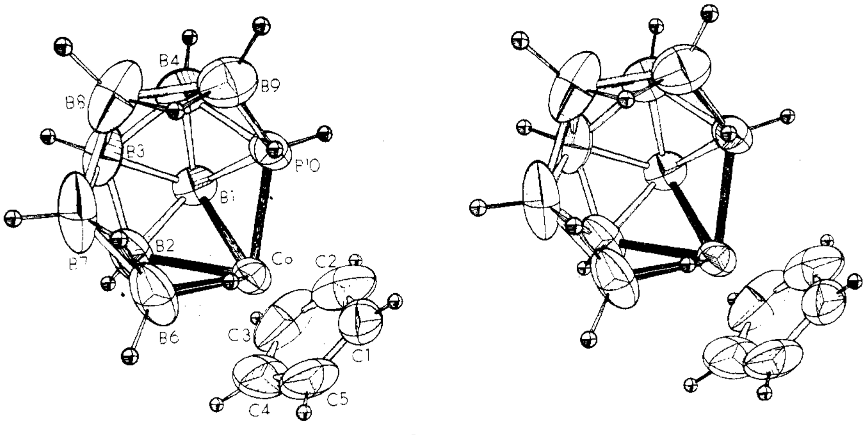

Figure 2. Stereoview of the molecule as seen from above the open face.

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

Atom	x	y	z	$B_{1,1}$	$B_{2,2}$	$B_{3,3}$	$B_{1,2}$	$B_{1,3}$	$B_{2,3}$
Co	0.22155 (8)	0.17167 (6)	−0.15952 (6)	0.01193 (9)	0.00657 (5)	0.00701 (5)	0.0028 (2)	0.0058 (1)	0.0024 (1)
C1	0.1528 (8)	0.0410 (5)	−0.0854 (6)	0.017 (1)	0.0092 (5)	0.0140 (7)	−0.005 (1)	0.001 (2)	0.006 (1)
C2	0.1961 (8)	0.0152 (5)	−0.1872 (7)	0.026 (1)	0.0079 (5)	0.0300 (10)	−0.012 (1)	0.031 (2)	−0.017 (1)
C3	0.0976 (10)	0.0676 (7)	−0.2850 (6)	0.040 (2)	0.0194 (8)	0.0090 (6)	−0.033 (2)	0.010 (2)	−0.002 (1)
C4	−0.0106 (9)	0.1260 (7)	−0.2431 (7)	0.015 (1)	0.0182 (8)	0.0142 (7)	0.001 (2)	−0.002 (2)	0.009 (1)
C5	0.0262 (8)	0.1076 (6)	−0.1195 (6)	0.018 (1)	0.0153 (7)	0.0135 (6)	−0.004 (2)	0.019 (1)	0.003 (1)
B1	0.3824 (8)	0.2134 (5)	−0.2551 (5)	0.0149 (10)	0.0068 (5)	0.0077 (5)	−0.002 (1)	0.009 (1)	−0.0032 (9)
B2	0.2326 (9)	0.3077 (6)	−0.2566 (6)	0.0239 (13)	0.0087 (6)	0.0077 (6)	0.010 (2)	0.010 (1)	0.0038 (10)
B3	0.4306 (11)	0.3459 (5)	−0.2473 (6)	0.0328 (16)	0.0060 (5)	0.0102 (6)	−0.004 (2)	0.017 (2)	0.0022 (10)
B4	0.5791 (9)	0.2559 (6)	−0.1769 (6)	0.0173 (12)	0.0096 (6)	0.0104 (7)	−0.006 (2)	0.009 (2)	−0.0034 (11)
B6	0.1904 (11)	0.3261 (6)	−0.1188 (7)	0.0324 (14)	0.0081 (5)	0.0130 (6)	0.017 (2)	0.022 (1)	0.0038 (12)
B7	0.3297 (14)	0.4099 (6)	−0.1584 (10)	0.0505 (24)	0.0047 (5)	0.0144 (8)	0.008 (2)	0.026 (2)	0.0036 (11)
B8	0.5582 (12)	0.3731 (6)	−0.1032 (7)	0.0399 (19)	0.0085 (6)	0.0101 (7)	−0.017 (2)	0.017 (2)	−0.0019 (11)
B9	0.6128 (10)	0.2533 (7)	−0.0233 (7)	0.0182 (13)	0.0106 (7)	0.0110 (7)	−0.006 (2)	0.005 (2)	−0.0031 (12)
B10	0.4840 (8)	0.1574 (5)	−0.1136 (7)	0.0117 (9)	0.0053 (5)	0.0129 (7)	0.002 (1)	0.004 (1)	−0.0003 (10)

