Professor Ekk Sinn for assistance during the x-ray data collection and refinement.

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.

References and Notes

(1) (a) N. N. Greenwood and I. M. Ward, *Chem. Soc. Rev.*, **3**, 231 (1974); (b) E. L. Muetterties, *Pure Appl. Chem.*, **29**, 585 (1972).

(2) (a) K. P. Callahan and M. F. Hawthorne, *Pure Appl. Chem.*, **39**, 475 (1974); (b) R. N. Grimes, "Organometallic Reactions and Syntheses", Vol. 6, Plenum Press, New York, N.Y., 1977, Chapter 2, pp 63–221 (comprehensive review).

(3) Several known metalloboron compounds have no structural analogues among the boranes, e.g., the 13-[4] and 14-vertex[5] metallocarboranes and (η^5-C_5H_5)$_3Co_3B_4H_4$,[6] a capped octahedron.

(4) (a) D. F. Dustin, G. B. Dunks, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **95**, 1109 (1973); (b) D. F. Dustin and M. F. Hawthorne, *ibid.*, **96**, 3462 (1974); (c) W. J. Evans and M. F. Hawthorne, *Inorg. Chem.*, **13**, 869 (1974); (d) W. M. Maxwell, V. R. Miller, and R. N. Grimes, *J. Am. Chem. Soc.*, **96**, 7116 (1974); (e) C. G. Salentine and M. F. Hawthorne, *ibid.*, **97**, 426 (1975); W. M. Maxwell, R. F. Bryan, and R. N. Grimes, *ibid.*, **99**, 4008 (1977).

(5) (a) W. J. Evans and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 38 (1974); (b) W. M. Maxwell, E. Sinn, and R. N. Grimes, *ibid.*, 389 (1976); (c) W. M. Maxwell, R. Weiss, E. Sinn, and R. N. Grimes, *J. Am. Chem. Soc.*, **99**, 4016 (1977).

(6) (a) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **98**, 1600 (1976); (b) V. R. Miller, R. Weiss, and R. N. Grimes, *ibid.*, **99**, 5646 (1977).

(7) K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976).

(8) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 5078 (1973).

(9) L. G. Sneddon and D. Voet, *J. Chem. Soc., Chem. Commun.*, 118 (1976).

(10) J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, in press.

(11) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(12) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.

(13) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(14) D. T. Cromer and J. A. Ibers, ref 12.

(15) D. P. Freyberg, G. M. Mockler, and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 447 (1976).

(16) Supplementary material.

(17) (a) The original x-ray investigation of $B_{10}H_{14}$ was by J. S. Kasper, C. M. Lucht, and D. Harker, *Acta Crystallogr.*, **3**, 436 (1950), and the data were reanalyzed by E. B. Moore, R. E. Dickerson, and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 209 (1957). The best data currently available are from a neutron diffraction study of $^{11}B_{10}D_{14}$ by A. Tippe and W. C. Hamilton, *Inorg. Chem.*, **8**, 464 (1969), and the latter results are used in our comparison. (b) In the x-ray study the corresponding distances are 1.34 and 1.42 Å.

(18) K. P. Callahan, F. Y. Lo, C. E. Strouse, A. L. Sims, and M. F. Hawthorne, *Inorg. Chem.*, **13**, 2842 (1974).

(19) (a) J. W. Lott, D. F. Gaines, H. Shenhav, and R. Schaeffer, *J. Am. Chem. Soc.*, **95**, 3042 (1973); (b) J. W. Lott and D. F. Gaines, *Inorg. Chem.*, **13**, 2261 (1974).

(20) D. F. Gaines, J. W. Lott, and J. C. Calabrese, *Inorg. Chem.*, **13**, 2419 (1974).

(21) The Mn–bridge hydrogen distances in the manganacarboranes range from 1.64 to 1.83 (10) Å and thus appear substantially larger than the Co–bridge hydrogen distances in (η^5-C_5H_5)CoB_9H_{13} (1.49 (1) Å) or in (η^5-C_5H_5)$CoC_2B_7H_{11}$ (1.40 (4) Å)[18] (the latter value increased to 1.53 (4) Å when only low-angle data were used). However, these differences may well simply reflect the fact that manganese occupies the 6 (outer) position in the MB_9 framework.

(22) A. R. Kane, L. J. Guggenberger, and E. L. Muetterties, *J. Am. Chem. Soc.*, **92**, 2571 (1970).

(23) W. R. Pretzer and R. W. Rudolph, *J. Am. Chem. Soc.*, **98**, 1441 (1976).

(24) There is a strong probability that (η^5-C_5H_5)CoB_9H_{13} forms via attack of $B_5H_8^-$ on the 2-(η^5-C_5H_5)CoB_4H_8 which is produced initially during the reaction.

(25) M. R. Churchill and R. Mason, *Proc. R. Soc. London, Ser. A*, **279**, 191 (1964).

Contribution from the Department of Chemistry,
University of Virginia, Charlottesville, Virginia 22901

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

J. ROBERT PIPAL and RUSSELL N. GRIMES*

Received June 7, 1977

AIC70405H

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 diffraction and microwave spectroscopy. Other 6-vertex boron systems such as $(CO)_3FeC_2B_3H_5$ and $(\eta^5\text{-}C_5H_5)CoC_2B_3H_5$ have been characterized[7] by ^{11}B and ^{1}H NMR, but molecular parameters are not available.

Recently, synthetic studies in our laboratory[8] have afforded some novel air-stable metalloboron cage compounds which are composed of both boron and transition-metal atoms in comparable numbers, thus constituting hybrid species between the metal cluster and boron hydride families. Since these compounds have, in effect, a foot in both camps, they are ideally suited for detailed structural and chemical investigations designed to elucidate more clearly the relationship between these two large classes of inorganic clusters. In this paper we report the crystal structure determinations of two such compounds, $(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$ and the electron-hyperdeficient system $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$, which are respectively the first octahedral and the first capped octahedral metalloboron species to be crystallographically characterized and which also claim several other structural distinctions to be discussed below.

Experimental Section

Irregular dark brown diamond-shaped crystals of $(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$ were grown over a 36-h period by the vapor diffusion of pentane into a methylene chloride solution of the metalloborane. One of the diamond-shaped platelets was cut to a suitable size and mounted on a glass fiber and on the basis of good preliminary precession photographs was selected for data collection. Crystal data: $Co_3C_{15}B_3H_{20}$, mol wt 409.6, space group *Pnma*, $Z = 4$; $a = 11.992$ (3), $b = 15.197$ (6), $c = 8.954$ (3) Å; $V = 1631.8$ (8) Å^3; $\mu(\text{Mo K}\alpha) = 30.9$ cm^{-1}; $\rho_c = 1.657$ g cm^{-3}; $F(000) = 824$. For the chosen crystal, the Enraf-Nonius program SEARCH was used to obtain 15 accurately centered reflections which were then employed in the program INDEX to obtain an orientation matrix for data collection and also to provide approximate cell constants. 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 found to be very good.

The initial choice of the centric space group *Pnma* instead of the acentric $Pna2_1$ was based on the high symmetry of the molecule, C_{3v}, as deduced from solution ^1H and ^{11}B NMR spectra.[8b,c] In *Pnma* with $Z = 4$, the molecule must be on a special position, namely, the mirror at $y = {}^1/_4$. This choice was later confirmed by the successful solution and refinement of the structure.

A single large yellow needle-shaped crystal of $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$ was grown from a very small sample (<5 mg) of the compound in the same manner as described for the preceding compound. This crystal was cut into two fragments (0.08 × 0.08 × 0.5 mm) and both were cemented to glass fibers. Preliminary precession photos indicated that both crystals were of very high quality. Crystal data: $Co_3C_{15}B_4H_{19}$, mol wt 419.4, space group *Pnma*, $Z = 4$; $a = 12.353$ (3), $b = 14.996$ (4), $c = 8.999$ (2) Å; $V = 1666.9$ (7) Å^3; $\mu(\text{Mo K}\alpha) = 31.2$ cm^{-1}; $\rho_c = 1.671$ g cm^{-3}; $F(000) = 840$. The same procedures as described above for the first compound were employed to produce an orientation matrix and refined cell constants. The mosaicity of the crystal was examined by the ω-scan technique and found to be very good. Given that the cell constants for $(C_5H_5)_3Co_3B_4H_4$ were nearly the same as for $(C_5H_5)_3Co_3B_3H_5$, with identical sets of systematic absences, we assumed that the compounds were isomorphous. This judgment was proved correct by the successful resolution of the structure.

