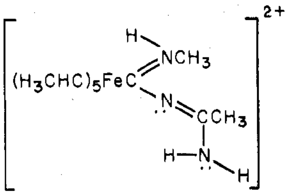
deprotonate rapidly and reversibly in solvents such as water and methanol. By acidifying to near pH 2 the color of the solution changes from bright yellow to deep red-orange, and the solubility increases dramatically; both effects are readily reversed when the solution is made more basic. It is reasonable, then, that in solution the ring hydrogen might move from one side of the ring to the other fairly rapidly at room temperature.

The reaction by which the Fe complex is formed probably takes place via nucleophilic attack on a coordinated isocyanide carbon atom and involves an intermediate similar to **3**. If the



3

same nitrogen which attacked the first isocyanide carbon also attacks the second, compound **1** will result; if, on the other hand, the other acetamidine nitrogen attacks the second carbon, a cation like **2** will be formed. Since the structure is now known to be similar to **2**, one may conclude that the second nucleophilic attack involved in forming the chelate ring is carried out by the second nitrogen.

Application of infrared and Mössbauer spectroscopy resulted in different proposed structures for the Fe complex described. The differences between both of those structures and that found by X-ray methods are significant. This once more illustrates the hazards involved in attempting to determine molecular structures by spectroscopic methods where precedents do not exist.

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Registry No. $Fe(CNCH_3)_4(C_6N_4H_{12})(PF_6)_2$ (**1**), 49631-73-4; $Fe(CNCH_3)_4(C_6N_4H_{12})(PF_6)_2$ (**2**), 56292-62-7.

Supplementary Material Available: Table II, a listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of a Cobaltocenium Cobaltacarborane Zwitterion. Cobaltocenium and Tetrahydrofuran Derivatives of *nido,closo*-$[2,3\text{-}(CH_3)_2C_2B_3H_5]CoH[2,3\text{-}(CH_3)_2C_2B_4H_4]$

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The preparation and characterization of the title compounds are described. The species 5-$[(\eta^5\text{-}C_5H_5)Co(\eta^5\text{-}C_5H_4)]$-$[2,3\text{-}(CH_3)_2C_2B_4H_3]Co[2,3\text{-}(CH_3)_2C_2B_3H_5]$ and σ-$(CH_2)_4O$-$[2,3\text{-}(CH_3)_2C_2B_4H_3]Co[2,3\text{-}(CH_3)_2C_2B_3H_5]$ were obtained from the reaction of $[2,3\text{-}(CH_3)_2C_2B_3H_5]CoH[2,3\text{-}(CH_3)_2C_2B_4H_4]$ with $(\eta^5\text{-}C_5H_5)Co(CO)_2$ in tetrahydrofuran under ultraviolet light, separated via thick-layer chromatography, and characterized from their NMR, infrared, and mass spectra. A single-crystal x-ray diffraction study of the cobaltocenium derivative established its structure. The molecule is a zwitterion composed of a $[(CH_3)_2C_2B_4H_3]Co^{III}[(CH_3)_2C_2B_3H_5]^-$ unit and a $(C_5H_5)Co^{III}(C_5H_4)^+$ group, with the latter substituent attached to the closo portion of the metallocarborane system at B(5). The metallocarborane structure is in agreement with that originally proposed for $[(CH_3)_2C_2B_4H_4]CoH[(CH_3)_2C_2B_3H_5]$ on the basis of spectroscopic evidence and consists formally of a Co^{3+} ion face-bonded to a pyramidal C_2B_4 and a cyclic C_2B_3 ligand. The latter group has two B–H–B hydrogen bridges which were located and refined. Crystal data: mol wt 438.98; space group *Pbca* (No. 61); $a = 11.339$ (6), $b = 16.703$ (22), $c = 22.332$ (18) Å; $V = 4230$ (7) Å^3; $d_{calcd} = 1.386$ g cm^{-3} for $Z = 8$. The structure was refined by full-matrix least-squares methods to a final R value of 0.063 and R_w of 0.071 for the 1725 reflections for which $F_o^2 > 3\sigma(F_o^2)$.

A series of metallocarboranes containing the cyclic 2,3-$C_2B_3H_7^{2-}$, 2,3-$C_2B_3H_5^{4-}$, and 2,4-$C_2B_3H_5^{4-}$ ligands and the pyramidal 2,3- and 2,4-$C_2B_4H_6^{2-}$ ligands (or their C-substituted derivatives) has been reported from this laboratory.[1] The formal $C_2B_3H_7^{2-}$ and $C_2B_3H_5^{4-}$ groups are isoelectronic with $C_5H_5^-$; however, due to the presence of two B–H–B bridges, $C_2B_3H_7^{2-}$ functions only as a capping group, whereas $C_2B_3H_5^{4-}$ face-bonds simultaneously to two metal atoms, as in the triple-decked sandwich species[1a–d,2a–c] $(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$. The pyramidal $C_2B_4H_6^{2-}$ ligands are, of course, of the capping type.

Because of their close relationship to the metallocene sandwich compounds, the metal complexes of these ligands are of interest structurally and stereochemically. Several crystallographic studies of metallocarboranes containing substituted derivatives of $C_2B_3H_5^{4-}$ or $C_2B_4H_6^{2-}$ have been conducted,[2–4] but the only prior structural investigation of a $C_2B_3H_7^{2-}$ complex has been that of 1,2,3-$(CO)_3FeC_2B_3H_7$.[5]

In that study the $C_2B_3H_7^{2-}$ ligand was shown to contain a planar C_2B_3 ring with the bridging hydrogens directed away from the metal atom, as originally proposed.[1i] Recent molecular orbital calculations[6] on that molecule indicate a transfer of two electrons from the $Fe(CO)_3$ group to the cyclocarborane ring, consistent with the earlier description of this structure as a $C_2B_3H_7^{2-}$ complex.[7]

The related yellow compound[1d] $[2,3-(CH_3)_2C_2B_4H_4]Co-H[2,3-(CH_3)_2C_2B_3H_5]$ (IA), which incorporates the *C,C′*-dimethyl derivatives of both the $C_2B_3H_7^{2-}$ and the $C_2B_4H_6^{2-}$ ligands in the same molecule, has held special interest for us because of its proposed nido,closo structure[1d] in which the metal atom is common to both an open and a closed polyhedral system. This molecule was originally prepared from the *commo*-metallocarborane $[2,3-(CH_3)_2C_2B_4H_4]_2CoH$ by acid hydrolysis and its structure was postulated from ^{11}B and ^1H NMR data.[1d] Attempts to grow crystals of IA suitable for X-ray analysis have been unsuccessful, but treatment with $(\eta^5-C_5H_5)Co(CO)_2$ under ultraviolet light in tetrahydrofuran (THF) produced, inter alia, a σ-THF derivative and a cobaltocenium-substituted derivative of IA. The preparation of these species and a structural investigation of the latter compound are the subject of this article.

