reported herein, four-coordinate gallium is present with either five- or six-coordinate iron.

It can be noted that for the usual nitrogen base systems, where monomeric species are formed, gallium tends to behave more like zinc (which favors $B_3ZnFe(CO)_4$ monomers)[1j] than germanium (which favors $R_2GeFe(CO)_4$ dimers).[2b,d] This is also the first case where the strength of the Lewis base has determined whether the complex was associated or not (chelation has been shown to be important in this regard also).[1h–j] From this observation, it would appear rather crudely that the favorability of iron in forming a second bond to another gallium atom is intermediate between the favorability of oxygen and nitrogen atom donors bonding to gallium. It is thus possible that, in other systems where nitrogen donor ligands favor monomeric complexes (notably the $B_nZnFe(CO)_4$ series), oxygen donor ligands might well favor oligomeric complexes (e.g., $B_2ZnFe(CO)_4$).

The reaction of ethylgallium diiodide with $Na_2Fe(CO)_4$ in toluene yielded a product which was nearly inseparable from some dark impurity. Less than 0.1 g of purified product could be isolated (see the Experimental Section), and as a result, only its infrared spectrum could be used for characterization. Nevertheless, this spectrum seems to unambiguously identify the material as $[(C_2H_5)GaFe(CO)_4]_n$. As this compound contains one less electron-donating base than $[(THF)(C_2H_5)GaFe(CO)_4]_2$, there should be less bending of the axial carbonyls, and hence the compound is expected to be dimeric. The lower electronic population of the CO π^* orbitals is readily seen by a comparison of the infrared spectrum of this compound with that of the THF adduct. Essentially identical patterns are observed, with the C–O stretching modes of the base-free compound coming at slightly higher frequency. In addition, bands attributable to Fe–C modes follow the expected pattern,[14] with the base-free complex absorbing at 610 cm^{-1} while the THF adduct absorbs at 613 cm^{-1}.

The present study demonstrates that stable $B_nRGaFe(CO)_4$ species may readily be prepared, in which the gallium atom tends to behave more like zinc in the fairly ionic $B_nZnFe(CO)_4$ complexes (n = 0–3) than like germanium in the considerably more covalent $B_nR_2GeFe(CO)_4$ complexes (n = 0, 1). Preliminary studies have also shown that analogous indium compounds may also be prepared and that their properties are intermediate between those of isoelectronic cadmium and tin species. These and related studies and their implications will be reported upon completion in the near future.[15]

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Registry No. $Na_2Fe(CO)_4$, 14878-31-0; $Fe(CO)_5$, 13463-40-6; $[(C_2H_5)GaI_2]_2$, 57286-39-2; $(THF)(C_2H_5)GaFe(CO)_4$, 73513-07-2; $(TMEDA)(C_2H_5)GaFe(CO)_4$, 73513-06-1; $(bpy)(C_2H_5)GaFe(CO)_4$, 73513-05-0; $(py)_2(C_2H_5)GaFe(CO)_4$, 73513-04-9; $(C_2H_5)GaFe(CO)_4$, 73513-03-8.

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[14] (14) For comparison,[10] the Ga–C stretching mode for $[(C_2H_5)GaI_2]_2$ comes at 546 cm^{-1}. The bands at 610 and 613 cm^{-1} are therefore consistently assigned to Fe–C stretching modes and compare well with those of other related compounds.[1h–j]

[15] (15) J. Vanderhooft, D. R. Wilson, T. H. Cymbaluk, and R. D. Ernst, experiments in progress.

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Small Metallacarboranes with Metal–Metal Bonds. Crystal and Molecular Structures of $2,3\text{-}(CH_3)_2\text{-}1,2,4,5\text{-}(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_3$ and $2,3\text{-}(CH_3)_2\text{-}1,2,4,5\text{-}(\eta^5\text{-}C_5H_5)_2CoFe(H)C_2B_3H_3$

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The structures of the title compounds were determined by single-crystal X-ray diffraction and in both cases were found to contain 7-vertex pentagonal-bipyramidal $M_2C_2B_3$ cages (M = Fe or Co) with cobalt in an equatorial vertex and cobalt or iron in an apical vertex. In both cases, the framework carbon atoms occupy adjacent positions in the equator. Both structures are in agreement with those proposed earlier from NMR data, except that the presumed face-bridging proton in the iron–cobalt cluster was not directly observed. The parent $1,2,4,5\text{-}(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ isomer is an isolable intermediate in the previously studied thermal rearrangement of the triple-decked complex $1,7,2,3\text{-}(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ to the 1,7,2,4 isomer via the 1,2,3,5 and 1,2,4,5 species. The present structures provide the first structural confirmation of equatorial metal atoms in pentagonal-bipyramidal metallaboron cages and are the smallest metallacarboranes containing metal–metal bonds to be crystallographically established. Crystal data for $2,3\text{-}(CH_3)_2\text{-}1,2,4,5\text{-}(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_3$: mol wt 338, space group $P2_1/c$, $Z = 4$; $a = 9.240$ (3), $b = 12.314$ (7), $c = 13.933$ (4) Å; $\beta = 108.94$ (4)°; $V = 1499$ Å^3; $R = 0.057$ for 1230 independent reflections having $F_o^2 > 3\sigma(F_o^2)$. Crystal data for $2,3\text{-}(CH_3)_2\text{-}1,2,4,5\text{-}(\eta^5\text{-}C_5H_5)_2CoFe(H)C_2B_3H_3$: mol wt 338, space group $P2_1/c$, $Z = 8$ (two molecules per asymmetric unit); $a = 9.385$ (3), $b = 22.431$ (7), $c = 14.133$ (4) Å; $\beta = 90.86$ (4)°; $V = 2975$ Å^3; $R = 0.056$ for 3548 independent reflections for which $F_o^2 > 3\sigma(F_o^2)$.

Introduction

Metallacarboranes in which metal atoms occupy adjacent vertices in the polyhedral framework are of interest for several reasons. The understanding of metal–metal interactions in such systems presents a challenging theoretical and experimental problem, which is, of course, related to the general question of bonding in metal clusters. In metallacarboranes and metallaboranes having two or more metal atoms, the relationship between metal–metal interactions and thermodynamic stability is often complex;[1] thus, in certain systems such as the 9-vertex $Co_2C_2B_5$ and 7-vertex $Co_2C_2B_3$ closo cages, studies in this laboratory have found *reversible* thermally induced metal atom migrations between adjacent and nonadjacent vertices.[1c,e] Moreover, electrochemical studies of

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several isomers of the $(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ and $(\eta^5\text{-}C_5H_5)CoC_2B_4H_6$ systems indicate a high degree of electron delocalization in which the metal atoms participate.[2] As a consequence of this delocalization, and also of the fact that the cage matrix imposes severe constraints on orbital overlap between metals, there is no simple correlation between metal–metal distance and bond order.

Metal–metal bonding in boron clusters also affords intriguing synthetic possibilities, since coordination of organic substrates to two or more contiguous metal atoms in metal clusters has led to the development of active homogeneous catalysts.[3]

Numerous metallaboranes and metallacarboranes having adjacent transition metals in the cage have been isolated and characterized, and about a dozen of these have been structurally established by X-ray crystallography.[4] In the present article we describe X-ray studies on two 7-vertex *closo*-dimetallacarboranes, $1,2,4,5\text{-}(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$ and $1,2,4,5\text{-}(\eta^5\text{-}C_5H_5)_2CoFe(H)(CH_3)_2C_2B_3H_3$, which form an isoelectronic and isostructural (but not isomorphous) pair. These species were obtained from different reactions (vide infra) but are reported together here because of their close structural relationship. They are the smallest known metallacarboranes containing adjacent metal centers (several smaller metallaboranes[5a,6] having this feature are known, however). Although the structures of these compounds were previously assigned from NMR data,[7,8] the present study was undertaken in order to confirm the proposed geometries in these prototype species, to establish the metal–metal distances, and to attempt to define more precisely the metal-bound hydrogen atom in $(\eta^5\text{-}C_5H_5)_2CoFe(H)(CH_3)_2C_2B_3H_3$.

Experimental Section

Dark green plates of $1,2,4,5\text{-}(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$, obtained from the reaction of $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2CoH$ with $(\eta^5\text{-}C_5H_5)Co(CO)_2$ as described elsewhere,[7] were grown from cold hexane solution by slow evaporation. The crystal selected for data collection was mounted in an arbitrary orientation on a glass fiber. Crystal data: $Co_2C_{14}B_3H_{19}$, mol wt 338; space group $P2_1/c$; $Z = 4$; $a = 9.240$ (3), $b = 12.314$ (7), $c = 13.933$ (4) Å; $\beta = 108.94$ (4)°; $V = 1499$ Å^3; $\mu(\text{Mo K}\alpha) = 22.8$ cm^{-1}; $\rho_c = 1.50$ g cm^{-3}; crystal dimensions (distances in mm from centroid) (100) 0.17, $(\bar{1}00)$ 0.17, (010) 0.05, $(0\bar{1}0)$ 0.05, (001) 0.09, $(00\bar{1})$ 0.09, $(10\bar{2})$ 0.07, $(\bar{1}02)$ 0.07. The Enraf-Nonius program SEARCH was used to obtain 25 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 these same 25 accurately centered reflections. The mosaicity of the crystal was examined by the ω-scan technique and found satisfactory. Systematic absences for $k = 2n + 1$ on $0k0$ and $l = 2n + 1$ on $h0l$ uniquely established the space group as $P2_1/c$ (No. 14).