Collection and Reduction of the Data. Diffraction data for both compounds 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 monochromator. The θ–2θ scan technique was used to record the unique intensities for all reflections for which $1 < 2\theta < 52°$. 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 and Kα_2 splitting. The values of A and B respectively were 0.5 and 0.3 for $(C_5H_5)_3Co_3B_3H_5$ and 0.6 and 0.3 for $(C_5H_5)_3Co_3B_4H_4$. 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 the intensities registered less than ten counts above background on a rapid prescan, such reflections being rejected automatically by the computer. The intensities of three standard reflections, monitored for each crystal at 100 reflection intervals, showed no systematic trends. The raw intensity data were corrected for Lorentz-polarization effects and their standard deviations were calculated in the usual manner from counting statistics ($\rho = 0.03$).[9] This resulted in 1428 reflections for $(C_5H_5)_3Co_3B_3H_5$ of which 1297 had $F_o^2 > 3\sigma(F_o^2)$ and 1435 reflections for $(C_5H_5)_3Co_3B_4H_4$ of which 1272 had $F_o^2 > 3\sigma(F_o^2)$. Only those reflections for which $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement of structural parameters.

Solution and Refinement of the Structures. $(C_5H_5)_3Co_3B_3H_5$. A three-dimensional Patterson synthesis was used to locate the position of the two unique Co atoms assuming the space group to be *Pnma*. The Patterson map in fact implied *Pnma* instead of its acentric counterpart $Pna2_1$, since the strongest peak in the map appeared at 0, 0.16, 0. This corresponds to an intramolecular Co–Co vector (2.38 Å) across the mirror at $y = {}^1/_4$. If the space group were $Pna2_1$, then an intramolecular Co–Co vector would have had to accidentally lie parallel to the y axis of the unit cell, a possible but less likely occurrence. The positions of these two cobalt atoms (one on the mirror, one in a general position) were used to phase an electron density map from which the positions of the two unique borons (one of which was on the mirror) were located. The map also yielded the positions of five cyclopentadienyl carbon atoms.

Additional cycles of least-squares refinement and several more maps were required in order to locate all of the unique nonhydrogen atoms. Unfortunately these maps also conclusively showed that all three cyclopentadienyl rings were disordered. Since one of the rings is bisected by the mirror and the other two related by it, the assumed twofold disorder resulted in a total of 16 half-weight carbon atoms that had to be located and refined. All 16 atoms were successfully located from this series of maps. Further refinement with all atoms anisotropic reduced R to 0.038. 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[10] and those for hydrogen from Stewart.[11] The effects of anomalous dispersion were included in F_c using Cromer and Ibers[12] 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 are described elsewhere.[13]

At this point an absorption correction was applied [$\mu(\text{Mo K}\alpha) = 30.95$], with maximum and minimum transmission coefficients 0.8278 and 0.5061. Several cycles of least-squares refinement reduced R to 0.036. A new electron density map was calculated, and from it the two unique hydrogen atoms bonded to borons were located; these atoms subsequently were refined with isotropic temperature factors. In addition, the map revealed three new peaks on the Co–Co–Co triangular face, one of which was on the mirror while the other two were related by the mirror. The cobalt–peak distances as well as the peak-to-peak distances suggested the possibility that these peaks corresponded to the two "extra" (nonterminal) hydrogen atoms which are known[8b,c] to be present in the $(C_5H_5)_3Co_3B_3H_5$ molecule; these two hydrogens would then occupy disordered bridging positions on the three Co–Co edges. Such a hypothesis is consistent with the ^1H and ^{11}B solution NMR spectra,[8b,c] which indicate (1) tautomerism of the two protons to produce C_{3v} symmetry on the NMR time scale and (2) close association of these protons with the metal atoms, as shown by the high-field ^1H NMR resonance (δ −14.48 ppm) associated with them.

An attempt was made to refine these new peaks. Initially only the positions were allowed to vary, but this produced movement in the two mirror-related peaks to positions unacceptably close (0.45 Å) to each other. When their isotropic thermal parameters were permitted to vary as well, there was no improvement, although the B values remained quite reasonable (<7.0 Å^2) and R was reduced to 0.033. Restriction of the two new atoms to the mirror plane was also unsuccessful, in that they refined to chemically unreasonable positions. Consequently the peaks were removed, causing R to increase to a final value of 0.035. At this stage another electron density map was synthesized and the "bridge hydrogen" peaks reappeared in their original locations on the Co_3 triangular face. The final value of R_w was 0.045 and the error in an observation of unit weight was 2.45.

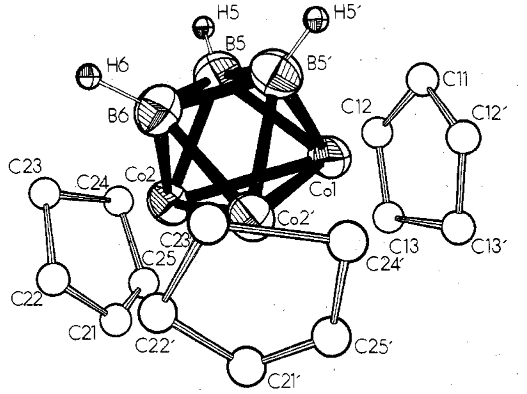


Figure 1. Structure and numbering system for $(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$, with hydrogen atoms omitted except for those bonded to boron. For each C_5H_5 ring, only one of the two disordered orientations is shown. Primed atoms are related by a crystallographic mirror plane to the corresponding unprimed atoms.

The largest parameter shift in the last cycle of refinement was 0.15 times its estimated standard deviation. A structure factor calculation including those reflections where $F_o^2 < 3\sigma(F_o^2)$ gave $R = 0.039$ indicating that nothing would be gained by accurately re-collecting these intensities. A table of structure factors is available (supplementary material).

$(C_5H_5)_3Co_3B_4H_4$. Assuming the two structures to be isomorphous (see above), a Patterson map was not calculated. Instead, the coordinates of the 20 nonhydrogen atoms (including the half-weight disordered cyclopentadienyl carbons) in the $(C_5H_5)_3Co_3B_3H_5$ structure were used in several cycles of refinement. The value of R rapidly dropped to 0.11 using anisotropic thermal parameters for the cobalt atoms and isotropic parameters for the remainder. A map phased on these refined coordinates clearly yielded the remaining boron atom (B7). Anisotropic refinement of all nonhydrogen atoms and an absorption correction ($\mu(\text{Mo K}\bar{\alpha}) = 31.15$, maximum and minimum transmission coefficients = 0.7827 and 0.7319) reduced R to 0.033. Another electron density map was synthesized, and from it the position of the terminal hydrogen bonded to B7 was unequivocally determined. Further refinement including the three other terminal hydrogen atoms (isotropic) reduced R to 0.032. All details of the refinement process, including programs, scattering factors, and computing equipment, were identical with those employed for $(C_5H_5)_3Co_3B_3H_5$. The final value of R_w was 0.042 and the error in an observation of unit weight was 2.2. During the last cycle of refinement, the largest parameter shift was 0.22 times its estimated standard deviation. A structure factor calculation including those reflections for which $F_o^2 < 3\sigma(F_o^2)$ yielded an R value of 0.038. A table of structure factors is available (supplementary material).

Results and Discussion

Final positional and thermal parameters are given in Tables I and II for $(C_5H_5)_3Co_3B_3H_5$ and $(C_5H_5)_3Co_3B_4H_4$, respectively. Tables III and IV list bond lengths for both compounds, while Tables V and VI contain selected bond angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figure quoted and were derived from the inverse matrix in the course of least-squares refinement calculations. Tables VII and VIII list selected mean planes and the dihedral angles between them. Tables giving the shortest intermolecular contacts between nonhydrogen atoms are available as supplementary material; the smallest such distances are 3.57 Å in $(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$ and 3.54 Å in $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$. The molecular structure and numbering for $(C_5H_5)_3Co_3B_3H_5$ are given in Figure 1, Figure 2 is a stereoview of the molecule viewed approximately along the pseudo-threefold axis, and a diagram of the unit cell contents is given in Figure 3. Two stereoviews of $(C_5H_5)_3Co_3B_4H_4$ are shown in Figure 4. In all of these structure drawings, each of the C_5H_5 rings is shown in just one of its two disordered orientations, arbitrarily selected.