Experimental Section

Materials. The complex $[2,3-(CH_3)_2C_2B_4H_4]CoH[2,3-(CH_3)_2-C_2B_3H_5]$ was prepared from $[2,3-(CH_3)_2C_2B_4H_4]_2CoH$ as described elsewhere.[1d] Tetrahydrofuran (THF) was dried over lithium aluminum hydride before use. All other materials were commercially obtained reagent grade and used as received.

Spectra. Boron-11 and proton pulse Fourier transform NMR, infrared, and unit- and high-resolution mass spectra were obtained on instruments described in other publications.[1d]

Preparation of $5-[(\eta^5-C_5H_5)Co(\eta^5-C_5H_4)]-[2,3-(CH_3)_2C_2B_4H_3]-Co[2,3-(CH_3)_2C_2B_3H_5]$ (I) and $\sigma-(CH_2)_4O-[2,3-(CH_3)_2C_2B_4H_3]Co-[2,3-(CH_3)_2C_2B_3H_5]$ (II). A 37-mg sample of solid yellow $[2,3-(CH_3)_2C_2B_4H_4]CoH[2,3-(CH_3)_2C_2B_3H_5]$ was placed together with 200 mg of $(\eta^5-C_5H_5)Co(CO)_2$ in a quartz reactor on a vacuum line, the reactor was evacuated, and 1 mL of THF was introduced by distillation. The solution was irradiated with a 275-W sun lamp for 40 h at room temperature, after which the vessel was opened to the atmosphere, methylene chloride was added, and the solution was stirred for several hours. The solution was filtered and the filtrate was placed on a 0.5-mm silica gel plate (F-254, Brinckmann Instruments), which was developed in 30% CCl_4/hexane to give two major bands. The first band was a brownish yellow material identified from its mass spectrum, color, and R_f value as the known compound[1h] $1,2,3-(\eta^5-C_5H_5)Co(CH_3)_2C_2B_3H_5$ (1 mg). The second band was yellowish solid II (2 mg), characterized as a derivative of the starting material with an attached THF substituent. The chemical ionization mass spectrum of II gave a mass of 325.2203 for the P + 1 peak (protonated parent ion); calcd for $^{59}Co^{16}O^{12}C_{12}{}^{11}B_7{}^1H_{29}{}^+$, 325.2202. The 32-MHz ^{11}B NMR spectrum in $CDCl_3$ contained a singlet of area 1 at δ 29.7 ppm (measured downfield from BF_3 etherate), assigned to the THF-substituted boron, and a broad doublet of area 6 at δ –0.09 ($J \approx 156$ Hz). The 100-MHz proton NMR spectrum in $CDCl_3$ contained methyl resonances of area 6 at δ 1.94 and 1.74 ppm downfield from $(CH_3)_4Si$ and multiplets centered at δ 4.77 (area 4, $J = 8$ Hz) and 2.35 (area 4, $J = 4$ Hz), both assigned to the $(CH_2)_4O$ group. The B–H–B resonance appeared as a broad singlet of area 2 ($w_{1/2} = 128$ Hz) at δ – 6.32. The observation of only two CH_3 resonances indicates the presence of a mirror plane in II, so that the $(CH_2)_4O$ substituent could be located on B(5′), B(5), or B(7) (the numbering system in the parent metallocarborane system is shown in Figure 1). However, the nearly identical ^{11}B chemical shifts of the six nonsubstituted borons make B(7) the more likely location; furthermore, the fact that substitution in the cobaltocenium derivative I occurs at B(5) (vide infra) implies that B(5) is relatively more negative than B(7), in which case B(7) is the more probable point of attack for a basic $(CH_2)_4O$ group.

The IR spectrum of II in CH_2Cl_2 vs. CH_2Cl_2 contained absorptions (cm^{-1}) at 2945 (sh), 2920 (s), 2858 (m), 2530 (vs), 1855 (m), 1730 (m), 1600 (w), 1528 (m), 1445 (m), 1368 (m), 1190 (m), 1135 (m), 1110 (m), 997 (m), 932 (m), 870 (w), and 835 (w).

The original TLC plate was redeveloped in benzene, which eluted one red-brown band (5 mg) characterized crystallographically as a cobaltocenium-substituted derivative of the starting material (I). The high-resolution mass spectrum of I contained a P + 1 peak at 441.1663 (calcd for $^{59}Co_2{}^{12}C_{18}{}^{11}B_7{}^1H_{30}{}^+$, 441.1657). The 32.1-MHz ^{11}B NMR spectrum in $CDCl_3$ contained heavily overlapped broad resonances near δ 7.0; on proton decoupling this resolved into singlets of approximate areas 3 and 4, at δ 7.0 and 6.5, respectively. The proton NMR spectrum was poor and contained unidentified impurities which precluded definitive interpretation. Although elemental composition revealed by the mass spectroscopic analysis corresponded to $(\eta^5-C_5H_5)_2Co_2(CH_3)_4C_4B_7H_7$, the NMR data did not permit even a gross structural assignment, and consequently an X-ray diffraction study was undertaken.

Crystal Structure Analysis of I. Red crystals were grown by the vapor diffusion of pentane into a chloroform solution of the compound. One irregular wedge-shaped crystal with maximum dimensions 0.40 × 0.23 × 0.12 mm was mounted in an arbitrary orientation on a glass fiber. Preliminary precision photographs indicated good crystal quality, and this crystal was used for the collection of a data set. Crystal data: $Co_2C_{18}B_7H_{29}$; mol wt 438.98; space group *Pbca* (No. 61); $Z = 8$; $a = 11.339$ (6), $b = 16.703$ (22), $c = 22.332$ (18) Å; $V = 4230$ (7) Å^3; μ(Mo Kα) = 16.37 cm^{-1}; $d_{calcd} = 1.386$ g cm^{-3}; $F(000) = 1808$. 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 to provide approximate cell dimensions. Refined cell dimensions and their estimated standard deviations were obtained from 28 accurately centered reflections using the Enraf-Nonius program UNICELL. The mosaicity of the crystal was examined by the ω scan technique and found acceptable. Systematic absences of $k = 2n + 1$ for $0kl$, of $l = 2n + 1$ for $h0l$, and of $h = 2n + 1$ for $hk0$ uniquely determine the space group as *Pbca*. For $Z = 8$ this is consistent with the molecular formula assuming 19.6 Å^3 per nonhydrogen atom.