Dark green plates of $1,2,4,5\text{-}(\eta^5\text{-}C_5H_5)_2CoFe(H)(CH_3)_2C_2B_3H_3$, isolated from the reaction of $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2FeH_2$ with $CoCl_2$ and $C_5H_5^-$ in ethanolic KOH as reported in an earlier publication,[8] were grown from cold toluene solution by slow evaporation. A crystal was chosen and mounted on a glass fiber in arbitrary orientation. Crystal data: $FeCoC_{14}B_3H_{20}$ (two molecules per asymmetric unit), mol wt 338; space group $P2_1/c$; $Z = 8$; $a = 9.385$ (3), $b = 22.431$ (7), $c = 14.133$ (4) Å; $\beta = 90.86$ (4)°; $V = 2975$ Å^3; $\mu(\text{Mo K}\alpha) = 21.3$ cm^{-1}; $\rho_c = 1.49$ g cm^{-3}; crystal dimensions (given as above) (010) 0.105, $(0\bar{1}0)$ 0.105, (101) 0.315, $(\bar{1}0\bar{1})$ 0.315, (001) 0.25, $(\bar{1}03)$ 0.21. The same procedures as described above for the Co_2 compound were followed to produce an orientation matrix and refined cell constants. The mosaicity of the crystal as judged by the ω-scan technique was very good. The space group was identified as $P2_1/c$ from systematic absences, as described for the dicobalt complex.

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 monochromator. The θ–2θ scan technique was used to record the intensities for all reflections for which $1.4° < 2\theta < 46°$ for $(C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$ and $1° < 2\theta < 48°$ for $(C_5H_5)_2CoFe(H)(CH_3)_2C_2B_3H_3$. 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–Kα_2 splitting. The values of A and B respectively were 0.60 and 0.35° for both compounds. 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, and their standard deviations were calculated in the usual manner from counting statistics ($\rho = 0.03$).[9] This resulted in 1903 reflections for $(C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$ of which 1230 had $F_o^2 > 3\sigma(F_o^2)$ and 4499 reflections for $(C_5H_5)_2CoFe(H)(CH_3)_2C_2B_3H_3$ of which 3548 had $F_o^2 > 3\sigma(F_o^2)$, after averaging of equivalent reflections. 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. For both compounds, three-dimensional Patterson syntheses were used to locate the metal atoms, whose positions phased the data sufficiently well to locate the other nonhydrogen atoms from difference Fourier maps. In each case, anisotropic refinement of these atomic positions with subsequent difference Fourier maps disclosed the location of most of the hydrogen atoms, and the remaining hydrogen positions were calculated except for those on C(M5) and the unique hydrogen associated with the metal(s) in the iron–cobalt complex. From the characteristic high-field ^{1}H NMR peak (δ −16.5),[8] this hydrogen atom is assumed to be bonded to one or both metal atoms and is proposed[8] to occupy a capping position over an Fe–Co–B face, as in the established structure[5a] of $(\eta^5\text{-}C_5H_5)_2Co_2B_4H_6$ which contains hydrogens capping Co–Co–B faces. In the present case, the mirror symmetry present on the NMR time scale suggests that the unique hydrogen tautomerizes between two equivalent Fe–Co–B faces; in the solid state, it could well be disordered between the two faces. Not surprisingly, difference Fourier maps failed to reveal the location of the metal-bound hydrogen.

For both structures, thermal parameters of the nonhydrogen atoms were made anisotropic, and absorption corrections were applied (maximum and minimum transmission coefficients 0.89 and 0.79, respectively, for $(C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$ and 0.73 and 0.42 for $(C_5H_5)_2CoFe(H)(CH_3)_2C_2B_3H_3$). In each case, hydrogen atom positions were allowed to refine for three cycles and thereafter held fixed.

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

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(4) For a tabulation see ref 5a. More recent additions to the list include $[1,2,3\text{-}(\eta^5\text{-}C_5H_5)_2Co_2CB_9H_{10}]^{-}$ [5b] and $2,3,10\text{-}(\eta^5\text{-}C_5H_5)_2NiCoCB_7H_8$.[5c]

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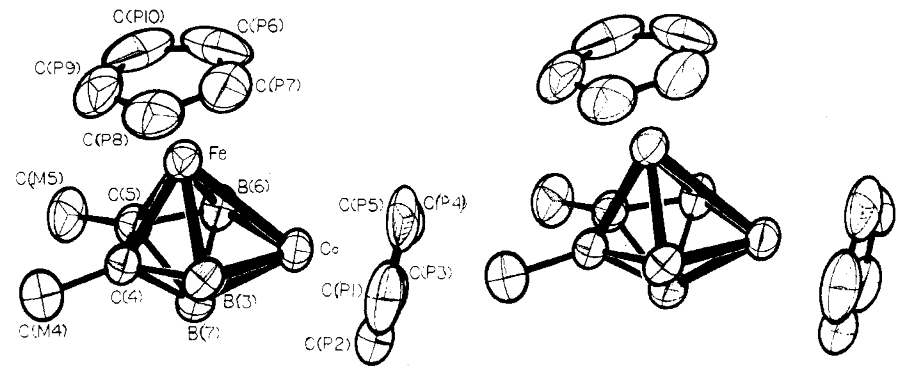

Figure 1. Stereoview of the molecular structure of 1,2,4,5-(η^5-C_5H_5)$_2$CoFe(H)(CH_3)$_2C_2B_3H_3$ with hydrogen atoms omitted. The bridging hydrogen is proposed to cap the Fe–Co–B(3) and/or Fe–Co–B(6) faces. The same cage structure and numbering system apply to 1,2,4,5-(η^5-C_5H_5)$_2Co_2$(CH_3)$_2C_2B_3H_3$ with Co(1) and Co(2) occupying the apical and equatorial metal locations, respectively.

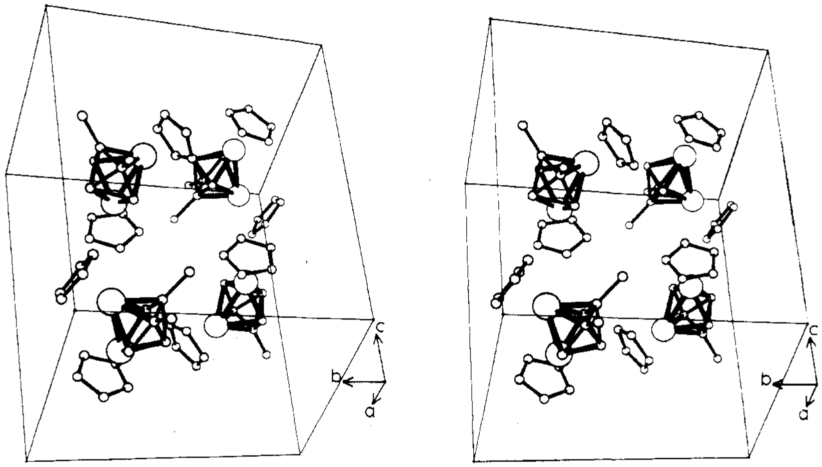

Figure 2. Unit cell packing in (η^5-C_5H_5)$_2Co_2$(CH_3)$_2C_2B_3H_3$.

included in F_c by using Cromer and Ibers'[12] values of $\Delta f'$ and $\Delta f''$. The computing system and programs are described elsewhere.[13] Tables of observed and calculated structure factors are available (see paragraph at end of paper regarding supplementary material).

For the dicobalt complex, refinement converged with $R = 0.057$ and $R_w = 0.062$ where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o^2|)^{1/2}$. The maximum shift/error ratio was 0.15 and the error in an observation of unit weight was 2.0. A final difference Fourier map contained no significant features.

In the iron–cobalt structure, the assignment of iron and cobalt atoms to their respective positions was made initially on the basis of the synthetic route,[8] specifically, the fact that iron occupies an apical position in the original reagent, [2,3-(CH_3)$_2C_2B_4H_4$]$_2FeH_2$. However, as a crystallographic test of this assignment the thermal parameters for the two metal atoms in each of the two independent molecules were converted back to their isotropic forms and were found to be of similar magnitude on refinement. Interchange of the Co and Fe positions produced an increase in R and significant dissimilarity of the isotropic temperature factors, demonstrating that the original assignment of metal locations was correct.