Description of the Structures. The two molecules are closely related (indeed isomorphous), each species containing a distorted Co_3B_3 octahedron with a triangular Co_3 face bisected

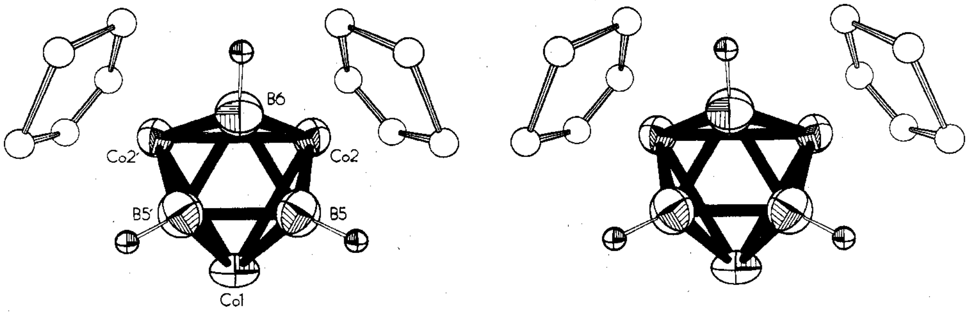


Figure 2. Stereopair view of $(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$ as seen from above the B_3 face.

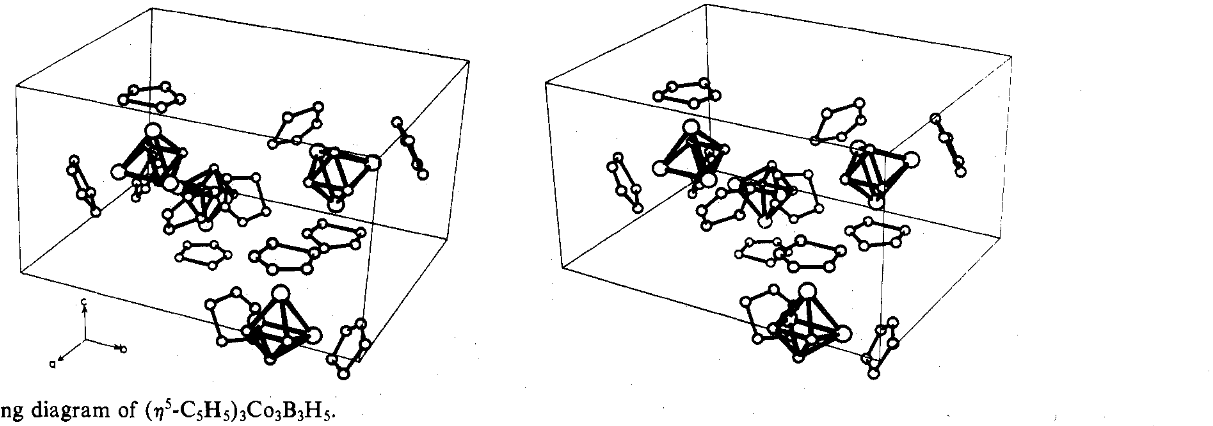


Figure 3. Packing diagram of $(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$.

Table I. Final Positional and Thermal Parameters and Their Estimated Standard Deviations for $(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co1	0.10262 (6)	0.25000 (0)	−0.16387 (7)	0.00502 (5)	0.00540 (4)	0.00730 (7)	0.00000 (0)	−0.00058 (12)	0.00000 (0)
Co2	0.15938 (4)	0.16867 (3)	0.06505 (5)	0.00581 (3)	0.00290 (2)	0.01029 (6)	0.00052 (5)	−0.00218 (8)	−0.00036 (6)
C11	0.0092 (11)	0.2500 (0)	−0.353 (1)	0.0064 (9)	0.0102 (9)	0.008 (1)	0.0000 (0)	0.001 (2)	0.000 (0)
C12	0.0788 (12)	0.1777 (7)	−0.343 (1)	0.0205 (13)	0.0094 (6)	0.016 (1)	0.0067 (15)	−0.023 (2)	−0.017 (1)
C13	0.1894 (12)	0.1914 (9)	−0.349 (1)	0.0159 (13)	0.0180 (11)	0.011 (1)	0.0081 (20)	0.002 (2)	−0.014 (2)
C11A	0.1983 (11)	0.2500 (0)	−0.354 (1)	0.0075 (10)	0.0106 (10)	0.009 (1)	0.0000 (0)	0.007 (2)	0.000 (0)
C12A	0.1388 (23)	0.1673 (13)	−0.333 (2)	0.0699 (34)	0.0333 (15)	0.014 (2)	0.0687 (29)	−0.006 (4)	−0.025 (2)
C13A	0.0384 (14)	0.2024 (13)	−0.363 (1)	0.0357 (17)	0.0355 (25)	0.010 (1)	−0.0389 (27)	−0.030 (2)	0.005 (2)
C21	0.3115 (7)	0.1159 (5)	0.124 (1)	0.0052 (5)	0.0045 (4)	0.019 (1)	0.0024 (8)	−0.007 (1)	0.004 (1)
C22	0.2509 (8)	0.1339 (6)	0.251 (1)	0.0111 (8)	0.0044 (3)	0.017 (1)	0.0022 (10)	−0.009 (2)	0.007 (1)
C23	0.1508 (9)	0.0731 (7)	0.223 (2)	0.0071 (8)	0.0105 (5)	0.077 (3)	−0.0043 (11)	−0.007 (3)	0.050 (1)
C24	0.1705 (10)	0.0277 (7)	0.049 (2)	0.0123 (11)	0.0044 (4)	0.059 (4)	−0.0046 (12)	−0.014 (4)	0.014 (2)
C25	0.2759 (8)	0.0686 (5)	0.032 (1)	0.0091 (7)	0.0035 (3)	0.021 (1)	0.0037 (9)	−0.002 (2)	−0.004 (1)
C21A	0.3022 (11)	0.1206 (7)	0.180 (1)	0.0364 (12)	0.0044 (4)	0.048 (2)	0.0141 (13)	−0.074 (2)	−0.013 (2)
C22A	0.1906 (10)	0.1042 (6)	0.257 (1)	0.0175 (12)	0.0048 (4)	0.013 (1)	0.0028 (12)	−0.005 (2)	0.009 (1)
C23A	0.1299 (8)	0.0457 (5)	0.160 (1)	0.0106 (8)	0.0030 (3)	0.022 (1)	−0.0009 (9)	−0.005 (2)	0.007 (1)
C24A	0.2011 (9)	0.0403 (4)	0.037 (1)	0.0127 (9)	0.0010 (2)	0.026 (2)	−0.0014 (8)	0.000 (2)	−0.004 (1)
C25A	0.3004 (12)	0.0807 (8)	0.019 (3)	0.0103 (11)	0.0057 (6)	0.095 (7)	0.0034 (14)	−0.012 (5)	0.007 (4)
B5	0.0005 (4)	0.1936 (3)	−0.0071 (6)	0.0059 (3)	0.0039 (2)	0.0130 (5)	−0.0020 (4)	−0.0005 (7)	0.0006 (6)
B6	0.0413 (6)	0.2500 (0)	0.1507 (7)	0.0066 (5)	0.0043 (3)	0.0106 (8)	0.0000 (0)	0.0026 (11)	0.0000 (0)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H5	−0.059 (4)	0.143 (3)	−0.027 (5)	7 (1)	H6	0.001 (4)	0.250 (0)	0.268 (5)	3 (1)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