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 $1 \leq 2\theta \leq 52°$. Scan widths were calculated from the formula $SW = A + B \tan \theta$ where A is estimated from the mosaicity of the crystal and B compensates for the increase in the width of the peak due to Kα_1 and Kα_2 splitting. The values of A and B were 0.5 and 0.30°, 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 for intensities registering less than ten counts above background on a rapid prescan, and these reflections were rejected automatically by the computer. The intensities of three standard reflections were monitored at intervals of 100 reflections and showed no systematic trends. Raw intensity data were corrected for Lorentz–polarization effects which resulted in a total of 2720 intensities of which 1725 had $F_o^2 \geq 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics using an ignorance factor of 0.03.[9] These latter reflections were used in the final refinement of the structural parameters after correction for absorption (maximum transmission factor = 0.9049, minimum = 0.8138).

Solution and Refinement of the Structure. The coordinates of the two cobalt atoms were determined from a three-dimensional Patterson synthesis. An electron density map phased with these atoms after isotropic refinement yielded 20 of the remaining 25 nonhydrogen atoms. A second map was used to locate the remaining five carbons. After several cycles of isotropic and then anisotropic refinement, another electron density map was calculated. From it the positions of 14 hydrogen atoms including one bridging hydrogen on the open C_2B_3 face were determined. A second map following more refinement, including these hydrogens, served to locate three additional hydrogen atoms, one of which was the second bridging hydrogen on the C_2B_3 face. The remaining 12 hydrogen positions had to be calculated. Refinement was continued with the inclusion of all 29 hydrogens with isotropic temperature factors. The thermal parameters of the cyclopentadienyl hydrogens, however, refined to unreasonable values and consequently were reset to 4.0 and held fixed. During the last few cycles of refinement, the thermal parameters of the remaining hydrogen atoms were maintained constant at their refined values. Final

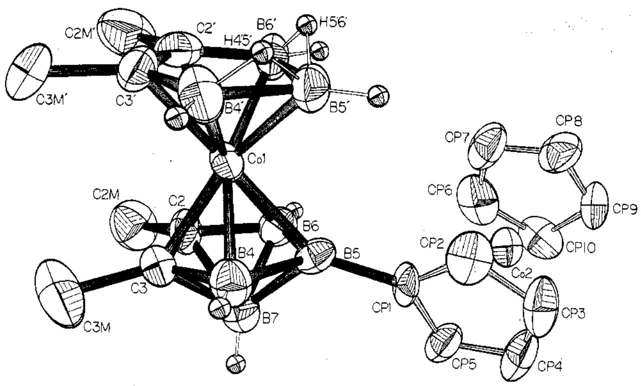

Figure 1. Structure and numbering system of 5-[(η^5-C_5H_5)Co(η^5-C_5H_4)]-[2,3-$(CH_3)_2C_2B_4H_3$]Co[2,3-$(CH_3)_2C_2B_3H_5$]. Nonhydrogen atoms are shown as 50% probability ellipsoids.

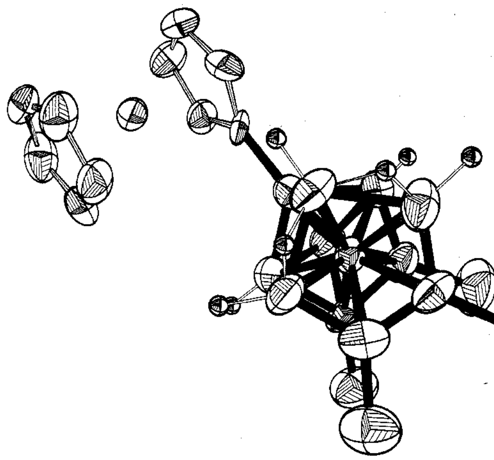

Figure 2. View of the cobaltocenium cobaltacarborane complex from above the open face.

residuals were $R = 0.063$ and $R_w = 0.071$, 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 estimated standard deviation of an observation of unit weight was 2.6. The final data to parameter ratio was 7.1 and the largest shift in the final refinement cycle was 0.03 times its estimated standard deviation. A final difference map was featureless.

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 of $\Delta f'$ and $\Delta f''$. The computing system and programs are described elsewhere.[13]

Results and Discussion

The two new compounds described herein can be conveniently regarded as derivatives of the $[(CH_3)_2C_2B_3H_5]Co^{III}$-$[(CH_3)_2C_2B_4H_4]^-$ anion which forms by loss of the metal-bound proton from the neutral starting material, $[(CH_3)_2C_2B_3H_5]Co^{III}H[(CH_3)_2C_2B_4H_4]$. In a formal electron-bookkeeping sense, the THF derivative is obtained from the anion by replacement of :H^- with :$O(CH_2)_4$ to yield a neutral product, while the substitution of $\cdot H^0$ by $\cdot(C_5H_4)$-$Co^{III}(C_5H_5)^+$ on the anion yields the neutral cobaltocenium species. In both derivatives, the hydrogen atom originally associated with the cobalt atom[1d] has been lost, as shown by the ^{11}B and ^1H NMR data (see Experimental Section). The position of attachment of the THF ligand is probably the apical boron atom B(7), as discussed above. The cobaltocenium derivative, however, involves substitution at B(5), as shown by the X-ray diffraction results which we now describe.

Structure of 5-[(η^5-C_5H_5)Co(η^5-C_5H_4)]-[2,3-$(CH_3)_2C_2B_4H_3$]Co[2,3-$(CH_3)_2C_2B_3H_5$]. The final positional and thermal parameters are given in Table I while Tables II and III contain intramolecular distances and 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 IV and V list selected mean planes and intermolecular contacts, respectively. A view of the molecule with the numbering system is shown in Figure 1 and Figure 2 illustrates the relative orientation of the C_2B_3 rings as viewed from above the open face. A diagram of the unit cell packing is given in Figure 3.

The geometry of the cobaltacarborane portion of the molecule is in agreement with the structure proposed earlier[1d] for the parent species $[2,3-(CH_3)_2C_2B_3H_5]CoH[2,3-(CH_3)_2C_2B_4H_4]$ and consists of a cobalt atom sandwiched between a pyramidal C_2B_4 unit and a planar C_2B_3 ring. The C_2B_3 ring and the basal ring of the C_2B_4 pyramid are not quite parallel, having a dihedral angle of 6.5°; the tilt is such as to move the cage carbon atoms on the two ligands away from each other. The relative orientation of the two rings is very nearly eclipsed, as seen in the view down the Co–B(7) axis in Figure 2.