A final difference Fourier map of the iron–cobalt complex was featureless, revealing no trace of the unique hydrogen atom discussed above. An effort to locate this atom via refinement with only low-angle data was unsuccessful. Refinement converged with $R = 0.056$ and $R_w = 0.067$; the maximum shift/error was 0.03, and the error in an observation of unit weight was 2.2.

Results and Discussion

Final positional and thermal parameters are given in Tables I and II for (η^5-C_5H_5)$_2Co_2$(CH_3)$_2C_2B_3H_3$ and (η^5-C_5H_5)$_2$CoFe(H)(CH_3)$_2C_2B_3H_3$, respectively. Tables III and IV list bond lengths for the two 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. The closest nonhydrogen intermolecular contacts in the dicobalt complex are 3.542 Å between C(P4) and C(P8) (symmetry operation $1 - x, y + {}^1/_2, {}^1/_2 - z$) and 3.599 Å between C(M4) and C(P2) (symmetry operation $\bar{x}, y - {}^1/_2, {}^1/_2 - z$). For the iron–cobalt compound, the closest intermolecular contacts are 3.601, 3.674, 3.733, and 3.742 Å corresponding respectively to the C(P7)–C(P3′), C(M4)–C(P2), C(M4)–C(P1), and C(P9)–C(P10′) interactions; in each case the symmetry operation is $x - 1, y, z$.

Figure 1 depicts the molecular structure of (η^5-C_5H_5)$_2$CoFe(H)(CH_3)$_2C_2B_3H_3$ with hydrogen atoms omitted. The heavy-atom geometry of (η^5-C_5H_5)$_2Co_2$(CH_3)$_2C_2B_3H_3$ is closely similar, as a comparison of bond distances (Table III and IV) clearly shows. Figures 2 and 3 exhibit the unit cell contents of the two structures. As noted above, the iron–cobalt complex structure contains two independent molecules in the asymmetric unit.

(η^5-C_5H_5)$_2Co_2$(CH_3)$_2C_2B_3H_3$. This compound was obtained in small yield by reaction of (η^5-C_5H_5)Co(CO)$_2$ with the bis(carboranyl) complex [2,3-(CH_3)$_2C_2B_3H_3$]$_2$CoH in THF solution under ultraviolet light and was isolated as a green solid and characterized from its ^{11}B and ^1H NMR, IR, and mass spectra.[7] Comparison with the spectra[1c] of the parent species, 1,2,4,5-(η^5-C_5H_5)$_2Co_2C_2B_3H_5$, suggested that the new material was the *C,C′*-dimethyl derivative of that compound, and the present crystallographic results confirm this assignment as well

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(12) Cromer, D. T.; Ibers, J. A., ref 10.

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

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co(1)	0.2355 (1)	−0.1681 (1)	0.1506 (1)	4.29 (5)	2.82 (5)	4.50 (5)	0.10 (5)	1.92 (4)	−0.16 (6)
Co(2)	0.4643 (1)	−0.2342 (1)	0.1100 (1)	3.56 (5)	3.98 (7)	6.00 (7)	0.13 (6)	2.12 (4)	0.95 (6)
C(4)	0.193 (1)	−0.3258 (8)	0.1407 (7)	4.7 (4)	2.8 (4)	3.5 (4)	0.4 (4)	2.0 (3)	−0.2 (4)
C(5)	0.134 (1)	−0.2749 (8)	0.0418 (8)	4.1 (4)	3.6 (5)	5.7 (5)	0.0 (4)	1.9 (3)	−1.8 (4)
C(M4)	0.086 (1)	−0.3981 (9)	0.1780 (9)	6.1 (4)	4.0 (5)	12.7 (7)	0.4 (4)	6.1 (4)	2.2 (6)
C(M5)	−0.027 (1)	−0.2878 (11)	−0.0297 (9)	3.7 (5)	8.5 (8)	7.1 (7)	−0.3 (5)	1.2 (4)	−2.2 (6)
C(P1)	0.078 (1)	−0.0503 (10)	0.1519 (11)	5.5 (6)	8.1 (7)	12.0 (9)	4.4 (5)	−1.2 (6)	−4.9 (6)
C(P2)	0.134 (1)	−0.1015 (11)	0.2449 (9)	17.2 (6)	4.9 (7)	13.6 (6)	0.5 (6)	13.4 (4)	−0.9 (5)
C(P3)	0.286 (2)	−0.0916 (11)	0.2864 (9)	9.2 (8)	8.3 (8)	6.0 (7)	2.4 (7)	0.7 (6)	−2.5 (6)
C(P4)	0.327 (1)	−0.0274 (10)	0.2188 (11)	9.3 (6)	4.7 (6)	16.1 (8)	−3.3 (5)	8.5 (5)	−4.8 (6)
C(P5)	0.205 (2)	−0.0044 (10)	0.1384 (9)	11.4 (8)	4.6 (6)	6.4 (6)	2.8 (6)	2.8 (6)	0.5 (6)
C(P6)	0.606 (1)	−0.1955	0.0287 (10)	3.3 (4)	16.3 (12)	9.7 (7)	0.1 (6)	3.8 (4)	4.5 (8)
C(P7)	0.649 (1)	−0.2897 (12)	0.0793 (12)	4.9 (4)	9.4 (9)	20.0 (10)	0.5 (6)	7.1 (5)	−3.9 (8)
C(P8)	0.691 (1)	−0.2656 (10)	0.1801 (12)	2.7 (5)	6.7 (7)	14.6 (10)	0.5 (5)	0.3 (6)	5.8 (7)
C(P9)	0.668 (1)	−0.1577 (12)	0.1902 (11)	3.5 (5)	9.5 (9)	10.3 (8)	−1.9 (5)	1.4 (5)	1.4 (7)
C(P10)	0.614 (1)	−0.1178 (10)	0.0967 (11)	6.9 (6)	6.0 (6)	14.6 (9)	0.5 (6)	4.0 (6)	5.7 (6)
B(3)	0.364 (1)	−0.311 (1)	0.1935 (9)	5.3 (5)	3.5 (6)	4.9 (5)	0.5 (5)	2.6 (4)	0.8 (5)
B(6)	0.262 (1)	−0.214 (1)	0.0105 (9)	5.8 (6)	3.6 (6)	4.8 (6)	−0.5 (5)	2.4 (4)	−0.5 (5)
B(7)	0.302 (1)	−0.349 (1)	0.0614 (9)	3.2 (4)	3.3 (6)	5.4 (6)	−0.5 (4)	1.5 (4)	−0.6 (5)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(3)	0.429 (8)	−0.346 (6)	0.270 (5)	3 (2)	H(P8)	0.730 (8)	−0.296 (6)	0.223 (5)	2 (2)
H(6)	0.238 (9)	−0.177 (7)	−0.064 (6)	5 (2)	H(P9)	0.705 (14)	−0.126 (10)	0.262 (9)	12 (4)
H(7)	0.317 (11)	−0.430 (8)	0.019 (7)	9 (3)	H(P10)	0.599 (9)	−0.065 (6)	0.084 (6)	3 (2)
H(P1)	0.001 (10)	−0.053 (7)	0.103 (6)	5 (2)	H(M41)	0.138 (10)	−0.427 (8)	0.260 (7)	7 (3)
H(P2)	0.089 (8)	−0.136 (6)	0.262 (6)	2 (2)	H(M42)	0.002 (10)	−0.364 (8)	0.178 (7)	7 (3)
H(P3)	0.342 (12)	−0.128 (9)	0.364 (8)	9 (3)	H(M43)	0.095 (10)	−0.481 (8)	0.147 (7)	6 (3)
H(P4)	0.406 (9)	−0.014 (7)	0.213 (6)	4 (2)	H(M51)	−0.072 (14)	−0.241 (10)	−0.094 (9)	12 (4)
H(P5)	0.185 (14)	0.026 (10)	0.076 (9)	10 (4)	H(M52)	−0.060 (11)	−0.354 (8)	−0.062 (7)	8 (3)
H(P6)	0.580 (12)	−0.168 (9)	−0.028 (8)	8 (3)	H(M53)	−0.090 (11)	−0.277 (8)	0.009 (7)	6 (3)
H(P7)	0.659 (8)	−0.338 (6)	0.066 (6)	3 (2)					

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{11}h^2(a^*)^2 + B_{22}k^2(b^*)^2 + B_{33}l^2(c^*)^2)/4 + (B_{12}hka^*b^* + B_{13}hla^*c^* + B_{23}klb^*c^*)/2]$. For all hydrogen atoms, standard isotropic B values are reported.