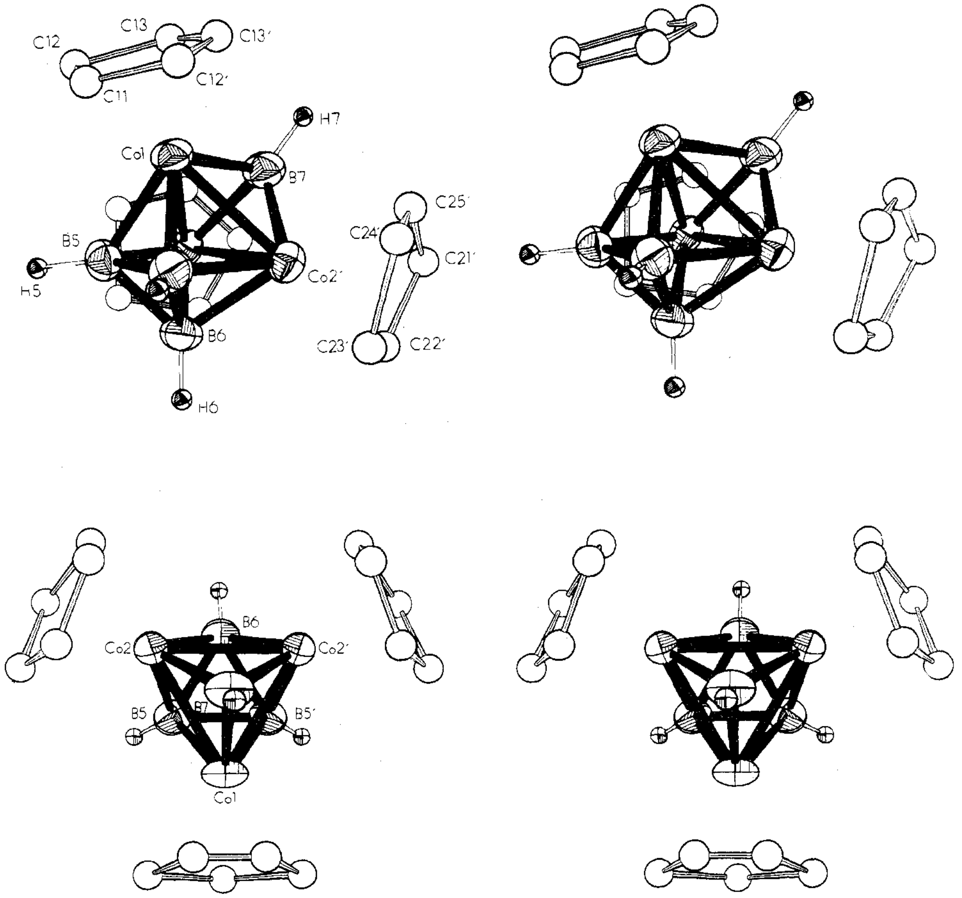


Figure 4. Stereopair drawings of $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$ as viewed obliquely (top) and down the pseudo-C_3 axis (bottom). In the latter illustration, the Co_3 ring is nearer the viewer than is the B_3 ring; in the drawing of $(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$ in Figure 2, the B_3 ring is nearer.

by a crystallographic mirror plane; in $(C_5H_5)_3Co_3B_4H_4$ this Co_3 face is capped by an additional BH unit, but in $(C_5H_5)_3Co_3B_3H_5$ it evidently accommodates the two "extra" hydrogen atoms as discussed below. Both structures are in agreement with those originally proposed[8b,c] from ^{11}B and ^1H Fourier transform NMR spectra. In the case of $(C_5H_5)_3Co_3B_4H_4$, an alternative possibility having the capping BH group on the B_3 rather than the Co_3 face had not been entirely eliminated by the NMR data, but the Co_3-capped geometry was strongly favored;[8b] the x-ray result confirms this judgment. Each of the molecules possesses pseudo-C_{3v} symmetry, in conformity with solution NMR data[8b,c] which indicate equivalence of the three $(\eta^5\text{-}C_5H_5)Co$ units and of three BH groups. Thus, the two crystallographically independent cobalt–cobalt bond lengths in $(C_5H_5)_3Co_3B_3H_5$ are nearly identical (2.488 (1) Å for Co1–Co2 vs. 2.472 (1) Å for

Table II. Final Positional and Thermal Parameters and Their Estimated Standard Deviations for $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co1	0.12012 (6)	0.25000 (0)	−0.12335 (7)	0.00480 (5)	0.00535 (4)	0.00550 (7)	0.00000 (0)	−0.00055 (11)	0.00000 (0)
Co2	0.14935 (4)	0.16881 (3)	0.10872 (5)	0.00557 (3)	0.00280 (2)	0.00822 (6)	0.00048 (5)	−0.00248 (8)	−0.00017 (6)
C11	0.0472 (11)	0.2500 (0)	−0.3201 (13)	0.0043 (9)	0.0291 (25)	0.0044 (14)	0.0000 (0)	−0.0055 (18)	0.000 (0)
C12	0.1074 (13)	0.1653 (12)	−0.3125 (11)	0.0232 (14)	0.0318 (14)	0.0107 (11)	−0.0355 (20)	0.0156 (22)	−0.028 (2)
C13	0.2184 (7)	0.2125 (9)	−0.2841 (5)	0.0131 (7)	0.0220 (17)	−0.0063 (4)	0.0098 (15)	0.0050 (9)	−0.003 (1)
C11A	0.2200 (11)	0.2500 (0)	−0.3317 (6)	0.0104 (10)	0.0494 (33)	−0.0121 (5)	0.0000 (0)	0.0082 (11)	0.000 (0)
C12A	0.1578 (8)	0.1761 (7)	−0.3108 (9)	0.0095 (8)	0.0084 (5)	0.0080 (9)	0.0044 (11)	−0.0029 (15)	−0.009 (1)
C13A	0.0472 (10)	0.1992 (7)	−0.3157 (9)	0.0146 (10)	0.0072 (5)	0.0054 (9)	0.0057 (12)	−0.0006 (16)	−0.004 (1)
C21	0.2951 (7)	0.1066 (6)	0.2225 (12)	0.0109 (5)	0.0090 (5)	0.0640 (15)	−0.0008 (8)	−0.0533 (10)	0.033 (1)
C22	0.1814 (10)	0.1027 (6)	0.2996 (9)	0.0166 (10)	0.0062 (5)	0.0069 (10)	0.0098 (12)	−0.0008 (18)	0.003 (1)
C23	0.1033 (10)	0.0484 (7)	0.2118 (11)	0.0161 (11)	0.0068 (5)	0.0206 (14)	0.0090 (13)	0.0160 (22)	0.017 (1)
C24	0.1792 (9)	0.0294 (6)	0.0632 (14)	0.0109 (9)	0.0040 (4)	0.0282 (20)	0.0021 (11)	−0.0026 (25)	0.002 (2)
C25	0.2663 (8)	0.0735 (6)	0.0817 (13)	0.0091 (7)	0.0054 (4)	0.0339 (20)	0.0083 (9)	−0.0123 (20)	0.011 (2)
C21A	0.2385 (7)	0.1222 (6)	0.2811 (11)	0.0092 (6)	0.0050 (4)	0.0290 (14)	−0.0026 (9)	−0.0262 (14)	0.013 (1)
C22A	0.1264 (8)	0.0951 (6)	0.3069 (10)	0.0117 (9)	0.0050 (4)	0.0121 (10)	0.0020 (11)	−0.0020 (18)	0.008 (1)
C23A	0.1157 (8)	0.0425 (5)	0.1704 (10)	0.0105 (7)	0.0020 (3)	0.0148 (12)	−0.0033 (8)	−0.0072 (17)	0.003 (1)
C24A	0.1935 (11)	0.0391 (5)	0.0932 (9)	0.0243 (13)	0.0027 (3)	0.0106 (11)	0.0104 (11)	−0.0035 (22)	−0.005 (1)
C25A	0.2778 (5)	0.0975 (7)	0.1620 (10)	0.0036 (4)	0.0164 (6)	0.0440 (12)	0.0001 (7)	−0.0283 (9)	0.044 (1)
B5	0.0056 (4)	0.1936 (3)	0.0069 (5)	0.0047 (3)	0.0041 (2)	0.0102 (5)	−0.0011 (4)	−0.0015 (7)	0.0006 (6)
B6	0.0261 (5)	0.2500 (0)	0.1701 (7)	0.0051 (4)	0.0042 (3)	0.0088 (7)	0.0000 (0)	0.0025 (10)	0.0000 (0)
B7	0.2473 (5)	0.2500 (0)	0.0060 (7)	0.0054 (4)	0.0052 (3)	0.0082 (8)	0.0000 (0)	−0.0002 (10)	0.0000 (0)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H5	−0.057 (3)	0.147 (2)	−0.021 (4)	2.8 (8)	H7	0.344 (5)	0.250	−0.034 (8)	6.3 (17)
H6	−0.014 (4)	0.250	0.279 (6)	3.6 (12)					