Comparison with Related Nido Cages. The parameters of the $(CH_3)_2C_2B_3H_5^{2-}$ open ring can be compared with those

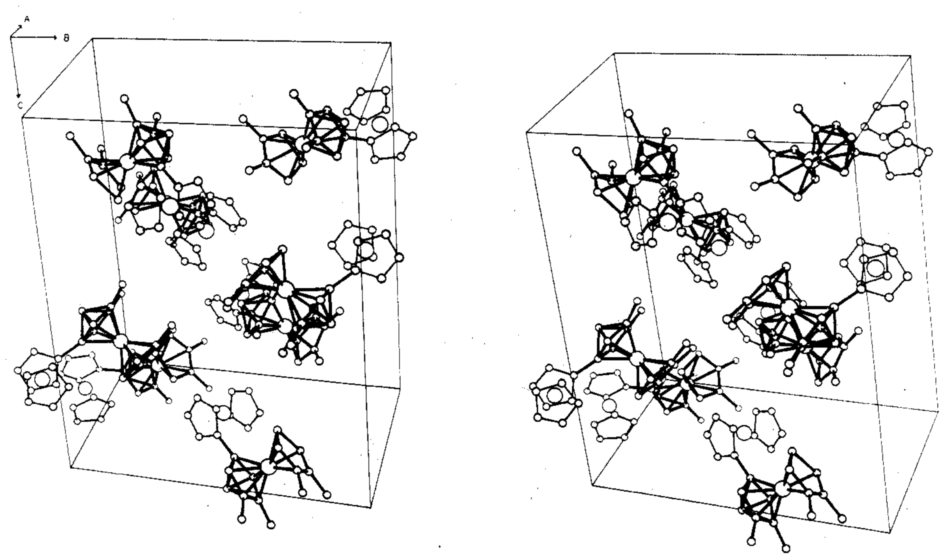

Figure 3. Stereoview of the contents of a unit cell.

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

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	0.1181 (1)	0.29441 (8)	0.13104 (6)	0.00428 (9)	0.00324 (5)	0.00149 (2)	0.0005 (2)	0.0007 (1)	0.00030 (7)
Co(2)	−0.2100 (1)	0.48964 (8)	0.15080 (6)	0.00538 (10)	0.00331 (5)	0.00154 (2)	0.0012 (2)	0.0000 (1)	−0.00019 (8)
C(2)	0.1620 (9)	0.3259 (6)	0.0452 (4)	0.0071 (10)	0.0041 (5)	0.0017 (2)	0.003 (1)	0.0029 (8)	−0.0005 (6)
C(3)	0.2503 (8)	0.3562 (6)	0.0890 (5)	0.0050 (8)	0.0033 (5)	0.0027 (3)	0.000 (1)	0.0014 (9)	−0.0001 (6)
C(2M)	0.1952 (11)	0.2868 (8)	−0.0116 (5)	0.0119 (13)	0.0063 (7)	0.0023 (3)	0.001 (2)	0.0028 (11)	−0.0011 (8)
C(3M)	0.3825 (11)	0.3424 (9)	0.0751 (7)	0.0072 (11)	0.0093 (9)	0.0043 (4)	0.001 (2)	0.0027 (13)	0.0004 (10)
C(2′)	0.1021 (9)	0.1714 (6)	0.1259 (4)	0.0105 (11)	0.0025 (4)	0.0018 (2)	−0.001 (1)	0.0016 (9)	0.0005 (5)
C(3′)	0.1975 (9)	0.1924 (6)	0.1638 (4)	0.0085 (10)	0.0029 (4)	0.0020 (2)	0.004 (1)	0.0016 (9)	0.0004 (5)
C(2M′)	0.1216 (12)	0.1167 (8)	0.0716 (6)	0.0140 (14)	0.0052 (6)	0.0031 (3)	−0.004 (2)	0.0024 (13)	−0.0010 (8)
C(3M′)	0.3240 (11)	0.1603 (7)	0.1522 (6)	0.0102 (12)	0.0038 (5)	0.0049 (4)	0.007 (1)	0.0017 (13)	0.0020 (8)
CP(1)	−0.0277 (7)	0.4796 (6)	0.1508 (4)	0.0025 (7)	0.0033 (4)	0.0022 (2)	0.003 (1)	−0.0008 (7)	−0.0009 (6)
CP(2)	−0.0765 (10)	0.4854 (7)	0.2105 (4)	0.0092 (11)	0.0047 (5)	0.0013 (2)	0.001 (1)	−0.0019 (8)	−0.0012 (6)
CP(3)	−0.1398 (10)	0.5584 (7)	0.2149 (5)	0.0085 (11)	0.0057 (6)	0.0020 (2)	0.004 (1)	0.0003 (9)	−0.0029 (6)
CP(4)	−0.1341 (10)	0.5951 (7)	0.1600 (5)	0.0092 (11)	0.0035 (5)	0.0032 (3)	0.005 (1)	−0.0006 (11)	−0.0016 (7)
CP(5)	−0.0676 (9)	0.5497 (6)	0.1230 (5)	0.0062 (9)	0.0023 (4)	0.0027 (3)	0.002 (1)	−0.0013 (9)	−0.0008 (6)
CP(6)	−0.2849 (9)	0.4252 (8)	0.0841 (5)	0.0062 (10)	0.0070 (6)	0.0029 (3)	−0.003 (1)	−0.0014 (10)	−0.0034 (7)
CP(7)	−0.2826 (9)	0.3808 (6)	0.1371 (5)	0.0073 (10)	0.0036 (5)	0.0039 (3)	0.004 (1)	−0.0019 (11)	−0.0011 (7)
CP(8)	−0.3482 (10)	0.4239 (7)	0.1767 (6)	0.0079 (10)	0.0032 (5)	0.0035 (3)	0.002 (1)	−0.0011 (11)	0.0009 (7)
CP(9)	−0.3919 (8)	0.4907 (6)	0.1532 (6)	0.0033 (8)	0.0040 (5)	0.0050 (4)	0.007 (1)	0.0016 (10)	−0.0004 (8)
CP(10)	−0.3503 (10)	0.4956 (7)	0.0934 (5)	0.0069 (10)	0.0062 (6)	0.0023 (3)	0.000 (1)	−0.0016 (8)	0.0030 (7)
B(4)	0.199 (1)	0.4060 (8)	0.1374 (5)	0.006 (1)	0.0042 (6)	0.0021 (3)	0.000 (1)	−0.001 (1)	−0.0006 (7)
B(5)	0.056 (1)	0.4131 (7)	0.1229 (5)	0.007 (1)	0.0023 (5)	0.0017 (3)	0.001 (1)	−0.001 (1)	0.0005 (6)
B(6)	0.038 (1)	0.3611 (7)	0.0618 (5)	0.007 (1)	0.0033 (5)	0.0019 (3)	0.001 (1)	−0.001 (1)	0.0003 (7)
B(7)	0.154 (1)	0.4265 (8)	0.0639 (6)	0.007 (1)	0.0042 (6)	0.0021 (3)	0.000 (1)	0.001 (1)	−0.0005 (8)
B(4′)	0.172 (1)	0.2509 (9)	0.2125 (6)	0.007 (1)	0.0063 (7)	0.0017 (3)	0.003 (2)	0.001 (1)	0.0021 (7)
B(5′)	0.017 (1)	0.2757 (8)	0.2039 (6)	0.009 (1)	0.0040 (6)	0.0022 (3)	0.003 (2)	0.003 (1)	0.0005 (7)
B(6′)	−0.014 (1)	0.2129 (7)	0.1390 (6)	0.006 (1)	0.0034 (5)	0.0026 (3)	0.002 (1)	0.001 (1)	−0.0010 (8)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
HB(4)	0.246 (7)	0.426 (5)	0.163 (3)	1 (2)	H2M′(2)	0.126 (12)	0.072 (8)	0.085 (6)	8 (4)
HB(6)	−0.023 (10)	0.347 (7)	0.034 (5)	5 (3)	H2M′(3)	0.187 (13)	0.147 (9)	0.057 (6)	9 (4)
HB(7)	0.182 (10)	0.473 (7)	0.040 (5)	5 (3)	H3M′(1)	0.330 (8)	0.110 (6)	0.167 (4)	3 (2)
HB(4′)	0.242 (8)	0.275 (5)	0.248 (4)	3 (2)	H3M′(2)	0.353 (13)	0.215 (8)	0.160 (6)	9 (4)
HB(5′)	−0.043 (9)	0.313 (6)	0.231 (4)	4 (3)	H3M′(3)	0.341 (12)	0.176 (8)	0.107 (6)	9 (4)
HB(6′)	−0.108 (9)	0.216 (5)	0.121 (4)	3 (2)	HCP(2)	−0.070 (7)	0.459 (5)	0.239 (4)	4
H(4′5′)	0.098 (11)	0.245 (7)	0.245 (6)	8 (4)	HCP(3)	−0.181 (9)	0.569 (6)	0.243 (5)	4
H(5′6′)	−0.038 (9)	0.212 (6)	0.188 (4)	4 (3)	HCP(4)	−0.158 (7)	0.634 (5)	0.155 (3)	4
H2M(1)	0.233 (11)	0.327 (7)	−0.027 (5)	6 (3)	HCP(5)	−0.064 (10)	0.559 (7)	0.086 (5)	4
H2M(2)	0.153 (8)	0.273 (5)	−0.026 (4)	3 (2)	HCP(6)	−0.251 (9)	0.405 (6)	0.059 (4)	4
H2M(3)	0.252 (14)	0.234 (10)	−0.009 (6)	10 (4)	HCP(7)	−0.249 (6)	0.344 (4)	0.136 (3)	4
H3M(1)	0.409 (8)	0.301 (6)	0.090 (4)	3 (2)	HCP(8)	−0.343 (11)	0.403 (7)	0.199 (5)	4
H3M(2)	0.409 (14)	0.375 (10)	0.094 (7)	12 (5)	HCP(9)	−0.426 (6)	0.533 (4)	0.161 (3)	4
H3M(3)	0.393 (13)	0.335 (8)	0.037 (6)	9 (4)	HCP(10)	−0.364 (0)	0.537 (0)	0.066 (0)	4
H2M′(1)	0.069 (9)	0.138 (6)	0.047 (4)	4 (2)					