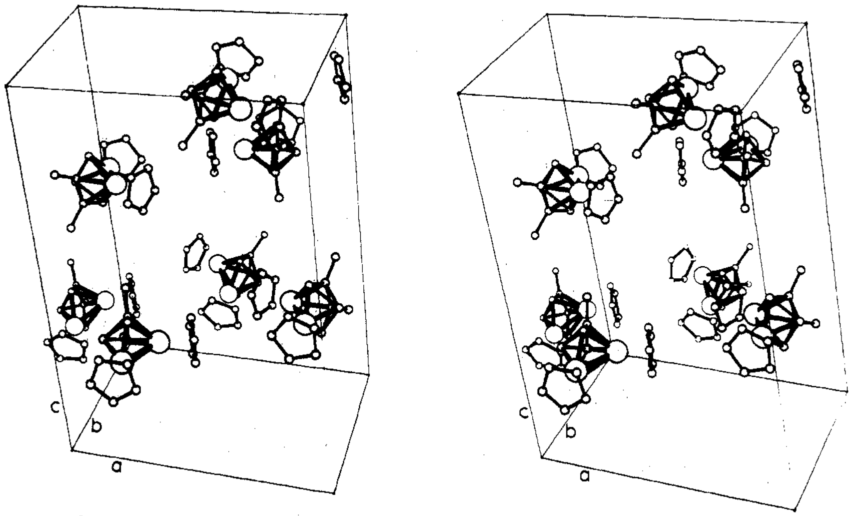

Figure 3. Unit cell packing in $(\eta^5\text{-}C_5H_5)_2CoFe(H)(CH_3)_2C_2B_3H_3$.

as that of the parent species, which had not itself been crystallographically established.

The 1,2,4,5 isomer of the $(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ system is an isolable intermediate in the thermal rearrangement of the triple-decker sandwich 1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ to its 1,7,2,4 isomer,[1c] the net effect of which is to separate the cage carbon atoms (Figure 4). Although the initial and final isomers (1,7,2,3 and 1,7,2,4) have been structurally characterized by crystallographic analyses of their *C*-monomethyl derivatives,[14,15] the structures of the intermediate 1,2,4,5 and 1,2,3,5 species had been based solely on NMR evidence.[1c] A significant feature in these two isomers, which has also been postulated in certain other metallacarboranes, is the presence of a metal atom in a low-coordinate (equatorial) vertex of the pentagonal bipyramid. The X-ray results reported herein establish unequivocally the stable existence of this type of metallacarborane. In turn, the confirmation of the proposed structure[7] of 1,2,4,5-$(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$ proves that in the 1,7,2,3 → 1,7,2,4 polyhedral rearrangement *the metal atoms do indeed move toward, and then away from, each other* as shown.[1c]

The 1,2,4,5-$Co_2C_2B_3$ cage is a pentagonal bipyramid with no distortion other than that attributable to the large covalent radius of cobalt. Indeed, the equatorial Co–B(3)–C(4)–C(5)–B(6) ring is virtually planar (Table VII), with the largest deviations from the plane less than 0.04 Å. The equatorial

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Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $(\eta^5\text{-}C_5H_5)_2Fe(H)Co(CH_3)_2C_2B_3H_3$[a]

atom[b]	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	−0.25981 (7)	0.88053 (3)	0.39682 (5)	2.35 (3)	4.99 (4)	3.16 (3)	−0.28 (3)	0.11 (2)	−0.09 (3)
Co′	0.24052 (7)	0.88138 (3)	−0.16179 (5)	2.70 (3)	4.89 (4)	3.29 (3)	−0.54 (3)	0.04 (2)	0.33 (3)
Fe	−0.49558 (8)	0.86097 (3)	0.30885 (5)	2.71 (3)	4.59 (4)	2.75 (3)	−0.17 (3)	−0.10 (2)	−0.01 (3)
Fe′	−0.00144 (8)	0.86603 (4)	−0.08527 (5)	2.80 (3)	4.83 (4)	2.90 (3)	−0.32 (3)	0.27 (2)	−0.14 (3)
C(4)	−0.5678 (5)	0.9021 (2)	0.4275 (3)	2.3 (2)	4.6 (3)	3.3 (2)	−0.0 (2)	−0.1 (2)	−0.5 (2)
C(5)	−0.5523 (5)	0.8390 (3)	0.4444 (3)	2.5 (2)	5.3 (3)	2.8 (2)	−0.1 (2)	−0.0 (2)	−0.1 (2)
C(M4)	−0.7036 (6)	0.9351 (3)	0.4485 (4)	3.6 (3)	6.1 (3)	5.4 (3)	0.2 (2)	0.6 (2)	−0.8 (3)
C(M5)	−0.6699 (6)	0.8015 (3)	0.4885 (4)	3.7 (3)	6.4 (3)	5.6 (3)	−1.4 (2)	1.3 (2)	1.0 (3)
C(4′)	−0.0608 (5)	0.9076 (3)	−0.2078 (4)	2.9 (2)	4.9 (3)	3.7 (2)	0.6 (2)	−0.1 (2)	0.1 (2)
C(5′)	−0.0508 (5)	0.8431 (3)	−0.2221 (3)	3.0 (2)	5.3 (3)	2.9 (2)	−0.3 (2)	−0.1 (2)	−1.2 (2)
C(M4′)	−0.1897 (7)	0.9423 (3)	−0.2387 (5)	5.5 (3)	7.5 (4)	8.0 (4)	1.9 (3)	−0.9 (3)	1.2 (3)
C(M5′)	−0.1694 (6)	0.8080 (3)	−0.2684 (4)	3.8 (3)	7.3 (4)	5.0 (3)	−1.4 (3)	−0.4 (2)	−0.8 (3)
C(P1)	−0.0634 (6)	0.8650 (3)	0.4625 (5)	2.8 (2)	7.2 (4)	5.4 (3)	−0.4 (2)	−0.5 (2)	0.7 (3)
C(P2)	−0.0938 (6)	0.9258 (3)	0.4591 (5)	2.9 (2)	7.7 (4)	6.4 (3)	−0.7 (3)	0.2 (2)	−1.6 (3)
C(P3)	−0.1059 (6)	0.9447 (3)	0.3698 (5)	3.2 (3)	6.6 (3)	9.3 (4)	−0.9 (3)	0.7 (3)	2.8 (3)
C(P4)	−0.0884 (6)	0.8941 (4)	0.3096 (4)	2.8 (2)	16.4 (6)	3.4 (2)	−2.1 (3)	1.1 (2)	1.3 (3)
C(P5)	−0.0595 (6)	0.8446 (3)	0.3693 (5)	2.9 (2)	7.8 (4)	8.5 (4)	0.4 (3)	1.0 (3)	−3.3 (3)
C(P6)	−0.4730 (8)	0.8171 (3)	0.1817 (4)	10.2 (4)	8.7 (4)	4.2 (3)	5.0 (3)	−2.1 (3)	−2.9 (3)
C(P7)	−0.4563 (7)	0.8789 (3)	0.1708 (4)	5.3 (3)	10.0 (5)	2.7 (2)	−1.7 (3)	0.0 (2)	0.6 (3)
C(P8)	−0.5765 (7)	0.9060 (3)	0.1947 (4)	6.6 (3)	6.4 (3)	3.7 (2)	0.6 (3)	−1.5 (2)	0.4 (3)
C(P9)	−0.6733 (7)	0.8632 (3)	0.2216 (4)	4.0 (3)	11.0 (5)	4.0 (3)	−0.3 (3)	−1.5 (2)	−0.2 (3)
C(P10)	−0.6108 (8)	0.8088 (3)	0.2134 (5)	9.3 (4)	7.2 (4)	4.4 (3)	−3.1 (3)	−2.5 (3)	0.0 (3)
C(P1′)	0.4320 (7)	0.8795 (4)	−0.2288 (5)	2.9 (3)	14.9 (7)	5.0 (3)	−2.1 (3)	0.9 (2)	0.0 (4)
C(P2′)	0.4412 (6)	0.8418 (4)	−0.1513 (5)	3.3 (3)	8.4 (4)	7.4 (4)	1.0 (3)	−0.7 (3)	−1.0 (3)
C(P3′)	0.4163 (6)	0.8744 (3)	−0.0707 (4)	3.6 (2)	8.3 (4)	4.4 (3)	−1.5 (3)	−1.2 (2)	0.7 (3)
C(P4′)	0.3941 (7)	0.9323 (3)	−0.0947 (6)	4.4 (3)	6.5 (4)	9.9 (5)	−0.9 (3)	−1.0 (3)	−2.7 (3)
C(P5′)	0.4020 (7)	0.9368 (4)	−0.1939 (6)	3.8 (3)	10.4 (4)	11.6 (5)	−3.3 (3)	−1.8 (3)	6.1 (3)
C(P6′)	−0.1032 (8)	0.9104 (3)	0.0196 (5)	8.9 (4)	7.1 (4)	5.0 (3)	1.1 (3)	3.2 (3)	−1.0 (3)
C(P7′)	−0.1854 (7)	0.8600 (4)	−0.0091 (5)	3.7 (3)	14.2 (6)	4.6 (3)	−1.0 (3)	1.4 (2)	−0.9 (4)
C(P8′)	−0.1005 (9)	0.8110 (3)	0.0097 (5)	10.2 (4)	6.6 (4)	4.8 (3)	−2.2 (3)	3.0 (3)	0.2 (3)
C(P9′)	0.0257 (8)	0.8301 (4)	0.0490 (5)	6.4 (4)	10.5 (5)	4.1 (3)	1.5 (4)	0.1 (3)	1.7 (3)
C(P10′)	0.0231 (8)	0.8923 (4)	0.0533 (4)	6.7 (4)	11.2 (5)	3.3 (2)	−3.3 (3)	0.8 (3)	−1.8 (3)
B(3)	−0.4282 (6)	0.9342 (3)	0.3929 (4)	2.9 (2)	4.8 (3)	4.0 (3)	−0.3 (2)	−0.5 (2)	−0.8 (2)
B(6)	−0.3976 (6)	0.8149 (3)	0.4290 (4)	2.7 (2)	4.3 (3)	4.4 (3)	−0.1 (2)	−0.1 (2)	0.3 (2)
B(7)	−0.4177 (6)	0.8840 (3)	0.4944 (4)	3.0 (2)	5.7 (3)	2.3 (2)	−0.3 (2)	0.1 (2)	−0.5 (2)
B(3′)	0.0785 (7)	0.9374 (3)	−0.1684 (5)	3.8 (3)	4.3 (3)	4.1 (3)	−0.5 (2)	−0.1 (2)	0.7 (2)
B(6′)	0.0994 (6)	0.8172 (3)	−0.1995 (4)	3.4 (3)	4.2 (3)	4.0 (3)	−0.6 (2)	0.8 (2)	−0.3 (2)
B(7′)	0.0910 (6)	0.8858 (3)	−0.2664 (4)	2.8 (2)	5.1 (3)	3.3 (2)	−0.3 (2)	0.3 (2)	0.1 (2)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
H(P1)	−0.048 (7)	0.840 (3)	0.521 (5)	9 (2)	H(P9′)	0.096 (6)	0.808 (3)	0.071 (4)	8 (2)
H(P2)	−0.107 (6)	0.954 (2)	0.510 (4)	5 (1)	H(P10′)	0.086 (7)	0.908 (3)	0.081 (4)	8 (2)
H(P3)	−0.127 (7)	0.985 (3)	0.353 (4)	7 (2)	H(3)	−0.436 (5)	0.985 (2)	0.388 (3)	4 (1)
H(P4)	−0.093 (6)	0.890 (2)	0.239 (4)	6 (2)	H(6)	−0.377 (6)	0.766 (2)	0.457 (4)	6 (1)
H(P5)	−0.044 (6)	0.803 (2)	0.354 (4)	6 (1)	H(7)	−0.416 (5)	0.892 (2)	0.567 (4)	4 (1)
H(P6)	−0.418 (6)	0.789 (3)	0.171 (4)	7 (2)	H(3′)	0.087 (6)	0.988 (2)	−0.164 (4)	6 (1)
H(P7)	−0.385 (7)	0.895 (2)	0.153 (4)	6 (2)	H(6′)	0.122 (6)	0.770 (2)	−0.210 (4)	5 (1)
H(P8)	−0.591 (5)	0.951 (2)	0.203 (4)	6 (1)	H(7′)	0.099 (6)	0.895 (3)	−0.347 (4)	7 (2)
H(P9)	−0.770 (9)	0.865 (3)	0.231 (6)	10 (2)	H(M41)	−0.727 (6)	0.940 (2)	0.508 (4)	7 (1)
H(P10)	−0.646 (6)	0.773 (3)	0.228 (4)	7 (2)	H(M42)	−0.695 (6)	0.974 (3)	0.421 (4)	7 (2)
H(P1′)	0.439 (8)	0.871 (3)	−0.303 (6)	10 (2)	H(M43)	−0.786 (6)	0.915 (3)	0.416 (4)	7 (2)
H(P2′)	0.454 (6)	0.800 (3)	−0.158 (4)	8 (2)	H(M41′)	−0.217 (5)	0.940 (2)	−0.271 (3)	5 (1)
H(P3′)	0.413 (6)	0.863 (2)	−0.011 (4)	5 (1)	H(M42′)	−0.263 (5)	0.936 (2)	−0.192 (4)	6 (1)
H(P4′)	0.376 (6)	0.959 (3)	−0.062 (4)	7 (2)	H(M43′)	−0.165 (6)	0.983 (2)	−0.238 (4)	6 (1)
H(P5′)	0.380 (6)	0.966 (3)	−0.227 (4)	7 (2)	H(M51′)	−0.251 (5)	0.794 (2)	−0.230 (4)	6 (1)
H(P6′)	−0.119 (6)	0.952 (2)	0.014 (4)	5 (1)	H(M52′)	−0.126 (6)	0.774 (3)	−0.294 (4)	8 (2)
H(P7′)	−0.278 (9)	0.858 (3)	−0.038 (6)	11 (2)	H(M53′)	−0.206 (6)	0.831 (3)	−0.323 (4)	7 (2)
H(P8′)	−0.115 (7)	0.768 (3)	−0.004 (4)	8 (2)					