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table III. Bond Distances (Å) in $(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$

Co1–Co2	2.488 (1)	Co2–C21A	2.13 (2)
Co2–Co2′	2.472 (1)	Co2–C22A	2.02 (1)
Co1–B5	2.051 (3)	Co2–C23A	2.08 (2)
Co1–B6	2.911 (4)	Co2–C24A	2.03 (1)
Co2–B5′	2.904 (3)	Co2–C25A	2.20 (3)
Co2–B5	2.047 (3)	C11–C12	1.38 (2)
Co2–B6	2.030 (4)	C12–C13	1.34 (4)
B5–B5′	1.716 (6)	C13–C13′	1.78 (12)
B5–B6	1.724 (5)	C11A–C12A	1.46 (9)
B5–H5	1.06 (4)	C12A–C13A	1.34 (6)
B6–H6	1.15 (3)	C13A–C13′A	1.45 (8)
Co1–C11	2.03 (2)	C21–C22	1.37 (3)
Co1–C12	1.97 (1)	C22–C23	1.53 (4)
Co1–C13	2.15 (4)	C23–C24	1.72 (6)
Co1–C11A	2.05 (2)	C24–C25	1.42 (4)
Co1–C12A	2.02 (5)	C21–C25	1.18 (3)
Co1–C13A	2.07 (2)	C21A–C22A	1.53 (4)
Co2–C21	2.06 (1)	C22A–C23A	1.44 (3)
Co2–C22	2.06 (1)	C23A–C24A	1.40 (3)
Co2–C23	2.03 (3)	C24A–C25A	1.35 (4)
Co2–C24	2.15 (2)	C21A–C25A	1.56 (4)
Co2–C25	2.09 (2)		

Table IV. Bond Distances (Å) in $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$

Co1–Co2	2.444 (1)	Co2–C23	2.11 (2)
Co2–Co2′	2.435 (1)	Co2–C24	2.16 (3)
Co1–B5	2.023 (3)	Co2–C25	2.05 (1)
Co2–B5	2.032 (3)	Co2–C21A	2.03 (2)
Co2–B6	2.026 (4)	Co2–C22A	2.12 (2)
Co1–B7	1.956 (5)	Co2–C23A	2.02 (1)
Co2–B7	1.950 (4)	Co2–C24A	2.03 (3)
Co1–B6	2.885 (5)	Co2–C25A	1.97 (2)
Co2–B5′	2.872 (3)	C11–C12	1.47 (4)
B5–B7	3.104 (6)	C12–C13	1.56 (2)
B6–B7	3.106 (7)	C13–C13′	1.12 (3)
B5–B5′	1.692 (7)	C11A–C12A	1.36 (2)
B5–B6	1.713 (5)	C12A–C13A	1.41 (2)
B5–H5	1.07 (2)	C13A–C13A′	1.52 (4)
B6–H6	1.10 (4)	C21–C22	1.57 (4)
B7–H7	1.24 (5)	C22–C23	1.49 (3)
Co1–C11	1.99 (2)	C23–C24	1.66 (6)
Co1–C12	2.13 (2)	C24–C25	1.27 (4)
Co1–C13	1.97 (1)	C21–C25	1.41 (4)
Co1–C11A	2.24 (1)	C21A–C22A	1.46 (2)
Co1–C12A	2.07 (1)	C22A–C23A	1.47 (4)
Co1–C13A	2.10 (2)	C23A–C24A	1.19 (6)
Co2–C21	2.27 (3)	C24A–C25A	1.50 (4)
Co2–C22	2.02 (2)	C21A–C25A	1.23 (3)

Co2–Co2′), as are the two kinds of B–B bonds (1.724 (5) Å for B5–B6 vs. 1.716 (6) Å for B5–B5′). A similar comparison holds for $(C_5H_5)_3Co_3B_4H_4$, with metal–metal distances of 2.444 (1) Å for Co1–Co2 and 2.435 (1) Å for Co2–Co2′, and boron–boron lengths of 1.713 (5) Å for B5–B6 and 1.692 (7) Å for B5–B5′. Significantly, the average Co–Co distance in the boron-capped system (2.441 (1) Å) is slightly smaller than the corresponding value in the uncapped species (2.483 (1) Å), reflecting a small, but real, contraction induced by the capping BH group in the former (this BH cap is analogous to a triply bridging CO or CR group as found in various metal cluster systems, a point to which we shall return). The average B–B distances in the two structures, on the other hand, are not significantly different.

All non-cyclopentadienyl hydrogen atoms in the two molecules were located and refined, except for the two "extra" hydrogens in $(C_5H_5)_3Co_3B_3H_5$. Electron density maps yielded three peaks in the vicinity of the tricobalt face which are attributed to these hydrogens in disordered locations. Although they could not be successfully refined (see Experimental Section), these peaks appear to be real; the assumption that they are the extra hydrogens is consistent with proton NMR evidence[8b,c] which shows that the extra protons in the molecule are bonded to cobalt and are tautomerizing rapidly in solution. Additional support for this assignment is the fact that the final electron density map exhibited no extra peaks of significant intensity in any other region of the cage. Thus, there is little doubt that the bridging hydrogens are associated with the tricobalt face, but their exact locations on this face have not been established.

The cobalt–cobalt bond lengths in these molecules can be compared with those in the 9-vertex system 1,7,5,6-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_5H_7$ (2.444 (3) Å),[14] 10-vertex 2,6,1,10-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_6H_8$ (2.489 (1) Å),[15] and 12-vertex 2,3,1,7-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_8H_{10}$ (2.387 (2) Å),[16] which are the only other structurally characterized cobalt–boron cages having adjacent cobalt atoms.[34] There is no clear trend here, other than variations which can reasonably be attributed to the different geometries involved (e.g., it can be argued that the short Co–Co distance in the $Co_2C_2B_8$ system arises from the

Table V. Selected Bond Angles (deg) in $(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$

Co2–Co1–Co2′	59.57 (2)	C21–Co2–C22	38.9 (7)
Co1–Co2–Co2′	60.22 (1)	C22–Co2–C23	44 (1)
Co2–Co1–B5	52.5 (1)	C23–Co2–C24	48 (1)
B5–Co1–B5′	49.5 (2)	C24–Co2–C25	39 (1)
Co1–Co2–B5	52.7 (1)	C21–Co2–C25	32.9 (8)
Co2′–Co2–B6	52.5 (1)	C21A–Co2–C22A	43 (1)
B5–Co2–B6	50.0 (2)	C22A–Co2–C23A	41.2 (9)
Co1–B5–Co2	74.8 (1)	C23A–Co2–C24A	39.7 (9)
Co1–B5–B5′	65.3 (1)	C24A–Co2–C25A	37 (1)
Co2–B5–B6	64.5 (2)	C21A–Co2–C25A	42 (1)
B5′–B5–B6	60.2 (1)	C12–C11–C12′	105 (2)
Co2–B6–Co2′	75.0 (2)	C11–C12–C13	118 (2)
Co2–B6–B5	65.5 (2)	C12–C13–C13′	99 (2)
B5–B6–B5′	59.7 (3)	C12A–C11A–C12A′	119 (3)
Co1–B5–H5	126 (2)	C11A–C12A–C13A	94 (5)
Co2–B5–H5	123 (2)	C12A–C13A–C13A′	113 (5)
B5′–B5–H5	136 (2)	C22–C21–C25	121 (1)
B6–B5–H5	134 (2)	C21–C22–C23	99 (3)
Co2–B6–H6	129 (1)	C22–C23–C24	106 (2)
B5–B6–H6	129 (1)	C23–C24–C25	93 (2)
C11–Co1–C12	40.4 (6)	C21–C25–C24	121 (2)
C12–Co1–C13	37.8 (11)	C22A–C21A–C25A	110 (3)
C13–Co1–C13′	49 (3)	C21A–C22A–C23A	105 (1)
C11A–Co1–C12A	42 (2)	C22A–C23A–C24A	102 (1)
C12A–Co1–C13A	38 (2)	C23A–C24A–C25A	127 (2)
C13A–Co1–C13A′	41 (2)	C21A–C25A–C24A	94 (3)