Atom	x	y	z	B, A^2	Atom	x	y	z	B, A^2
H1CP	0.214 (6)	0.023 (4)	−0.015 (4)	5	H6	0.082 (8)	0.370 (5)	−0.093 (5)	8 (2)
H2CP	0.250 (7)	−0.017 (4)	−0.211 (4)	5	H7	0.312 (9)	0.490 (5)	−0.159 (6)	9 (2)
H3CP	0.083 (6)	0.086 (4)	−0.349 (4)	5	H8	0.639 (7)	0.448 (5)	−0.064 (5)	8 (2)
H4CP	−0.087 (6)	0.176 (4)	−0.296 (4)	5	H9	0.723 (7)	0.235 (4)	0.048 (5)	5 (1)
H5CP	−0.023 (6)	0.138 (4)	−0.073 (4)	5	H10	0.530 (7)	0.082 (4)	−0.096 (5)	6 (1)
H1	0.370 (6)	0.169 (4)	−0.340 (4)	4 (1)	HB10	0.498 (6)	0.197 (4)	−0.009 (4)	5 (1)
H2	0.154 (7)	0.317 (4)	−0.336 (5)	6 (1)	HB56	0.234 (6)	0.245 (3)	−0.057 (4)	3 (1)
H3	0.450 (7)	0.398 (4)	−0.322 (5)	6 (2)	HB67	0.306 (7)	0.392 (4)	−0.051 (5)	7 (2)
H4	0.687 (6)	0.236 (4)	−0.198 (4)	5 (1)	HB89	0.553 (8)	0.336 (5)	0.009 (5)	8 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{1,1}h^2 + B_{2,2}k^2 + B_{3,3}l^2 + B_{1,2}hk + B_{1,3}hl + B_{2,3}kl)]$.

Table II. Bond Distances (Å)

Co–C1	2.047 (5)	B4–B9	1.712 (8)
Co–C2	2.034 (5)	B4–B10	1.776 (7)
Co–C3	2.031 (6)	B6–B7	1.77 (1)
Co–C4	2.044 (5)	B7–B8	1.95 (1)
Co–C5	2.049 (5)	B8–B9	1.784 (9)
Co–B1	2.082 (5)	B9–B10	1.779 (7)
Co–B2	2.091 (5)	Co–HB56	1.49 (1)
Co–B6	2.072 (6)	B6–HB56	1.26 (1)
Co–B10	2.183 (5)	B6–HB67	1.36 (1)
B1–B2	1.768 (7)	B7–HB67	1.33 (1)
B1–B3	1.746 (7)	B8–HB89	1.40 (1)
B1–B4	1.765 (7)	B9–HB89	1.28 (1)
B1–B10	1.767 (7)	B9–HB10	1.28 (1)
B2–B3	1.754 (8)	B10–HB10	1.28 (1)
B2–B6	1.749 (8)	C1–C2	1.373 (7)
B2–B7	1.777 (9)	C2–C3	1.376 (9)
B3–B4	1.743 (8)	C3–C4	1.391 (9)
B3–B7	1.734 (8)	C4–C5	1.389 (7)
B3–B8	1.743 (8)	C5–C1	1.353 (7)
B4–B8	1.763 (8)	⟨B–H⟩	1.10 (1)
		⟨C–H⟩	0.84 (1)