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

of one other metallocarborane and two carboranes, viz., $(CO)_3FeC_2B_3H_7$,[5] 2,3-$C_2B_4H_8$,[14] and the *C,C′*-dimethyl derivative[14] of the latter species (the $C_2B_4H_8$ system can be regarded for our purposes as an η^5 complex of $C_2B_3H_7^{2-}$ with a BH^{2+} group). As expected, the B–B, B–C, and C–C bond lengths in compound I are very similar (within 3 esd's) to those of $(CO)_3FeC_2B_3H_7$. The short carbon–carbon distance of 1.418 (9) Å, for example, is matched by the 1.410 (4) Å value in the iron complex; short C–C bonds are typical features of pyramidal and bipyramidal carboranes containing equatorial carbon atoms, as discussed elsewhere.[1c,2b,15] In 2,3-$C_2B_4H_8$ and 2,3-$(CH_3)_2C_2B_4H_6$ the framework C–C bond distances[14] are similar to the metal complexes (1.418 (6) and 1.432 (6) Å, respectively), but the basal boron–boron distances are shorter, having a range of 1.778 (6) – 1.801 (6) Å; these values can be compared with lengths of 1.852 (3) and 1.82 (1) Å in $(CO)_3FeC_2B_3H_7$ and I.

The B–H–B bridging groups in the cobalt complex require comment in that they are highly asymmetric, with both hydrogens much closer to the outer boron atoms [B(4′) and B(6′)] than to the middle boron, B(5′). Since the difference amounts to 0.17 Å for one bridge hydrogen atom and 0.28 Å for the other, with esd's of 0.01 Å for all of the bond lengths involved, the asymmetry can be assigned a high level of significance. In contrast, the B–H–B bridges in $(CO)_3Fe-C_2B_3H_7$ and the two carboranes are all symmetrical or nearly so. In $(CH_3)_2C_2B_4H_6$ the bridging hydrogens are each 0.10 Å closer to the outer borons than to the middle boron,[14] but the effect may not be real inasmuch as the esd's are 0.03 Å for each distance.

Comparison with Related Closo Cages. Crystallographic studies have been reported for at least nine other 7-vertex metalloboron cage compounds, all of them pentagonal-bipyramidal species (a listing of selected structural parameters in these molecules has been presented earlier[2b]). The closo portion of I [Co(1)–C(2)–C(3)–B(4)–B(5)–B(6)–B(7)] is structurally similar to its close relatives 1,2,3-$(\eta^5-C_5H_5)Co-(CH_3)_2C_2B_4H_4$,[3] 2-$CH_3$-1,7,2,3-$(\eta^5-C_5H_5)_2Co_2C_2B_3H_4$,[2c] and μ(2,3)-C_3H_4-1,7,2,3-$(\eta^5-C_5H_5)_2Co_2C_2B_3H_3$.[2b] However, the equatorial carbon–carbon distance [C(2)–C(3)] of 1.489 (9) Å in I is longer than any other bonded C–C interaction in a 7-vertex species except for the propenylene-bridged triple-decked sandwich μ(2,3)-C_3H_4-1,7,2,3-$(\eta^5-C_5H_5)_2Co_2C_2B_3H_3$,[2b] in which the corresponding distance is statistically identical (1.485 (4) Å). In compound I, this long C–C distance in the closo portion contrasts sharply with the short C–C length in the nido section of the molecule (vide supra) which is nearly 5% smaller; once again, we can invoke the qualitative argument[15] that the closo-cage carbon atoms C(2) and C(3) interact with more neighboring atoms than the open-ring carbons C(2′) and C(3′), resulting in a lower C–C bond order in the former case. Note, however, that even the relatively