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{11}h^2(a^*)^2 + B_{22}k^2(b^*)^2 + B_{33}l^2(c^*)^2)/4 + (B_{12}hka^*b^* + B_{13}hla^*c^* + B_{23}klb^*c^*)/2]$. For all hydrogen atoms, standard isotropic *B* values are reported. [b] Primed and unprimed atoms are associated with independent molecules 2 and 1, respectively.

plane is nearly parallel with that of the cyclopentadienyl ring on the apex cobalt, so that the molecule is a well-behaved sandwich with the central metal atom 1.58 Å from the CoC_2B_2 ring and 1.67 Å from its C_5H_5 ligand.

The C(4)–C(5) bond length of 1.450 (9) Å is typical of carbon–carbon bonds in pentagonal-pyramidal or pentagonal-bipyramidal metallaboron clusters;[16] as in 2,3-$C_2B_4H_8$, 1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$, and related systems, this distance suggests a localized C–C interaction with a bond order greater than unity.[17]

$(\eta^5\text{-}C_5H_5)_2CoFe(H)(CH_3)_2C_2B_3H_3$. The isolation of this complex as one of a number of products of the reaction of $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2FeH_2$ with $CoCl_2$ and $C_5H_5^-$ in ethanolic KOH has been described elsewhere.[8] Although no evidence directly bearing on the mechanism is available, the compound is assumed to form via displacement of one $(CH_3)_2C_2B_4H_4^{2-}$ ligand by $C_5H_5^-$ and of one BH unit by $Co(\eta^5\text{-}C_5H_5)$, with removal of one of the metal-bound protons to maintain elec-

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Table III. Bond Distances (Å) in $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$

Co(1)–Co(2)	2.495 (1)	C(4)–C(5)	1.450 (9)
Co(1)–C(P1)	2.058 (8)	C(4)–C(M4)	1.540 (9)
Co(1)–C(P2)	2.021 (8)	C(4)–B(7)	1.74 (1)
Co(1)–C(P3)	2.028 (9)	C(5)–C(M5)	1.506 (9)
Co(1)–C(P4)	2.024 (9)	C(5)–B(6)	1.58 (1)
Co(1)–C(P5)	2.035 (9)	B(6)–B(7)	1.79 (1)
Co(1)–B(3)	2.092 (8)	C(P1)–C(P2)	1.38 (2)
Co(1)–C(4)	1.978 (6)	C(P2)–C(P3)	1.34 (2)
Co(1)–C(5)	1.997 (7)	C(P3)–C(P4)	1.38 (2)
Co(1)–B(6)	2.124 (8)	C(P4)–C(P5)	1.33 (2)
Co(2)–C(P6)	2.043 (9)	C(P5)–C(P1)	1.37 (2)
Co(2)–C(P7)	2.007 (9)	C(P6)–C(P7)	1.35 (2)
Co(2)–C(P8)	2.037 (9)	C(P7)–C(P8)	1.36 (2)
Co(2)–C(P9)	2.075 (8)	C(P8)–C(P9)	1.36 (1)
Co(2)–C(P10)	2.04 (1)	C(P9)–C(P10)	1.33 (1)
Co(2)–B(3)	1.950 (8)	C(P10)–C(P6)	1.33 (2)
Co(2)–B(7)	2.007 (7)	⟨B–H⟩	1.14
Co(2)–B(6)	1.945 (9)	⟨C–H⟩(CH_3)	1.01
B(3)–C(4)	1.52 (1)	⟨C–H⟩(C_5H_5)	0.82
B(3)–B(7)	1.80 (1)		