Table VI. Selected Bond Angles (deg) in $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$

Co2–Co1–Co2′	59.75 (2)	C11A–Co1–C12A	36.5 (4)
Co1–Co2–Co2′	60.12 (1)	C12A–Co1–C13A	39.6 (6)
Co2–Co1–B5	53.1 (1)	C13A–Co1–C13A′	43 (1)
Co2–Co1–B7	51.2 (1)	C21–Co2–C22	42 (1)
B5–Co1–B5′	49.4 (2)	C22–Co2–C23	42.2 (9)
Co1–Co2–B5	52.8 (1)	C23–Co2–C24	46 (2)
Co1–Co2–B7	51.4 (1)	C24–Co2–C25	35 (1)
Co2′–Co2–B6	53.1 (1)	C21–Co2–C25	38 (1)
Co2′–Co2–B7	51.4 (1)	C21A–Co2–C22A	41.2 (7)
B5–Co2–B6	49.9 (2)	C22A–Co2–C23A	41 (1)
Co1–B5–Co2	74.1 (1)	C23A–Co2–C24A	34 (2)
Co1–B5–B5′	65.3 (1)	C24A–Co2–C25A	44 (1)
Co2–B5–B6	64.8 (2)	C21A–Co2–C25A	35.9 (7)
B5′–B5–B6	60.4 (1)	C12–C11–C12′	119 (2)
Co2–B6–Co2′	73.9 (2)	C11–C12–C13	93 (2)
Co2–B6–B5	65.2 (2)	C12–C13–C13′	117 (1)
B5–B6–B5	59.2 (3)	C12A–C11A–C12A′	109 (2)
Co1–B7–Co2	77.5 (2)	C11A–C12A–C13A	110 (1)
Co2–B7–Co2′	77.3 (2)	C12A–C13A–C13A′	104 (1)
Co1–B5–H5	130 (1)	C22–C21–C25	99 (2)
Co2–B5–H5	128 (1)	C21–C22–C23	111 (2)
B5′–B5–H5	131 (1)	C22–C23–C24	99 (2)
B6–B5–H5	129 (1)	C23–C24–C25	107 (2)
Co2–B6–H6	125 (1)	C21–C25–C24	121 (3)
B5–B6–H6	134 (1)	C22A–C21A–C25A	115 (2)
Co1–B7–H7	127 (2)	C21A–C22A–C23A	96 (2)
Co2–B7–H7	137 (1)	C22A–C23A–C24A	116 (2)
C11–Co1–C12	41.8 (9)	C23A–C24A–C25A	107 (2)
C12–Co1–C13	44.6 (6)	C21A–C25A–C24A	105 (2)
C13–Co1–C13′	33.1 (9)		

Table VII. Selected Molecular Planes in $(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$

Atom	Dev, Å	Atom	Dev, Å
Plane 1: Co1, Co2, Co2′ $0.9491x - 0.3151z = 1.6304$			
Plane 2: B5, B5′, B6 $0.9448x - 0.3276z = 0.0262$			
Plane 3: C11, C12, C12′, C13, C13′ $0.0036x - 1.000z = 3.1161$			
C11	0.047	C13	0.015
C12	−0.038	C13′	0.015
C12′	−0.038		
Plane 4: C11A, C12A, C12A′, C13A, C13A′ $0.0976x - 0.9952z = 3.2421$			
C11A	0.140	C13A	0.040
C12A	−0.110	C13A′	0.040
C12A′	−0.110		
Plane 5: C21, C22, C23, C24, C25 $0.4576x - 0.7713y + 0.4423z = 0.8289$			
C21	−0.014	C24	0.022
C22	0.027	C25	−0.008
C23	−0.027		
Plane 6: C21A, C22A, C23A, C24A, C25A $0.4281x - 0.8119y + 0.3969z = 0.6523$			
C21A	−0.049	C24A	−0.015
C22A	0.044	C25A	0.039
C23A	−0.019		

Planes	Dihedral angle, deg	Planes	Dihedral angle, deg
1,2	0.76	1,4	66.0
3,4	5.40	1,5	72.8
5,6	3.88	1,6	73.7
1,3	71.4		

fact that a longer bond would produce an unacceptably large distortion of the icosahedral framework; in the smaller systems the metal atoms appear to be less constrained by the polyhedral geometry).

Comparison with Other Polyhedral Boron Cages. The $(C_5H_5)_3Co_3B_4H_4$ complex is unique in boron chemistry; no other examples of boron-containing capped octahedra exist. It is, however, directly analogous to the few capped octahedral metal clusters that have been reported, as discussed in the following section.

The octahedral $(C_5H_5)_3Co_3B_3H_5$ species, on the other hand, can be compared electronically and structurally with several other octahedral boron cages. Since all of these molecules can be viewed as 6-vertex closo polyhedra with 14 ($2n + 2$) skeletal electrons,[1,2] it is not surprising that the boron–boron distances in the Co_3B_3 cage (1.716 (6) and 1.724 (5) Å) are similar to those in the metal hexaborides, MB_6 (1.70–1.74 Å),[17] the $B_6H_6^{2-}$ ion (1.69 (1) Å),[3] 1,2- and 1,6-$C_2B_4H_6$ (1.721–1.752 Å from electron diffraction and microwave analyses[5,6]), and CB_5H_7 (1.70 (1)–1.72 (1) Å from microwave data,[4] excluding the proton-bridged B_3 face). Several additional octahedral cages which have been prepared in this laboratory ($(CO)_3FeC_2B_3H_5$,[7] $(\eta^5\text{-}C_5H_5)CoC_2B_3H_5$,[7] and 1,2-$(C_5H_5)_2Co_2B_4H_6$[8a,c]) have not yet been crystallographically examined; the last of these is, of course, closely related to $(C_5H_5)_3Co_3B_3H_5$, both being members of the hypothetical series $[(\eta^5\text{-}C_5H_5)Co]_n(BH)_{6-n}H_2$ which would be octahedra with two extra hydrogen atoms. The species for which n = 1, 4, 5, and 6 are yet to be found, but the n = 0 member exists as the $B_6H_6^{2-}$ ion[18] which can be regarded as B_6H_8 minus two protons.

Comparison with Metal Clusters. Perhaps the most interesting aspect of the $(C_5H_5)_3Co_3B_3H_5$ and $(C_5H_5)_3Co_3B_4H_4$ structures is their relationship to other metal cluster systems. While we know of no previous examples of structurally characterized octahedral clusters containing $(\eta^5\text{-}C_5H_5)Co$ units, there are a number of octahedral cobalt carbonyls, and it is important to note that all of them obey the skeletal electron-counting arguments mentioned earlier; that is, they all contain 14 ($2n + 2$) framework electrons. The Co–Co bond distances in $Co_6(CO)_{14}^{4-}$,[19] $Co_6(CO)_{15}^{2-}$,[20] $Co_4Ni_2(CO)_{14}^{2-}$ (with Co and Ni atoms indistinguishable),[21] and $(C_2H_5)_2C_2Co_4(CO)_{10}$[22] are between 2.42 and 2.55 Å, quite similar to the values in $(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$ and $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$ despite the fact that the carbonyl species all contain face-bridging and/or edge-bridging CO groups. In the paramagnetic carbido cluster[23] $Co_6(CO)_{14}C^-$, which has a carbon atom in the center of the octahedron and contains an extra (antibonding) skeletal electron, the Co–Co distances have an average value of 2.53 Å for the six carbonyl-bridged edges, 2.75 Å for five others, and 2.96 Å for the unique "stretched" bond. In relation to these "pure" metal cluster systems, the