Table II. Interatomic Distances (Å)

Co(1)–Co(2)	4.973 (1)	C(3')–B(4')	1.49 (1)
Co(1)–C(2)	2.050 (6)	B(4')–B(5')	1.82 (1)
Co(1)–C(3)	2.048 (7)	B(5')–B(6')	1.82 (1)
Co(1)–B(4)	2.082 (8)	B(4')–HB(4')	1.19 (1)
Co(1)–B(5)	2.111 (7)	B(5')–HB(5')	1.09 (1)
Co(1)–B(6)	2.113 (8)	B(6')–HB(6')	1.14 (1)
Co(1)–C(2')	2.065 (7)	B(4')–HB(4'5')	1.12 (1)
Co(1)–C(3')	2.061 (6)	B(5')–H(4'5')	1.40 (1)
Co(1)–B(4')	2.052 (8)	B(5')–H(5'6')	1.29 (1)
Co(1)–B(5')	2.017 (8)	B(6')–H(5'6')	1.12 (1)
Co(1)–B(6')	2.032 (8)	Co(2)–CP(1)	2.083 (6)
C(2)–C(3)	1.489 (9)	Co(2)–CP(2)	2.025 (6)
C(2)–C(2M)	1.476 (9)	Co(2)–CP(3)	2.004 (7)
C(2)–B(6)	1.57 (1)	Co(2)–CP(4)	1.975 (8)
C(2)–B(7)	1.73 (1)	Co(2)–CP(5)	2.007 (7)
C(3)–C(3M)	1.548 (9)	Co(2)–CP(6)	2.021 (7)
C(3)–B(4)	1.48 (1)	Co(2)–CP(7)	2.016 (8)
C(3)–B(7)	1.70 (1)	Co(2)–CP(8)	1.993 (8)
B(4)–B(5)	1.66 (1)	Co(2)–CP(9)	2.054 (6)
B(4)–B(7)	1.75 (1)	Co(2)–CP(10)	2.039 (7)
B(5)–CP(1)	1.589 (9)	CP(1)–CP(2)	1.446 (9)
B(5)–B(6)	1.63 (1)	CP(2)–CP(3)	1.42 (1)
B(5)–B(7)	1.74 (1)	CP(3)–CP(4)	1.37 (1)
B(6)–B(7)	1.72 (1)	CP(4)–CP(5)	1.350 (9)
B(4)–HB(4)	0.84 (1)	CP(5)–CP(1)	1.402 (8)
B(6)–HB(6)	0.97 (1)	CP(6)–CP(7)	1.40 (1)
B(7)–HB(7)	1.00 (1)	CP(7)–CP(8)	1.36 (1)
C(2')–C(3')	1.418 (9)	CP(8)–CP(9)	1.329 (9)
C(2')–C(2M')	1.54 (1)	CP(9)–CP(10)	1.42 (1)
C(2')–B(6')	1.52 (1)	CP(10)–CP(6)	1.41 (1)
C(3')–C(3M')	1.553 (9)		

long C–C distance in I is still not nearly as large as typical carbon–carbon interactions in large cages (e.g., 1.655 Å in derivatives of 1,2-$C_2B_{10}H_{12}$),[16] reflecting the still higher coordination (6) of these carbon atoms.

It is notable that the cobalt atom Co(1) is much closer to the open C_2B_3 ligand than it is to the C_2B_4 ligand; the vector distances from the metal to the planes C(2)–C(3)–B(4)–B(5)–B(6) and C(2')–C(3')–B(4')–B(5')–B(6') are respectively 1.599 and 1.510 Å. The first value appears normal for such structures, being slightly longer than the metal-equatorial ring vector in 1,2,3-(η^5-C_5H_5)Co$(CH_3)_2C_2B_4H_4$[3] (1.566 Å), 2-CH_3-1,7,2,3-(η^5-C_5H_5)$_2Co_2C_2B_3H_4$ (1.570 Å),[2c] and μ(2,3)-C_3H_4-1,7,2,3-(η^5-C_5H_5)$_2Co_2C_2B_3H_3$ (1.568 Å).[2b] The much shorter cobalt–C_2B_3 ring distance is harder to evaluate since the only other complex of $C_2B_3H_7^{2-}$ for which structural parameters are available is $(CO)_3FeC_2B_3H_7$, in which the Fe-ring vector is 1.617 Å.[5] The fact that this latter distance is 0.1 Å longer than the corresponding value in the cobalt species no doubt reflects the difference in oxidation states of the metals, i.e., Fe^{2+} vs. Co^{3+}.

The two cobalt–ring vector distances in the title compound indicate that the metal is more firmly bound to the C_2B_3 than to the C_2B_4 ligand, probably due to the higher coordination of the equatorial atoms in the latter. In the closo cage, the equatorial ring is face-bonded simultaneously to Co(1) and B(7), in contrast to the open C_2B_3 ring which is face-bonded on only one side; thus the electron density available for ligand–metal interaction is greater in the C_2B_3 than in the C_2B_4 group. In light of these observations, a quantitative molecular orbital treatment of the parent $(C_2B_3H_7)CoH(C_2B_4H_6)$ system would be of interest.

Comparison with 1-[(η^5-C_5H_5)Co(η^5-C_5H_4)]-1,2-$C_2B_9H_{11}$. One previous example of a structurally characterized metallocene-substituted boron cage species has been reported.[17] This compound, obtained as a side product in the reaction[18] of $C_2B_{10}H_{12}^{2-}$ ion with $Na^+C_5H_5^-$ and $CoCl_2$, has been shown via an X-ray diffraction study[17] to consist of an 11-vertex icosahedral-fragment $C_2B_9H_{11}^-$ cage with a cobaltocenium group attached to one of the carbon atoms on the open face. The carborane portion of this molecule is in no way similar to the present structure (I), but the cobaltocenium ligands do bear comparison. Although the cyclopentadienyl rings in I are less well defined than are those in the cobaltocenium carborane,[17] the following observations will be noted.