Table IV. Bond Distances (Å) in $(\eta^5\text{-}C_5H_5)_2CoFe(H)(CH_3)_2C_2B_3H_3$

molecule 1		molecule 2	
Fe–Co	2.560 (1)	Fe′–Co′	2.553 (1)
Fe–C(P6)	2.062 (4)	Fe′–C(P6′)	2.035 (4)
Fe–C(P7)	2.030 (3)	Fe′–C(P7′)	2.052 (4)
Fe–C(P8)	2.041 (3)	Fe′–C(P8′)	2.055 (4)
Fe–C(P9)	2.060 (4)	Fe′–C(P9′)	2.074 (4)
Fe–C(P10)	2.078 (4)	Fe′–C(P10′)	2.055 (4)
Fe–B(3)	2.117 (4)	Fe′–B(3′)	2.129 (4)
Fe–C(4)	2.039 (3)	Fe′–C(4′)	2.037 (3)
Fe–C(5)	2.056 (3)	Fe′–C(5′)	2.048 (3)
Fe–B(6)	2.179 (4)	Fe′–B(6′)	2.178 (4)
Co–B(3)	1.986 (4)	Co′–B(3′)	1.975 (4)
Co–B(7)	2.041 (3)	Co′–B(7′)	2.026 (4)
Co–B(6)	2.015 (4)	Co′–B(6′)	2.022 (4)
Co–C(P1)	2.081 (3)	Co′–C(P1′)	2.044 (4)
Co–C(P2)	2.048 (4)	Co′–C(P2′)	2.086 (4)
Co–C(P3)	2.078 (4)	Co′–C(P3′)	2.084 (3)
Co–C(P4)	2.064 (3)	Co′–C(P4′)	2.059 (4)
Co–C(P5)	2.088 (3)	Co′–C(P5′)	2.017 (4)
B(3)–C(4)	1.579 (5)	B(3′)–C(4′)	1.564 (5)
B(3)–B(7)	1.826 (5)	B(3′)–B(7′)	1.811 (5)
C(4)–C(5)	1.443 (5)	C(4′)–C(5′)	1.465 (5)
C(4)–C(M4)	1.507 (4)	C(4′)–C(M4′)	1.498 (5)
C(4)–B(7)	1.734 (4)	C(4′)–B(7′)	1.730 (5)
C(5)–C(M5)	1.528 (4)	C(5′)–C(M5′)	1.505 (4)
C(5)–B(6)	1.568 (4)	C(5′)–B(6′)	1.554 (5)
B(6)–B(7)	1.815 (5)	B(6′)–B(7′)	1.808 (5)
C(P1)–C(P2)	1.396 (5)	C(P1′)–C(P2′)	1.385 (6)
C(P2)–C(P3)	1.335 (6)	C(P2′)–C(P3′)	1.378 (6)
C(P3)–C(P4)	1.429 (6)	C(P3′)–C(P4′)	1.357 (6)
C(P4)–C(P5)	1.419 (7)	C(P4′)–C(P5′)	1.409 (7)
C(P5)–C(P1)	1.395 (6)	C(P5′)–C(P1′)	1.407 (7)
C(P6)–C(P7)	1.403 (6)	C(P6′)–C(P7′)	1.425 (7)
C(P7)–C(P8)	1.330 (6)	C(P7′)–C(P8′)	1.379 (6)
C(P8)–C(P9)	1.378 (6)	C(P8′)–C(P9′)	1.369 (6)
C(P9)–C(P10)	1.361 (6)	C(P9′)–C(P10′)	1.398 (7)
C(P10)–C(P6)	1.387 (7)	C(P10′)–C(P6′)	1.334 (6)
⟨B–H⟩	1.13	⟨B–H⟩	1.13
⟨C–H⟩(CH_3)	0.94	⟨C–H⟩(CH_3)	0.90
⟨C–H⟩(C_5H_5)	0.94	⟨C–H⟩(C_5H_5)	0.91

Table V. Selected Bond Angles (Deg) in $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$

B(3)–Co(1)–Co(2)	49.4 (3)	C(M5)–C(5)–C(4)	129.6 (7)
B(6)–Co(1)–Co(2)	49.0 (3)	C(M5)–C(5)–B(6)	122.5 (7)
B(3)–Co(1)–C(4)	43.8 (3)	C(M5)–C(5)–Co(1)	133.8 (5)
C(4)–Co(1)–C(5)	42.8 (3)	C(M5)–C(5)–B(7)	133.4 (6)
C(5)–Co(1)–B(6)	45.0 (3)	C(5)–B(6)–Co(2)	112.0 (6)
B(3)–Co(2)–B(6)	87.4 (4)	Co(1)–B(6)–B(7)	87.2 (4)
Co(1)–Co(2)–B(7)	73.2 (3)	B(3)–B(7)–Co(2)	61.3 (4)
Co(1)–Co(2)–B(6)	55.5 (3)	Co(2)–B(7)–B(6)	61.3 (4)
Co(1)–Co(2)–B(3)	54.5 (3)	B(3)–B(7)–C(4)	50.8 (4)
B(3)–Co(2)–B(7)	54.2 (3)	C(4)–B(7)–C(5)	49.1 (4)
B(6)–Co(2)–B(7)	53.9 (3)	C(5)–B(7)–B(6)	53.1 (4)
Co(2)–B(3)–C(4)	113.1 (5)	C(P2)–C(P1)–C(P5)	104.2 (1)
Co(1)–B(3)–B(7)	87.9 (4)	C(P1)–C(P2)–C(P3)	112.4 (1)
B(3)–C(4)–C(5)	114.6 (6)	C(P2)–C(P3)–C(P4)	103.9 (1)
Co(1)–C(4)–B(7)	93.4 (4)	C(P3)–C(P4)–C(P5)	111.0 (1)
C(M4)–C(4)–B(3)	126.0 (6)	C(P4)–C(P5)–C(P1)	108.8 (1)
C(M4)–C(4)–C(5)	119.1 (6)	C(P7)–C(P6)–C(P10)	107.9 (1)
C(M4)–C(4)–Co(1)	132.8 (4)	C(P6)–C(P7)–C(P8)	106.8 (1)
C(M4)–C(4)–B(7)	133.4 (6)	C(P7)–C(P8)–C(P9)	108.5 (1)
C(4)–C(5)–B(6)	112.6 (6)	C(P8)–C(P9)–C(P10)	106.3 (1)
Co(1)–C(5)–B(7)	92.8 (4)	C(P9)–C(P10)–C(P6)	110.4 (1)

Table VI. Selected Bond Angles (Deg) in $(\eta^5\text{-}C_5H_5)_2CoFe(H)(CH_3)_2C_2B_3H_3$