shorter than those in $B_{10}H_{14}$. There is an apparent difference in the attachment of the bridging hydrogens; in $B_{10}H_{14}$ the B–H–B bonds are unsymmetrical, with two of them having B–H lengths of 1.298 (5) and 1.355 (7) Å while the other two bridges have distances of 1.297 (5) and 1.339 (7) Å.[17b] In contrast, two of the B–H–B bridges in (η^5-C_5H_5)CoB_9H_{13} are symmetrical while the third (B8–HB89–B9) is highly unsymmetrical with B–H lengths of 1.40 (1) and 1.28 (1) Å. In the latter instance, the bridging hydrogen is closest to the "outer" boron (B9), whereas in $B_{10}H_{14}$ the H bridges are all *furthest* from the outer boron atoms B6 and B9. The B–H–Co bridge in the cobaltaborane is unsymmetrical (1.49 vs. 1.26 Å) with the longer leg attached to cobalt; this is similar to the situation in the *nido*-cobaltacarborane (η^5-C_5H_5)$CoC_2B_7H_{11}$,[18] which has a B–H–Co bridge whose hydrogen is 1.31 (4) Å from boron and 1.40(4) Å from cobalt, but differs from (η^5-C_5H_5)CoB_4H_8,[9] in which the bridging hydrogens are equidistant from boron and cobalt at 1.43 (5) Å. These observations are difficult to interpret in a chemically useful way at present, but the situation should improve as additional *nido*-cobaltaborane crystal structures are produced.

Table III. Bond Angles (deg)

B1–Co–B2	50.1 (2)	B3–B7–B8	56.1 (4)
B1–Co–B10	48.9 (2)	B6–B7–HB67	49.8 (4)
B2–Co–B6	49.7 (2)	B8–B7–HB67	94.0 (4)
B2–Co–HB56	84.1 (4)	B3–B8–B4	59.6 (3)
B6–Co–HB56	37.1 (4)	B3–B8–B7	55.7 (4)
B10–Co–HB56	91.6 (4)	B4–B8–B9	57.7 (3)
B2–B1–B3	59.9 (3)	B4–B8–HB89	101.1 (4)
B2–B1–Co	65.2 (2)	B9–B8–HB89	45.6 (4)
B3–B1–B4	59.5 (3)	B7–B8–HB89	94.6 (4)
B4–B1–B10	60.4 (3)	B4–B9–B8	60.5 (3)
Co–B1–B10	68.6 (2)	B4–B9–B10	61.1 (3)
B1–B2–B3	59.4 (3)	B4–B9–HB89	109.2 (4)
B1–B2–Co	64.7 (2)	B4–B9–HB10	103.8 (4)
B3–B2–B7	58.8 (4)	B8–B9–HB89	51.2 (4)
Co–B2–B6	64.6 (3)	B10–B9–HB10	46.0 (4)
B6–B2–B7	60.3 (4)	HB89–B9–HB10	91.9 (4)
B1–B3–B2	60.7 (3)	B1–B10–B4	59.7 (3)
B1–B3–B4	60.8 (3)	B1–B10–Co	62.6 (2)
B2–B3–B7	61.2 (4)	B4–B10–B9	57.6 (3)
B4–B3–B8	60.8 (4)	B4–B10–HB10	100.2 (4)
B7–B3–B8	68.2 (4)	B9–B10–HB10	45.8 (4)
B1–B4–B3	59.7 (3)	Co–B10–HB10	90.2 (4)
B1–B4–B10	59.9 (3)	Co–HB56–B6	97.3 (4)
B3–B4–B8	59.6 (4)	B6–HB67–B7	82.1 (4)
B8–B4–B9	61.8 (3)	B8–HB89–B9	83.2 (4)
B9–B4–B10	61.3 (3)	B9–HB10–B10	88.2 (4)
B2–B6–Co	65.7 (3)	C2–C1–C5	107.6 (5)
B2–B6–B7	60.6 (3)	C1–C2–C3	109.1 (6)
B2–B6–HB56	107.3 (4)	C2–C3–C4	107.2 (5)
B2–B6–HB67	106.9 (4)	C3–C4–C5	106.8 (5)
Co–B6–HB56	45.6 (4)	C1–C5–C4	109.3 (5)
B7–B6–HB67	48.2 (4)	C1–Co–C2	39.3 (2)
HB56–B6–HB67	97.8 (4)	C2–Co–C3	39.6 (3)
B2–B7–B3	59.9 (3)	C3–Co–C4	39.9 (3)
B2–B7–B6	59.1 (4)	C4–Co–C5	39.7 (2)
B2–B7–HB67	107.0 (4)	C1–Co–C5	38.6 (2)