Table VIII. Selected Molecular Planes in $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$

Atom	Dev, Å	Atom	Dev, Å
Plane 1: Co1, Co2, Co2′ $0.9854x - 0.1704z = 1.6512$			
Plane 2: B5, B5′, B6 $0.9854x - 0.1701z = 0.0576$			
Plane 3: Co1, B6, B7 $y = 3.7491$			
Plane 4: Co2, B5′, B7 $0.1450x + 0.5030y + 0.8520z = 2.3745$			
Plane 5: Co2′, B5, B7 $-0.1450x + 0.5030y - 0.8520z = 1.3971$			
Plane 6: C11, C12, C12′, C13, C13′ $0.1615x - 0.9869z = 2.9664$			
C11	−0.030	C13	−0.008
C12	0.023	C13′	−0.008
C12′	0.023	Co1	−1.63
Plane 7: C11A, C12A, C12A′, C13A, C13A′ $-0.0374x - 0.9993z = 2.7920$			
C11A	0.089	C13A	0.025
C12A	−0.070	C13A′	0.025
C12A′	−0.070	Co1	−1.74
Plane 8: C21, C22, C23, C24, C25 $0.3318x - 0.8595y + 0.3888z = 0.5254$			
C21	−0.089	C24	−0.050
C22	0.058	C25	0.097
C23	−0.016	Co2	1.71
Plane 9: C21A, C22A, C23A, C24A, C25A $0.3414x - 0.8058y + 0.4838z = 0.7279$			
C21A	−0.024	C24A	−0.023
C22A	0.008	C25A	0.029
C23A	0.011	Co2	1.66

Planes	Dihedral angle, deg	Planes	Dihedral angle, deg
1,2	0.02	3,5	59.80
1,3	90.00	4,5	60.40
1,4	89.87	1,6	70.9
1,5	89.87	1,7	82.3
2,3	90.00	1,8	74.9
2,4	89.89	1,9	75.3
2,5	89.89	6,7	11.4
3,4	59.80	8,9	6.3

Co–Co distances in the two metalloboron cages appear to reflect a comparable degree of metal–metal interaction insofar as this can be judged from structural parameters.

The complex $(C_5H_5)_3Co_3B_4H_4$ is one of only three known examples of capped octahedral clusters to have been structurally characterized, the others being $Os_7(CO)_{21}$[24] and the $Rh_7(CO)_{16}{}^{3-}$ ion.[25] The adoption of this unusual geometry in place of the "normal" pentagonal-bipyramidal shape for 7-vertex clusters was originally attributed by Mason et al.,[24b] and later by others,[1c,2a,8b,c,26–28] to the presence of only 14 ($2n$) framework electrons, which is two electrons short of the $2n + 2$ required for regular closo polyhedra. These molecules compensate for their electron-hyperdeficiency[26] by assuming a capped octahedral structure, which has exactly the same capacity for skeletal bonding electrons (14) as an uncapped octahedron.[27] In more general terms, this "capping principle"[27] states that a $2n$-electron cluster will adopt the structure of an $(n - 1)$-vertex closo polyhedron capped on one face; other known examples include $Os_6(CO)_{18}$, a capped trigonal bipyramid;[24b] 1,6,2,3-$(\eta^5\text{-}C_5H_5)_2Fe_2C_2B_6H_8$, a capped tricapped trigonal prism;[28] and $(\eta^5\text{-}C_5H_5)CoFe(CH_3)_4C_4B_8H_8$,[26] which consists of two pentagonal bipyramids simultaneously capped by a BH unit.

Table IX. Comparison of Co_3BH and Co_3CR Groups in $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$ and $(CO)_9Co_3CR$

Av values[a]	$(C_5H_5)_3Co_3B_4H_4$	Av for $(CO)_9Co_3CR$ structures[29]
Co–Co, Å	2.441 (1)	2.47
Co–B(C), Å	1.953 (5)	1.92
Co–B(C)–Co, deg	77.4 (2)	81
Co–B–H, deg	134 (1)	
Co–C–R, deg		131

[a] Apex B or C atoms only.

The $(C_5H_5)_3Co_3B_4H_4$ system is also of interest in a different respect: it provides the only known case of a boron atom triply bonded to a triangular cluster of metal atoms (and is also unique in having a boron atom adjacent to no other borons in a polyboron cage). As such, it is reminiscent of the well-known tricobalt carbon clusters $(CO)_9Co_3CR$,[29] and a structural comparison with these species is of interest. The reported values[30] for Co–Co bonds in the known $(CO)_9Co_3CR$ structures are between 2.43 and 2.55 Å, so that the 2.444 (1) and 2.435 (1) Å distances in the Co_3B_4 system are near the lower end of that range. There is a remarkable similarity in the Co_3BH array in $(C_5H_5)_3Co_3B_4H_4$ and the Co_3CR group in the tricobalt carbon clusters, as illustrated in Table IX The difference of 0.03 Å in the Co–apex B and Co–apex C bond lengths is nearly identical with the 0.04 Å difference in covalent radii of boron and carbon as conventionally given.[31] This is consistent with the view that the Co_3B and Co_3C units are electronically similar, as would be expected since $(CO)_9Co_3CR$ species are delocalized systems[29] and can legitimately be compared to borane cages. A further indication of this similarity is the observation of extremely low field ^1H NMR signals for the apex protons in $(C_5H_5)_3Co_3B_4H_4$ (δ 14.45 relative to $(CH_3)_4Si$)[8b,c] and $(CO)_9Co_3CH$ (δ 12.08).[32] The tricobalt carbon clusters have also been compared[7] to the isomeric 10-vertex tricobaltacarboranes 2,3,8,1,6- and 2,3,4,1,10-$(\eta^5\text{-}C_5H_5)_3Co_3C_2B_5H_7$ which contain apex BH groups coordinated to two and three cobalt atoms, respectively; again, the NMR resonances exhibited by these apex protons (δ 10.65 and 15.81) are at very low field.[7]

What is now required is an investigation of the chemical properties of the unique BH unit in $(C_5H_5)_3Co_3B_4H_4$. Although the yield of this compound in the original preparation[8c] from $B_5H_8{}^-$, $CoCl_2$, and $C_5H_5{}^-$ was so low as to preclude a systematic study, a new route[33] based on the introduction of cobalt into the readily accessible complex 2-$(\eta^5\text{-}C_5H_5)CoB_4H_8$[8a,c] affords workable quantities of the Co_3B_4 system, and an examination of its chemistry is in progress.

Acknowledgment. This work was supported by the National Science Foundation, Grant No. CHE 76-04491. We thank Professor Ekk Sinn for assistance during the data collection and refinement.

Registry No. 1,2,3-$(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$, 59217-07-1; 1,2,3-$(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$, 59458-52-5.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes and tables of nearest intermolecular contacts (14 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) K. Wade, *J. Chem. Soc. D*, 792 (1971); (b) D. M. P. Mingos, *Nature (London), Phys. Sci.*, **236**, 99 (1972); (c) R. N. Grimes, *Ann. N.Y. Acad. Sci.*, **239**, 180 (1974); (d) K. Wade, *Chem. Br.*, 177 (1975).

(2) (a) K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976); (b) R. W. Rudolph, *Acc. Chem. Res.*, **9**, 446 (1976).

(3) R. Schaeffer, Q. Johnson, and G. S. Smith, *Inorg. Chem.*, **4**, 917 (1965).

(4) E. A. McNeill and F. R. Scholer, *Inorg. Chem.*, **14**, 1081 (1975).

(5) R. A. Beaudet and R. L. Poynter, *J. Chem. Phys.*, **53**, 1899 (1970).

(6) (a) G. L. McKown and R. A. Beaudet, *Inorg. Chem.*, **10**, 1350 (1971); (b) B. S. Mastryukov, O. V. Dorofeeva, L. V. Vilkov, A. F. Zhigach, V. T. Laptev, and A. B. Petrunin, *J. Chem. Soc., Chem. Commun.*, 276 (1973); (c) V. S. Mastryukov, O. V. Dorofeeva, L. V. Vilkov, A. V. Golubinskii, A. F. Zhigach, V. T. Laptev, and A. B. Petrunin, *Zh. Strukt. Khim.*, **16**, 171 (1975).