Table III. Selected Bond Angles (deg)

C(2)–Co(1)–C(3)	42.6 (3)	C(3)–B(7)–B(4)	50.9 (4)
C(3)–Co(1)–B(4)	42.1 (3)	B(4)–B(7)–B(5)	56.7 (4)
B(4)–Co(1)–B(5)	46.6 (3)	B(5)–B(7)–B(6)	56.3 (4)
B(5)–Co(1)–B(6)	45.4 (3)	B(6)–B(7)–C(2)	54.2 (4)
B(6)–Co(1)–C(2)	44.3 (3)	Co(1)–C(2')–C(3')	69.8 (4)
C(2')–Co(1)–C(3')	40.2 (3)	Co(1)–C(2')–C(2M')	128.6 (5)
C(3')–Co(1)–B(4')	42.5 (3)	C(3')–C(2')–C(2M')	120.6 (7)
B(4')–Co(1)–B(5')	53.1 (3)	B(6')–C(2')–C(2M')	123.3 (7)
B(5')–Co(1)–B(6')	53.5 (3)	Co(1)–C(2')–B(6')	67.1 (4)
B(6')–Co(1)–C(2')	43.4 (3)	C(3')–C(2')–B(6')	115.8 (6)
Co(1)–C(2)–C(3)	68.6 (4)	Co(1)–C(3')–C(3M')	129.0 (5)
Co(1)–C(2)–B(6)	70.0 (4)	C(2')–C(3')–C(3M')	121.3 (7)
C(3)–C(2)–B(7)	62.9 (5)	B(4')–C(3')–C(3M')	121.9 (7)
B(6)–C(2)–B(7)	62.3 (5)	Co(1)–C(3')–C(2')	70.0 (4)
Co(1)–C(2)–C(2M)	138.8 (6)	Co(1)–C(3')–B(4')	68.4 (4)
C(3)–C(2)–C(2M)	123.0 (6)	C(2')–C(3')–B(4')	116.6 (6)
B(6)–C(2)–C(2M)	126.7 (6)	Co(1)–B(4')–C(3')	69.1 (4)
B(7)–C(2)–C(2M)	130.5 (6)	Co(1)–B(4')–B(5')	62.5 (4)
Co(1)–C(3)–C(3M)	136.6 (6)	C(3')–B(4')–B(5')	105.2 (6)
C(2)–C(3)–C(3M)	117.9 (6)	B(5')–B(4')–H(4'5')	50.6 (4)
B(4)–C(3)–C(3M)	127.6 (7)	Co(1)–B(5')–B(4')	64.4 (4)
B(7)–C(3)–C(3M)	131.1 (6)	Co(1)–B(5')–B(6')	63.7 (4)
Co(1)–C(3)–C(2)	68.8 (4)	B(4')–B(5')–B(6')	97.9 (6)
Co(1)–C(3)–B(4)	70.2 (4)	B(4')–B(5')–H(4'5')	38.0 (3)
C(2)–C(3)–B(7)	65.6 (5)	B(6')–B(5')–H(5'6')	37.5 (4)
B(4)–C(3)–B(7)	66.5 (5)	Co(1)–B(6')–B(5')	62.8 (4)
Co(1)–B(4)–C(3)	67.7 (4)	Co(1)–B(6')–C(2')	69.4 (4)
Co(1)–B(4)–B(5)	67.7 (4)	C(2')–B(6')–B(5')	104.5 (6)
C(3)–B(4)–B(7)	62.6 (5)	B(5')–B(6')–H(5'6')	44.3 (4)
B(5)–B(4)–B(7)	61.4 (5)	B(4')–H(4'5')–B(5')	91.4 (5)
Co(1)–B(5)–B(4)	65.8 (4)	B(5')–H(5'6')–B(6')	98.2 (5)
Co(1)–B(5)–B(6)	67.4 (4)	B(5)–CP(1)–CP(2)	129.6 (6)
B(4)–B(5)–B(7)	62.0 (5)	B(5)–CP(1)–CP(5)	127.1 (6)
Co(1)–B(5)–CP(1)	145.3 (5)	CP(2)–CP(1)–CP(5)	103.2 (6)
B(4)–B(5)–CP(1)	123.9 (6)	CP(1)–CP(2)–CP(3)	108.4 (6)
B(6)–B(5)–CP(1)	128.7 (6)	CP(2)–CP(3)–CP(4)	107.4 (6)
B(7)–B(5)–CP(1)	126.2 (6)	CP(3)–CP(4)–CP(5)	108.8 (7)
B(6)–B(5)–B(7)	61.1 (5)	CP(4)–CP(5)–CP(1)	112.2 (7)
Co(1)–B(6)–B(5)	67.2 (4)	CP(7)–CP(6)–CP(10)	109.3 (7)
Co(1)–B(6)–C(2)	65.7 (4)	CP(6)–CP(7)–CP(8)	105.0 (7)
B(5)–B(6)–B(7)	62.6 (5)	CP(7)–CP(8)–CP(9)	113.0 (8)
C(2)–B(6)–B(7)	63.5 (5)	CP(8)–CP(9)–CP(10)	107.3 (7)
C(2)–B(7)–C(3)	51.5 (4)	CP(9)–CP(10)–CP(6)	105.4 (7)

(1) In both structures, the cyclopentadienyl carbon atom linked directly to the boron cage [CP(1)] is further from the cobaltocenium cobalt atom than are the other carbon atoms in the same C_5H_4 ring. In our structure the CP(1)–Co(2) distance is 2.083 (6) Å while the Co—CP(2)···Co—CP(5) distances range from 1.975 (8) to 2.025 (6) Å; in the $C_2B_9H_{11}$–cobaltocenium complex the CP(1)–Co bond length is 2.0666 (12) Å while the range for the other metal–carbon values is 2.0223 (14)–2.0369 (13) Å. Thus it can reasonably be assumed that the effect in both cases is a real one induced by the carborane or metallocarborane substituent at CP(1).

(2) In both structures the cyclopentadienyl rings are staggered and parallel within 1°.

(3) The angle CP(5)–CP(1)–CP(2) in I (103.2 (5)°) is smaller (by 2° or more) than any other internal angle in either ring. Although the range of values for these angles in compound I is large due to the imprecision in the locations of the cyclopentadienyl carbons arising from thermal motions, it is significant that a similar distortion of the angle at CP(1) has been noted in the cobaltocenium carborane structure and is ascribed[17] to the carborane substituent attached to CP(1); it appears that a comparable effect is present in I.