Table IV. Closest Intermolecular Contacts

Molecule 1	Molecule 2	Distance, Å	Symmetry operation
C1	C1	3.874	$-x, -y, -z$
C1	C5	3.709	$-x, -y, -z$
C3	B6	3.928	$-x, -^1/_2 + y, -^1/_2 - z$
C4	B7	3.843	$-x, -^1/_2 + y, -^1/_2 - z$

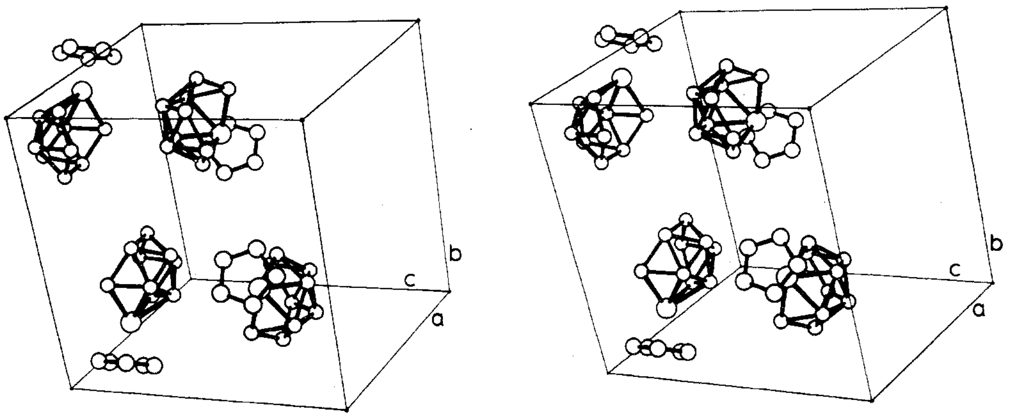

Figure 3. Stereoview of the unit cell contents.

Table V. Selected Molecular Planes[a]

Atom	Dev, Å	Atom	Dev, Å
Plane 1: Cyclopentadienyl Ring $0.6136X + 0.7703Y + 0.1736Z = 1.2225$			
C1	−0.007	C4	−0.001
C2	0.006	C5	0.005
C3	−0.003	*Co	−1.67
Plane 2: Borons Bonded to Cobalt $0.6429X + 0.7391Y + 0.2011Z = 4.1619$			
B1	0.029	B6	0.015
B2	−0.029	B10	−0.015
		*Co	1.31
Plane 3: Base of Pentagonal Pyramidal Unit $0.9083X - 0.1855Y - 0.3750Z = 4.3079$			
B1	0.022	B9	0.078
B3	0.029	B10	−0.062
B8	−0.066		
Plane 4: Base of Pentagonal Pyramidal Unit $-0.5174X + 0.1554Y - 0.8415Z = 0.6138$			
Co	−0.057	B6	0.080
B1	0.028	B7	−0.070
B3	0.020		
Plane 5: Co, B2, B3, B4, B10 $0.1452X - 0.5252Y - 0.8385Z = 0.6823$			
Co	−0.005	B4	0.054
B2	0.040	B10	−0.027
B3	−0.061		
Plane 6: B1, B2, B4, B7, B8 $0.3776X + 0.4772Y - 0.7936Z = 5.1769$			
B1	−0.063	B7	0.000
B2	0.038	B8	−0.036
B4	0.061		
Plane 7: B2, B4, B6, B9 $0.2518X + 0.9676Y + 0.0197Z = 4.5145$			
B2	0.032	B6	−0.026
B4	−0.032	B9	0.026
Plane 8: Co, B7, B8, B10 $0.2652X - 0.0512Y - 0.9628Z = 2.2732$			
Co	−0.039	B8	−0.048
B7	0.043	B10	0.044

Planes	Dihedral angle, deg	Planes	Dihedral angle, deg
1,2	2.9	4,7	90.2
2,8	86.5	5,6	62.0
3,7	92.4	7,8	89.9
3,4	100.6		

[a] Atoms marked with an asterisk are not included in the calculated plane.