molecule 1		molecule 2	
B(3)–Fe–Co	49.1 (1)	B(3′)–Fe′–Co′	48.9 (1)
B(6)–Fe–Co	49.5 (1)	B(6′)–Fe′–Co′	49.8 (1)
B(3)–Fe–C(4)	44.6 (1)	B(3′)–Fe′–C(4′)	44.0 (1)
C(4)–Fe–C(5)	41.3 (1)	C(4′)–Fe′–C(5′)	42.0 (1)
C(5)–Fe–B(6)	43.3 (1)	C(5′)–Fe′–B(6′)	43.0 (1)
B(3)–Co–B(6)	86.3 (2)	B(3′)–Co′–B(6′)	86.6 (2)
Fe–Co–B(7)	72.8 (1)	Fe′–Co′–B(7′)	72.9 (1)
Fe–Co–B(6)	55.4 (1)	Fe′–Co′–B(6′)	55.4 (1)
Fe–Co–B(3)	53.7 (1)	Fe′–Co′–B(3′)	54.3 (1)
B(3)–Co–B(7)	53.9 (2)	B(3′)–Co′–B(7′)	53.8 (2)
B(6)–Co–B(7)	53.2 (2)	B(6′)–Co′–B(7′)	53.1 (2)
Co–B(3)–C(4)	112.3 (2)	Co′–B(3′)–C(4′)	112.5 (2)
Fe–B(3)–B(7)	88.6 (2)	Fe′–B(3′)–B(7′)	88.2 (2)
B(3)–C(4)–C(5)	114.6 (2)	B(3′)–C(4′)–C(5′)	114.7 (3)
Fe–C(4)–B(7)	93.7 (2)	Fe′–C(4′)–B(7′)	93.5 (2)
C(M4)–C(4)–B(3)	123.1 (3)	C(M4′)–C(4′)–B(3′)	123.3 (3)
C(M4)–C(4)–C(5)	122.2 (3)	C(M4′)–C(4′)–C(5′)	121.7 (3)
C(M4)–C(4)–Fe	132.6 (2)	C(M4′)–C(4′)–Fe′	134.0 (3)
C(M4)–C(4)–B(7)	133.6 (2)	C(M4′)–C(4′)–B(7′)	132.4 (3)
C(4)–C(5)–B(6)	114.0 (2)	C(4′)–C(5′)–B(6′)	113.6 (3)
Fe–C(5)–B(7)	92.4 (2)	Fe′–C(5′)–B(7′)	92.1 (2)
C(M5)–C(5)–C(4)	122.4 (3)	C(M5′)–C(5′)–C(4′)	121.9 (3)
C(M5)–C(5)–B(6)	122.9 (3)	C(M5′)–C(5′)–B(6′)	123.9 (3)
C(M5)–C(5)–Fe	135.3 (2)	C(M5′)–C(5′)–Fe′	134.2 (2)
C(M5)–C(5)–B(7)	132.2 (2)	C(M5′)–C(5′)–B(7′)	133.4 (3)
C(5)–B(6)–Co	112.3 (2)	C(5′)–B(6′)–Co′	112.2 (2)
Fe–B(6)–B(7)	87.0 (2)	Fe′–B(6′)–B(7′)	86.8 (2)
B(3)–B(7)–Co	61.5 (2)	B(3′)–B(7′)–Co′	61.6 (2)
Co–B(7)–B(6)	62.7 (2)	Co′–B(7′)–B(6′)	63.4 (2)
B(3)–B(7)–C(4)	52.6 (2)	B(3′)–B(7′)–C(4′)	52.4 (2)
C(4)–B(7)–C(5)	48.8 (2)	C(4′)–B(7′)–C(5′)	49.6 (2)
C(5)–B(7)–B(6)	52.0 (2)	C(5′)–B(7′)–B(6′)	51.6 (2)
C(P2)–C(P1)–C(P5)	107.3 (4)	C(P2′)–C(P1′)–C(P5′)	107.0 (4)
C(P1)–C(P2)–C(P3)	110.9 (4)	C(P1′)–C(P2′)–C(P3′)	108.6 (4)
C(P2)–C(P3)–C(P4)	107.6 (4)	C(P2′)–C(P3′)–C(P4′)	109.2 (4)
C(P3)–C(P4)–C(P5)	106.9 (3)	C(P3′)–C(P4′)–C(P5′)	107.9 (4)
C(P4)–C(P5)–C(P1)	107.3 (4)	C(P4′)–C(P5′)–C(P1′)	107.3 (4)
C(P7)–C(P6)–C(P10)	105.9 (4)	C(P7′)–C(P6′)–C(P10′)	109.5 (4)
C(P6)–C(P7)–C(P8)	109.1 (4)	C(P6′)–C(P7′)–C(P8′)	105.6 (4)
C(P7)–C(P8)–C(P9)	108.4 (4)	C(P7′)–C(P8′)–C(P9′)	108.9 (4)
C(P8)–C(P9)–C(P10)	108.3 (4)	C(P8′)–C(P9′)–C(P10′)	108.2 (4)
C(P9)–C(P10)–C(P6)	108.2 (4)	C(P9′)–C(P10′)–C(P6′)	107.8 (4)

trical neutrality. The 1,2,4,5 structure, originally proposed from ^{11}B and ^{1}H NMR data,[8] is now confirmed by the X-ray results; however, as noted above, the proton associated with the metal(s) was not located in this investigation. The assignment of iron and cobalt atoms to apical and equatorial vertices, respectively, was based originally on the method of synthesis[8] and has been confirmed in this study by the application of statistical tests to the crystallographic data as described above.

The two crystallographically independent molecules are essentially identical, none of the differences in corresponding bond lengths having more than marginal statistical significance. As in the dicobalt system, the equatorial CoC_2B_2 ring is nearly planar; however, this plane is inclined at an angle of 10.9° to the plane of the apical C_5H_5 ring, in contrast to the dicobalt complex in which the corresponding planes are nearly parallel. The framework carbon–carbon distance (mean

Table VII. Selected Mean Planes for $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$

atom	dev, Å	atom	dev, Å
Plane 1: Co(2), B(3), C(4), C(5), B(6) $0.3032x - 0.8494y - 0.4320z = 2.9368$			
Co(2)	0.037	Co(1)	−1.583
B(3)	−0.036	B(7)	1.122
B(6)	−0.036	C(M4)	0.211
C(4)	0.018	C(M5)	0.209
C(5)	0.019		
Plane 2: C(P1), C(P2), C(P3), C(P4), C(P5) $0.3136x - 0.8287y - 0.4636z = -0.4082$			
C(P1)	0.004	C(P4)	−0.012
C(P2)	−0.012	C(P5)	0.005
C(P3)	0.015	Co(1)	1.672
Plane 3: C(P6), C(P7), C(P8), C(P9), C(P10) $-0.9829x - 0.1825y - 0.0261z = -4.9282$			
C(P6)	−0.014	C(P9)	−0.002
C(P7)	0.013	C(P10)	0.010
C(P8)	−0.007	Co(2)	1.689

planes	angle, deg	planes	angle, deg
1,2	2.3	2,3	98.3
1,3	97.6		

Table VIII. Selected Mean Planes for $(\eta^5\text{-}C_5H_5)_2CoFe(H)(CH_3)_2C_2B_3H_3$ [a]

atom	dev, Å	atom	dev, Å
Plane 1: Co, B(3), B(6), C(4), C(5) $-0.1810x - 0.1979y - 0.9634z = -8.8073$			
Co	−0.047	Fe	1.634
B(3)	0.054	B(7)	−1.119
B(6)	0.041	C(M4)	−0.238
C(4)	−0.036	C(M5)	−0.245
C(5)	−0.012		
Plane 2: C(P1), C(P2), C(P3), C(P4), C(P5) $0.9806x + 0.1940y - 0.0269z = 2.9051$			
C(P1)	0.003	C(P4)	−0.011
C(P2)	−0.010	C(P5)	0.005
C(P3)	0.013	Co	−1.699
Plane 3: C(P6), C(P7), C(P8), C(P9), C(P10) $-0.3186x - 0.0675y - 0.9455z = -2.2367$			
C(P6)	−0.002	C(P9)	−0.003
C(P7)	0.000	C(P10)	0.003
C(P8)	0.002	Fe	−1.690

planes	angle, deg	planes	angle, deg
1,2	101.0	2,3	107.5
1,3	10.9		

[a] Planes are given for molecule no. 1; planes for the other molecule are indentical within experimental error.

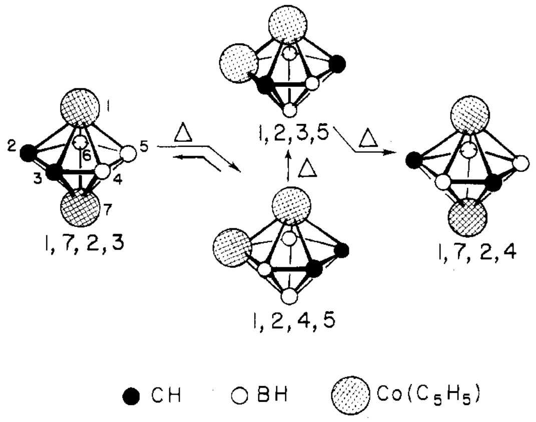

Figure 4. Rearrangement of the 1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ triple-decker complex to the 1,7,2,4 isomer via the 1,2,4,5 and 1,2,3,5 isolable intermediates (see ref 1c).

value 1.454 (4) Å) is virtually the same as in the dicobalt species and again suggests the presence of localized bonding electron density between the carbons.

Metal–Metal Interactions. The iron–cobalt distance in $(\eta^5\text{-}C_5H_5)_2CoFe(H)(CH_3)_2C_2B_3H_3$ [mean value 2.557 (1) Å] is significantly longer than the cobalt–cobalt bond length in $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$ [2.495 (1) Å]. The difference of ~0.06 Å can be attributed to the larger covalent radius of formal Fe(II) in comparison to Co(III); the effect is less than would be expected from the literature values[18] for Fe^{2+} and Co^{3+}, which differ by 0.13 Å, but this is not surprising given the electron delocalization in the cage, the steric constraints on the metal atoms, and the probability that the actual oxidation states of the metals are more nearly equal than the formal assignments would suggest.