The remaining parameters of the cobaltocenium group are similar to those given for the cobaltocenium carborane and for the structurally characterized cobaltocenium salts.[19]

Table IV

Selected Intramolecular Planes

Atom	Dev, Å	Atom	Dev, Å
Plane 1: C(2), C(3), B(4), B(5), B(6)			
$0.1694x + 0.8134y - 0.5565z = 4.1968$			
C(2)	−0.020	Co(1)[a]	−1.599
C(3)	0.017	C(2M)[a]	0.219
B(4)	−0.007	C(3M)[a]	0.257
B(5)	−0.005	B(7)[a]	1.100
B(6)	0.014		
Plane 2: C(2′), C(3′), B(4′), B(5′), B(6′)			
$0.2470x + 0.7513y - 0.6120z = 0.7246$			
C(2′)	−0.008	B(6′)	0.008
C(3′)	0.004	Co(1)[a]	1.510
B(4′)	0.001	C(2M′)[a]	0.101
B(5′)	−0.004	C(3M′)[a]	0.114
Plane 3: CP(1), CP(2), CP(3), CP(4), CP(5)			
$0.8257x + 0.4780y + 0.2995z = 4.5751$			
CP(1)	−0.003	CP(4)	0.010
CP(2)	0.009	CP(5)	−0.004
CP(3)	−0.011	Co(2)	1.631
Plane 4: CP(6), CP(7), CP(8), CP(9), CP(10)			
$0.8208x + 0.4867y + 0.2989z = 1.3775$			
CP(6)	0.011	CP(9)	0.013
CP(7)	−0.003	CP(10)	−0.014
CP(8)	−0.007	Co(2)[a]	−1.648

Angles between the Planes

Planes	Angle, deg	Planes	Angle, deg
1,2	6.5	2,3	112.3
1,3	111.2	2,4	112.7
1,4	111.6	3,4	0.58

[a] Not included in the calculated plane.

Table V. Intermolecular Contacts (≤3.8 Å) for Nonhydrogen Atoms

Atoms	Dist, Å	Relationship
C(3M′)–CP(5)	3.386	$^1/_2 - x, -^1/_2 + y, z$
C(3′)–CP(3)	3.575	$-x, -^1/_2 + y, ^1/_2 - z$
B(4′)–CP(3)	3.620	$-x, -^1/_2 + y, ^1/_2 - z$
C(3M′)–CP(4)	3.685	$^1/_2 - x, -^1/_2 + y, z$
CP(2)–CP(9)	3.696	$^1/_2 + x, y, ^1/_2 - z$
C(2M′)–CP(6)	3.702	$^1/_2 + x, ^1/_2 - y, -z$
C(2M′)–CP(10)	3.713	$-^1/_2 - x, -^1/_2 + y, z$
CP(2)–CP(8)	3.755	$^1/_2 + x, y, ^1/_2 - z$

Summary

The cobaltocenium cobaltacarborane (I) is the first structurally characterized example of a closo metallocarborane in which a cage metal atom is capped by a cyclocarborane ring ligand. Although other species containing the $C_2B_3H_7^{2-}$ or $(CH_3)_2C_2B_3H_5^{2-}$ ligands have been prepared, structural details are known only for $(CO)_3FeC_2B_3H_7$,[5] which of course contains no carborane ligand other than the $C_2B_3H_7^{2-}$ group itself.

There is a simple relationship between $(CO)_3FeC_2B_3H_7$ and I: disregarding for simplicity the methyl and cobaltocenium substituents, one can view the pyramidal $C_2B_4H_6^{2-}$ ligand as a six-electron donor analogous to $C_5H_5^-$ or to three CO groups; thus, $(CO)_3Fe^{II}C_2B_3H_7$ is an analogue of $(C_2B_4H_6)Fe^{II}$-$(C_2B_3H_7)^{2-}$, which in turn is equivalent to $(C_2B_4H_6)Co^{III}$-$(C_2B_3H_7)^-$, the parent species of compound I. By similar reasoning, the carborane portion of I is also analogous to $(\eta^5\text{-}C_5H_5)Co^{III}(C_2B_4H_6)$, $[(C_2B_4H_6)_2Co^{III}]^-$, and $[(\eta^5\text{-}C_5H_5)_2Co^{III}]^+$ (cobaltocenium ion). The last example, of course, is equivalent to saying that the entire zwitterionic system in I is an analogue of dicobaltocenium ion, $[(\eta^5\text{-}C_5H_5)Co^{III}(\eta^5\text{-}C_5H_4)]_2^{2+}$.

Finally, if one invokes the electronic equivalence[20] of a BH^{2+} unit with $(CO)_3Fe^{2+}$ and $[(C_2B_4H_6)Co^{III}$–$(C_5H_5)Co(C_5H_4)]^{2+}$, i.e., formally substitutes BH^{2+} for these groups in $(CO)_3$-$FeC_2B_3H_7$ and I, both of the latter two compounds are seen to be analogues of *nido*-2,3-$C_2B_4H_8$ (indeed, specific details of these structures have been compared earlier in the paper). Thus, I occupies a rather central position in a family of structurally and electronically related metallocenes, metallocarboranes, and carboranes for which relatively few crystal structures are currently available.

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Registry No. I, 66256-04-0; II, 66213-31-8; $[2,3\text{-}(CH_3)_2C_2B_4H_4]CoH[2,3\text{-}(CH_3)_2C_2B_3H_5]$, 60587-07-7; $(\eta^5\text{-}C_5H_5)Co(CO)_2$, 12078-23-8.

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

References and Notes

(1) (a) The earlier work has been reviewed: R. N. Grimes, *Pure Appl. Chem.*, **39**, 455 (1974); (b) R. N. Grimes, D. C. Beer, L. G. Sneddon, V. R. Miller, and R. Weiss, *Inorg. Chem.*, **13**, 1138 (1974); (c) R. Weiss and R. N. Grimes, *J. Organomet. Chem.*, **113**, 29 (1976); (d) W. M. Maxwell, V. R. Miller, and R. N. Grimes, *J. Am. Chem. Soc.*, **98**, 4818 (1976); (e) *Inorg. Chem.*, **15**, 1343 (1976); (f) K-S. Wong and R. N. Grimes, *ibid.*, **16**, 2053 (1977); (g) W. M. Maxwell, K-S. Wong, and R. N. Grimes, *ibid.*, **16**, 3094 (1977); (h) R. Weiss, J. R. Bowser, and R. N. Grimes, *ibid.*, in press; (i) R. N. Grimes, *J. Am. Chem. Soc.*, **93**, 261 (1971).

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(7) We question, however, the conclusion in ref 6 that the complex is held together primarily by ionic attraction between the formal $Fe(CO)_3^{2+}$ and $C_2B_3H_7^{2-}$ moieties; such a model is difficult to reconcile with the high stability of the molecule and the Fe–C and Fe–B bond distances, which are typical of covalent interactions. In addition, acceptance of an ionic-bonding description of $(CO)_3FeC_2B_3H_7$ implies that either metallocarboranes in general should be viewed as ionic or that $(CO)_3FeC_2B_3H_7$ should be regarded as a special case somehow distinct from other metallocarboranes. Neither of these conclusions seems justified when viewed in the broad context of metallocarborane chemistry.[8]

(8) This area has recently been comprehensively reviewed: R. N. Grimes in "Organometallic Reactions and Syntheses", Vol. 6, E. I. Becker and M. Tsutsui, Ed., Plenum Press, New York, N.Y., 1977, Chapter 2, pp 63–221.

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