The (η^5-C_5H_5)CoB_9H_{13} molecule is related also to several other metalloboranes containing an MB_9 nido framework, all of which bear a strong structural similarity to $B_{10}H_{14}$. These include a family of manganese and rhenium metalloboranes[19] of the formula $(CO)_3MB_9H_{12}R$ where M = Mn or Re and R = tetrahydrofuran or $(C_2H_5)_3N(CH_2)_4O$. Crystal structure determinations[19,20] on several derivatives of the manganese system have shown that the metal occupies the 6 rather than the 5 position as in (η^5-C_5H_5)CoB_9H_{13}, no doubt reflecting the difference in synthetic routes inasmuch as the manganese and rhenium species were prepared from $B_9H_{14}^-$. A comparison of distances and angles between the manganaborane derivatives and the cobalt species reveals no starting variations other than those directly attributable to the different metal locations[21] or to the external substituents. The previously mentioned cobaltacarborane (η^5-C_5H_5)$CoC_2B_7H_{11}$[18] also has a $B_{10}H_{14}$-type cage, with the cobalt in position 5 (in our numbering system) and the cage carbons in 9 and 10. This molecule is therefore essentially isostructural with (η^5-C_5H_5)CoB_9H_{13} except for the replacement of B_9, B_{10}, and their adjoining hydrogen bridges by carbon atoms; the two species are also, of course, isoelectronic.

We know of no other crystallographically established nido 10-vertex cage systems, but a structure having the metal in the 6 position and only two bridge hydrogens has been proposed[22] for $[(C_2H_5)_3P]_2PtB_9H_{11}L$ where L is an organic Lewis base. Similarly the thiaborane SB_9H_{11}[23] is thought to have a $B_{10}H_{14}$-like skeleton with sulfur in vertex 6; it may be significant that all of the heteroboranes produced from B_9 anions are 6 substituted while (η^5-C_5H_5)CoB_9H_{13}, produced[6b,8] from $B_5H_8^-$, has its heteroatom in the 5 position.[24] A number of other heteroboranes are related to the structures discussed here and have been cited in recent reviews.[1]

The (η^5-C_5H_5)CoB_9H_{13} molecule can alternatively be viewed as a metal sandwich complex containing formal Co^{3+} coordinated to η^5-$C_5H_5^-$ and $B_9H_{13}^{2-}$ ligands. The face which the borane ligand presents to the cobalt (B1–B2–B6–B10) is almost planar (Table V) and this plane is nearly parallel to the cyclopentadienyl ring, with a dihedral angle of 2.9°. The cobalt atom is 1.67 Å from the C_5H_5 plane and 1.31 Å from the plane of the four-boron face; the shortness of the latter distance is a consequence of the large "spread" of the B_4 group which requires the cobalt atom to move in close to the B_4 face in order to achieve normal Co–B bonding distances. In this respect it is instructive to compare this molecule with the organometallic complex[25] (η^5-C_5H_5)Co[η^4-$C_5H_5(C_6H_5)$] in which the metal is similarly coordinated to four carbon atoms in one of the C_5 rings, the fifth carbon (phenyl-substituted) being bent away from the metal. The four-carbon group linked to cobalt has internal C–C bond lengths of 1.49, 1.36, and 1.54 Å, which are much shorter than the corresponding B–B distances in the B_4 face of the cobaltaborane (1.75–1.77 Å). As a result, the cobalt atom in the hydrocarbon complex is nearly equidistant from the planes of the C_4 and C_5 faces (1.67–1.69 Å), in sharp contrast to the cobaltaborane.