Comparisons of the metal–metal distances in these species with those in other metallaboron clusters are difficult to interpret owing to the differences in cage geometry, but it will be noted that metal–metal bond lengths involving first-row transition metals in metallaboranes and metallacarboranes[4] range from 2.354 (1) Å in $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$ to 2.571 (1) Å in $(\eta^5\text{-}C_5H_5)_2Fe_2C_2B_6H_8$. The only previous confirmed example of a 7-vertex cage with a metal–metal bond is the structurally unique complex $(\eta^5\text{-}C_5H_5)_2CoFe(CH_3)_4C_4B_8H_8$, which contains a pentagonal-bipyramidal $CoFeC_2B_3$ unit with an apical Fe and an equatorial Co atom, one of the Fe–Co–B faces being capped by a BH group.[19] The Co–Fe distance of 2.480 (1) Å, which is significantly less than in the present $CoFeC_2B_3$ cluster, is shortened by the BH unit which bridges the metal–metal bond in that complex.[20]

The presence of a hydrogen atom bridging the Fe–Co–B faces in $(\eta^5\text{-}C_5H_5)_2CoFe(H)(CH_3)_2C_2B_3H_3$, discussed above, would be expected to lengthen the Fe–Co distance slightly.[21] Such an effect is particularly evident in the octahedral cluster $(\eta^5\text{-}C_5H_5)_2Co_2B_4H_6$,[5a] which has an unusually long Co–Co bond [2.557(1) Å] bridged by *two* hydrogen atoms. Bond lengthening is less evident, however, in the closely related species $(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$,[6a] whose three Co–Co interactions are bridged by two fluxional hydrogens (only two-thirds of a hydrogen atom per Co–Co bond), and the mean Co–Co distance [2.483 (1) Å] is somewhat shorter. In the present iron–cobalt cluster, bond lengthening arising from the bridging hydrogen might be detected by measuring the Co–Fe distance in the bridge-deprotonated anion $(\eta^5\text{-}C_5H_5)_2CoFe(CH_3)_2C_2B_3H_3^-$, but these data are not available.

Comparison with Related Nonboron Clusters. Several transition-metal–carbon clusters having 7-vertex pentagonal-bipyramidal (closo) or 6-vertex pentagonal-pyramidal (nido) geometry, and in which there are one or more metal–metal bonds between apical and equatorial metal atoms, have been crystallographically characterized. The 7-vertex organometallic species that is most relevant to the compounds described in the present paper is the black isomer of $(CO)_8Fe_3C_4(C_6H_5)_4$,[22] in which the iron atoms occupy an equatorial and both apical vertices with Fe–Fe distances of 2.428 (3) and

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(18) Pauling, L. "Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, N.Y., 1960; p 518.

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(20) Another illustration of this bond-shortening effect is given by the molecule[6a] 1,2,3-$(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$, an octahedral cluster with a mean Co–Co distance of 2.483(1) Å, and its boron-capped counterpart $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$,[6a] in which the mean Co–Co bond length decreases to 2.441 (1) Å. The BH-capping phenomenon can be regarded as analogous to triply bridging CO groups in metal cluster carbonyls.

(21) For discussions of the structural consequences of M–H–M bridging see: ref 5a; Huie, B. T.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1978**, *100*, 3059; Teller, R. G.; Wilson, R. D.; McMullan, R. K.; Koetzle, T. F.; Bau, R. *J. Am. Chem. Soc.* **1978**, *100*, 3071 and references therein.

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2.435 (3) Å, slightly shorter than those in the metallacarboranes in this study. The analogy between this species and the boron cages is strengthened by the fact that the three equatorial C–C bond lengths are identical within experimental error [mean value 1.45 (2) Å], suggesting considerable electron delocalization. Moreover, the molecule is isoelectronic, in terms of electrons involved in bonding the Fe_3C_4 skeleton together, with the $FeCoC_2B_3$ and $Co_2C_2B_3$ systems in the present investigation. All three molecules formally contain 16 skeletal valence electrons and thus are $(2n + 2)$-electron cages, in conformity with the well-known structural correlation originated by Wade.[23] A recently reported tetrametallic cluster, $(\eta^5\text{-}C_5H_5)NiRu_3(CO)_8(C_6H_9)$, is also a 7-vertex pentagonal-bipyramidal 16-electron cage, in which two ruthenium atoms occupy the apices while the remaining two metals are in vicinal positions in the equator.[24]

Among the family of 6-vertex nido clusters is $(CO)_5Co_2(C_8H_{12})_2$,[25] whose central core is a Co_2C_4 pyramid with a cobalt in the apex. The Co–Co distance of 2.4738 (7) Å and average framework C–C distance of 1.423 (2) Å compare closely with those in the metallacarboranes reported here. Several other 6-vertex pyramidal clusters contain an Fe_2C_4 core and were derived from an iron carbonyl and a cycloalkyne;[26] each has an apical and a basal iron atom, and the Fe–Fe bond lengths range from 2.46 to 2.54 Å with basal C–C distances around 1.42 Å, closely comparable to the clusters described above. All of these species are formal 16-electron cage systems whose nido geometry is in accord with electron-counting procedures.[23] Such comparisons emphasize the close relationship which exists among the different types of clusters, often overlooked because of their widely varying synthetic origins.

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Registry No. $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$, 60569-32-6; $(\eta^5\text{-}C_5H_5)_2CoFe(H)(CH_3)_2C_2B_3H_3$, 64091-68-5.

Supplementary Material Available: Listings of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 16.[1–6] Crystal Structure of $(\mu\text{-H})(\mu\text{-OMe})Os_3(CO)_{10}$ and a Comparison of the Hinged $Os(\mu\text{-H})_2Os$, $Os(\mu\text{-H})(\mu\text{-OMe})Os$, and $Os(\mu\text{-OMe})_2Os$ Bridges in Trinuclear $(\mu\text{-H})_n(\mu\text{-OMe})_{2-n}Os_3(CO)_{10}$ (n = 0–2) Complexes

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The complex $(\mu\text{-H})(\mu\text{-OMe})Os_3(CO)_{10}$ crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with a = 7.4156 (15) Å, b = 26.932 (11) Å, c = 8.9941 (22) Å, β = 106.325 (18)°, V = 1723.8 (9) Å^3, and ρ(calcd) = 3.40 g cm^{-3} for mol wt = 882.59 and Z = 4. Diffraction data were collected with a Syntex $P2_1$ diffractometer and the structure was solved and refined via a combination of Patterson, difference-Fourier, and full-matrix least-squares refinement techniques. The final discrepancy indices are R_F = 5.1% and R_{wF} = 3.4% for 2243 independent reflections with 3.5° $< 2\theta <$ 45° [Mo Kα radiation]. The molecule contains a triangular arrangement of osmium atoms in which atom Os(2) is linked to four terminal carbonyl ligands; atoms Os(1) and Os(3) are each linked to three terminal carbonyl and are bridged by a μ-hydride and a μ-methoxide ligand. The nonbridged osmium–osmium bond lengths (Os(1)–Os(2) = 2.8130 (12) Å, Os(2)–Os(3) = 2.8221 (10) Å) are not distinguishable from the μ-hydrido-μ-methoxy-bridged Os–Os distance (2.8120 (11) Å). Important distances and angles within the $Os(\mu\text{-H})(\mu\text{-OMe})Os$ bridge are as follows: Os(1)–O(B) = 2.112 (9) Å, Os(3)–O(B) = 2.093 (9) Å, Os(1)–O(B)–Os(3) = 83.9 (2)°; Os(1)–H(Os) = 1.93 (11) Å, Os(3)–H(Os) = 1.84 (11) Å, Os(1)–H(Os)–Os(3) = 96 (5)°. The geometry of the $(\mu\text{-H})(\mu\text{-OMe})Os_3(CO)_{10}$ molecule is compared to that of the species $(\mu\text{-H})_2Os_3(CO)_{10}$ and $(\mu\text{-OMe})_2Os_3(CO)_{10}$.

Introduction

Some years ago Mason and co-workers provided an interesting comparison of the structural geometry of the species $(\mu\text{-H})_2Os_3(CO)_{10}$, $(\mu\text{-H})(\mu\text{-SEt})Os_3(CO)_{10}$, and $(\mu\text{-OMe})_2Os_3(CO)_{10}$. It was explicitly indicated that "electron deficient" hydrido species were associated with formal metal–metal bonds, whereas the "electron precise" di-μ-methoxy complex required no metal–metal bond.[7–9] The details of the Mason–Mingos symmetry-based model[8] have been challenged by semiquantitative calculations of Teo et al.,[10] but the net formal bond orders of 2 for the $Os(\mu\text{-H})_2Os$ system (**1**) in $(\mu\text{-H})_2Os_3(CO)_{10}$, 1 for the $Os(\mu\text{-H})(\mu\text{-SEt})Os$ system (**2**) in

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(1) For recent parts in this series see ref 2–6.

(2) Part 15, $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHSO}_2C_6H_4Me)$: Churchill, M. R.; Hollander, F. J.; Shapley, J. R.; Keister, J. B. *Inorg. Chem.* **1980**, *19*, 1272–1277.

(3) Part 14, $(\mu\text{-H})_4Os_4(CO)_{11}(CNMe)$: Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1980**, *19*, 306–310.

(4) Part 13, $(\mu\text{-H})(\mu\text{-Br})Os_3(CO)_{10}$: Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 3261–3267.

(5) Part 12, $(\mu\text{-H})(\mu\text{-Cl})Os_3(CO)_{10}$: Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 1926–1930.

(6) Part 11, $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CHCH{=}NEt}_2)$: Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 848–853.

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