(7) V. R. Miller, L. G. Sneddon, D. C. Beer, and R. N. Grimes, *J. Am. Chem. Soc.*, **96**, 3090 (1974).
(8) (a) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 5078 (1973); (b) *ibid.*, **98**, 1600 (1976); (c) V. R. Miller, R. Weiss, and R. N. Grimes, *ibid.*, **99**, 5646 (1977).
(9) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(10) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," Vol. IV, The Kynoch Press, Birmingham, England, 1974.
(11) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(12) D. T. Cromer and J. A. Ibers, ref 10.
(13) D. P. Freyberg, G. M. Mockler, and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 447 (1976).
(14) R. N. Grimes, A. Zalkin, W. T. Robinson, *Inorg. Chem.*, **15**, 2274 (1976).
(15) E. L. Hoel, C. E. Strouse, and M. F. Hawthorne, *Inorg. Chem.*, **13**, 1388 (1974).
(16) K. P. Callahan, C. E. Strouse, A. L. Sims, and M. F. Hawthorne, *Inorg. Chem.*, **13**, 1397 (1974).
(17) N. N. Greenwood, "The Chemistry of Boron", Pergamon Press, Oxford, England, 1973, Chapter 3.
(18) J. L. Boone, *J. Am. Chem. Soc.*, **86**, 5036 (1964).
(19) V. G. Albano, P. L. Bellon, P. Chini, and V. Scatturin, *J. Organomet. Chem.*, **16**, 461 (1969).
(20) V. Albano, P. Chini, and V. Scatturin, *J. Oganomet. Chem.*, **15**, 423 (1968).
(21) V. Albano, G. Ciani, and P. Chini, *J. Chem. Soc., Dalton Trans.*, 432 (1974).
(22) L. F. Dahl and D. L. Smith, *J. Am. Chem. Soc.*, **84**, 2450 (1962).
(23) V. G. Albano, P. Chini, G. Ciani, M. Sansoni, D. Strumolo, B. T. Heaton, and S. Martinegro, *J. Am. Chem. Soc.*, **98**, 5027 (1976).
(24) (a) C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.*, **37**, C39 (1972); (b) R. Mason, K. M. Thomas, and D. M. P. Mingos, *J. Am. Chem. Soc.*, **95**, 3802 (1973); (c) C. R. Eady, B. F. G. Johnson, J. Lewis, R. Mason, P. B. Hitchcock, and K. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 385 (1977).
(25) V. G. Albano, P. L. Bellon, and G. F. Ciani, *J. Chem. Soc., Chem. Commun.*, 1024 (1969).
(26) W. M. Maxwell, E. Sinn, and R. N. Grimes, *J. Am. Chem. Soc.*, **98**, 3490 (1976).
(27) D. M. P. Mingos and M. Forsyth, *J. Chem. Soc., Dalton Trans.*, 610 (1977).
(28) K. P. Callahan, W. J. Evans, F. Y. Lo, C. E. Strouse, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **97**, 296 (1975).
(29) B. R. Penfold and B. H. Robinson, *Acc. Chem. Res.*, **6**, 73 (1973).
(30) (a) J. Lewis, *Pure Appl. Chem.*, **10**, 11 (1965); (b) B. R. Penfold, *Perspect. Struct. Chem.*, **2**, 71 (1968).
(31) (a) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960; (b) V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.*, **63**, 37 (1941).
(32) D. Seyferth, J. E. Hallgren, and P. L. K. Hung, *J. Organomet. Chem.*, **50**, 265 (1973).
(33) R. Weiss, J. R. Bowser, and R. N. Grimes, submitted for publication.
(34) Recent x-ray structure determinations of $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$ and $1,2\text{-}(\eta^5\text{-}C_5H_5)_2Co_2B_4H_6$ have yielded an average Co–Co bond length of 2.477 (1) Å in the former molecule and 2.53 Å in the latter: J. R. Pipal and R. N. Grimes, manuscript in preparation. (The structures of these clusters are described in ref 8c.)

Contribution from the Department of Chemistry,
Columbia University, New York, New York 10027

Synthesis and Characterization of the Pentacoordinate Mononitrosyliron Complexes $Fe(NO)[SCH_2CH_2N(CH_3)(CH_2)_nN(CH_3)CH_2CH_2S]$, $n = 2, 3$

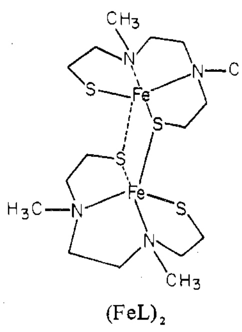
KENNETH D. KARLIN, HAROLD N. RABINOWITZ, DAVID L. LEWIS, and STEPHEN J. LIPPARD*

Received May 2, 1977 AIC70303R

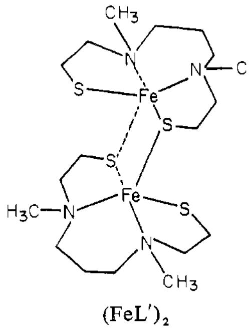
Addition of nitronium ion, nitrosonium ion, or nitric oxide to $(FeL)_2$ or $(FeL')_2$, where L and L′ are the tetradentate N_2S_2 donor ligands derived from *N,N′*-dimethyl-*N,N′*-bis(2-mercaptoethyl)ethylenediamine (LH_2) and *N,N′*-dimethyl-*N,N′*-bis(2-mercaptoethyl)-1,3-propanediamine ($L'H_2$), respectively, affords the crystalline green complexes FeL(NO) and FeL′(NO), respectively. A single-crystal x-ray diffraction study of FeL(NO) revealed a pentacoordinate structure in which the nitrosyl ligand occupies the apical position of a distorted square pyramid. The Fe–N–O angles in two crystallographically independent molecules are 155.2 (5) and 158.4 (5)°. The corresponding distances are Fe–N = 1.693 (5) and 1.702 (5) Å and N–O = 1.170 (6) and 1.130 (6) Å, respectively. Crystal data are as follows: orthorhombic space group $Pca2_1$; $a = 13.890$ (2), $b = 11.939$ (2), $c = 15.198$ (3) Å; ρ(obsd) = 1.529 (5) and ρ(calcd) = 1.540 g cm^{-3} for mol wt 292.2; $V = 2520$ (4) Å^3; $Z = 8$. Temperature-dependent magnetic susceptibility studies (to 80 K) show both FeL(NO) and FeL′(NO) to have $S = {}^1/_2$ ground states. Electron spin resonance, Mössbauer, and electronic spectral data are presented and shown to be consistent with results for other isoelectronic, sulfur-containing iron nitrosyl complexes.

Introduction

We have recently reported the synthesis and described the physical and chemical properties of the iron(II) complexes $(FeL)_2$ and $(FeL')_2$.[1-4] During the preparation of $[(FeL)_2NO]^+$ from $(FeL)_2$ and nitrosonium (NO^+) salts,[4] a green monomeric complex having the composition FeL(NO) was isolated. Here we describe the synthesis and characterization of this complex and its analogue FeL′(NO). These results are of interest because they reveal some further reactions of $(FeL)_2$ and $(FeL')_2$ and because the structure of FeL(NO), determined by x-ray diffraction, is one of the few known cases of a partially bent, ordered metal nitrosyl complex at room temperature.



$(FeL)_2$



$(FeL')_2$

Experimental Section

Materials and methods are as reported previously,[1] with the following additions. Nitric oxide was purchased from Matheson and passed through a dry ice–acetone trap prior to use to remove water and higher oxide impurities.[5] Electron spin resonance experiments were carried out using a Varian E-line ESR spectrometer at a modulation frequency of 100 kHz. Samples were made up on a vacuum line. Solvents were distilled into the solid samples in quartz tubes and then sealed under vacuum. Low-temperature spectra were taken employing a Varian variable-temperature controller, which was calibrated using an iron–constantan thermocouple. The g values were calibrated by comparison with the spectrum of strong pitch (a Varian standard, $g = 2.0028$)[6] and are accurate to ±0.005.