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Registry No. 5-(η^5-C_5H_5)CoB_9H_{13}, 43062-04-0.

Supplementary Material Available: Listing of observed and calculated structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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Structures of Metalloboron Clusters. X-Ray Studies of Octahedral (η^5-C_5H_5)$_3Co_3B_3H_5$ and Capped Octahedral (η^5-C_5H_5)$_3Co_3B_4H_4$, a Boron Analogue of Tricobalt Carbon Clusters

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The crystal and molecular structures of dark brown 1,2,3-(η^5-C_5H_5)$_3Co_3B_3H_5$ and yellow 1,2,3-(η^5-C_5H_5)$_3Co_3B_4H_4$, both air-stable solids, were determined from single-crystal x-ray diffraction data and found to incorporate an octahedron and a capped octahedron, respectively, in agreement with the structures originally postulated from NMR spectra by Miller and Grimes. In both molecules the three cobalt atoms occupy a single triangular face of the octahedron; in the Co_3B_4 system the Co_3 face is capped by a BH group and in the Co_3B_3 system the Co_3 face evidently accommodates the two "extra" hydrogen atoms in three disordered positions although these hydrogens could not be refined. Both compounds are regarded as hybrid cages linking the borane and metal cluster families and are electronically and structurally related to the octahedral borane anion $B_6H_6^{2-}$, several carboranes, and numerous octahedral metal cluster systems. The Co_3B_4 species is structurally unique among boron cages but is analogous to capped octahedral $Os_7(CO)_{21}$ and $Rh_7(CO)_{16}^{3-}$; in addition, its Co_3 face capped by a BH group is closely related to the $(CO)_9Co_3CR$ tricobalt carbon clusters. The two compounds are isomorphous and crystallize in the orthorhombic space group *Pnma* with $Z = 4$. Crystal data: $(C_5H_5)_3Co_3B_3H_5$, mol wt 409.6, $a = 11.992$ (3) Å, $b = 15.197$ (6) Å, $c = 8.954$ (3) Å, $V = 1631.8$ (8) Å^3, $R = 0.035$ for 1297 reflections having $F_o^2 > 3\sigma(F_o^2)$; $(C_5H_5)_3Co_3B_4H_4$, mol wt 419.4, $a = 12.353$ (3) Å, $b = 14.996$ (4) Å, $c = 8.999$ (2) Å, $V = 1666.9$ (7) Å^3, $R = 0.032$ for 1272 reflections having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

It is now widely recognized that boron hydrides and metal clusters are closely related electronically and structurally[1] and that to a considerable degree both classes obey a common set of electron-counting rules[1] which allow predictions of geometric shape. For example, the boron cage species $B_6H_6^{2-}$, $C_2B_4H_6$, and (η^5-C_5H_5)$CoC_2B_3H_5$ are seen as electronic analogues of metal clusters such as $H_2Ru_6(CO)_{18}$, $Rh_6(CO)_{16}$, and $(C_2H_5)_2C_2Co_4(CO)_{10}$, all of these molecules having 14 valence electrons in an octahedral cage framework; a similar comparison exists for the 7-vertex, 16-electron pentagonal-bipyramidal systems $B_7H_7^{2-}$, $C_2B_5H_7$, $[(CO)_3Fe]_2C_2B_3H_5$, and $(CO)_8Fe_3C_4(C_6H_5)_4$. Many other examples have been cited elsewhere.[1,2]

While the utility and predictive power of these correlations are obvious, detailed structural comparisons between the boron cages and the metal clusters are scarce, indeed almost nonexistent. The primary reason for this is that few of the boron systems that are most closely related to the metal clusters have been examined by x-ray diffraction or other rigorous structural methods. The only octahedral boron cage (other than in metal borides) for which an x-ray study has been published is $B_6H_6^{2-}$,[3] while the analogous carboranes CB_5H_7,[4] 1,2-$C_2B_4H_6$,[4,5] and 1,6-$C_2B_4H_6$[6] have been investigated by electron