

for the cis and trans geometrical isomers of chromic desferrioxamine B are very similar to the corresponding data for the previously reported model chromic complexes.¹ Further studies of the preparation and biological activities of these and related compounds are in progress.

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Structures of Metallocarboranes. V. Synthesis and Crystal and Molecular Structure of the Closo 20-Electron Bimetallocarborane 1,6-Bis(η -cyclopentadienyl)-1,6-diferrate-2,3-dicarba-closo-decaborane(8), 1,6-(η -C₅H₅)₂-1,6,2,3-Fe₂C₂B₆H₈¹

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Abstract: The polyhedral expansion of 4,5-C₂B₇H₉ with ferrous chloride and sodium cyclopentadienide produced a new ferroceneborane formulated as (C₅H₅)₂Fe₂C₂B₆H₈, which exists in paramagnetic and diamagnetic forms. The crystal and molecular structure of the diamagnetic form has been determined by a three-dimensional X-ray diffraction study at -160°. The compound crystallized in the monoclinic centrosymmetric space group *P*2₁/*n* with *a* = 8.999 (7) Å, *b* = 12.860 (10) Å, *c* = 11.989 (4) Å, β = 92.00 (5)°, and *Z* = 4. Observed (25°) and calculated (-160°) densities are 1.58 (3) and 1.623 g cm⁻³, respectively. Diffraction data to 2 θ (max) = 50° (Mo K α radiation) were collected on a Syntex P1 automated diffractometer, and the structure was solved by conventional Patterson, Fourier, and full-matrix least-squares techniques. The final discrepancy index is *R* = 3.6% for the 1642 independent nonzero reflections. All atoms were located. The polyhedral geometry observed in this compound is a new ten-vertex species which is derived from a bicapped square antiprism. Structures of the title compound and its cobalt analog are discussed in terms of the bonding theory of metallocarboranes.

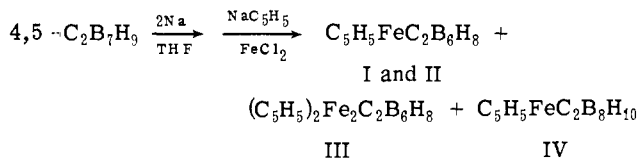
The polyhedral expansion reaction,² *i.e.*, the addition of NaC₅H₅ and a transition metal chloride to a solution of a reduced carborane or metallocarborane, has been used to synthesize numerous bimetallocarboranes of the general

formula (C₅H₅)₂Co₂C₂B_{*n*}H_{*n*+2} (*n* = 4-10)²⁻⁴ and (C₅H₅)₂CoNiCB₇H₈.⁵ Recently, paramagnetic bimetallocarboranes containing formally one Co(III) vertex and one Fe(III) vertex have also been prepared in this manner.⁶

Herein we report the synthesis of a new biferracarborane, $(C_5H_5)_2Fe_2C_2B_6H_8$, which exists in diamagnetic and paramagnetic forms, by the polyhedral expansion of 4,5- $C_2B_7H_9$, and the crystal and molecular structure of the diamagnetic isomer.

Chemistry

The addition of NaC_5H_5 and $FeCl_2$ to the product of the reduction of 4,5- $C_2B_7H_9$ resulted in the formation of several ferracarboranes.



Initially isolated by chromatography were two previously described² isomers of $C_5H_5FeC_2B_6H_8$, I and II. These ferracarboranes, 4-($\eta-C_5H_5$)-4,1,8- $FeC_2B_6H_8$ and 1-($\eta-C_5H_5$)-1,4,6- $FeC_2B_6H_8$, were first synthesized by the polyhedral expansion of 1,7- $C_2B_6H_8$.²

The mass spectrum of the next species separated chromatographically, the green III, contained a cutoff at m/e 340, corresponding to the molecular ion $^{11}B_6^{12}C_{12}^{1}H_{18}^{56}Fe_2^+$, and a parent envelope isotopic distribution consistent with the formula $(C_5H_5)_2Fe_2C_2B_6H_8$. Elemental analysis confirmed this formulation for III. The cyclic voltammogram of III was similar to that of other bimetallo-carboranes, exhibiting a reversible reduction wave at -1.17 V and a reversible oxidation wave at -0.80 V (vs. sce). The effective magnetic moment at 300°K is 3.05 BM.

The ^{11}B nmr spectrum at 80.5 MHz of the paramagnetic III in acetonitrile solution exhibited two resonances of equal intensity at +346 and +700 ppm ($W_{1/2} = 500$ Hz) relative to $BF_3 \cdot O(C_2H_5)_2$. The line widths observed are sufficiently broad to embody three nonequivalent signals in each, hence a structure for III could have three possible patterns of boron environments: 1:1:1:1:1:1, 2:2:1:1, or 3:3. The magnitudes of the two chemical shifts suggest that each boron atom is adjacent to at least one iron atom.

Upon standing at room temperature for a period of weeks in the solid state, III was observed to undergo transformation to an isomeric species, IIIa, primarily distinguished by its diamagnetism. Compound IIIa is also green, and exhibits a mass spectrum indistinguishable from that of III. The 80.5-MHz ^{11}B nmr spectrum of IIIa in acetone- d_6 solution exhibited six well-resolved doublets of equal relative intensities at -142.9 , -36.8 , -28.1 , -18.1 , -1.8 , and $+8.5$ ppm relative to $BF_3 \cdot O(C_2H_5)_2$.

The fourth ferracarborane isolated from the polyhedral expansion of 4,5- $C_2B_7H_9$ with iron(II) was 1-($\eta-C_5H_5$)-1,2,3- $FeC_2B_8H_{10}$ (IV), previously synthesized from 1,6- $C_2B_8H_{10}$.² While the formation of this larger metallocarborane is not unusual,^{2,3} the absence of significant amounts of the desired $C_5H_5FeC_2B_7H_9$ is surprising. Attempts to synthesize this species from 6,8- $C_2B_7H_{13}$ have similarly been unsuccessful, although the related commo ferracarborane, $[Fe(C_2B_7H_9)_2]^-$, has been obtained.⁷

Since the incorporation of two iron vertices into a carborane framework was likely to substantially alter the polyhedral geometry for electronic reasons (*vide infra*), because of the unusual isomerization observed for III, and since the spectral data did not uniquely define a structure for either III or IIIa, we have carried out a single-crystal X-ray diffraction study of the diamagnetic isomer IIIa at -160° .

Unit Cell and Space Group

A sample of the title compound was glued on a glass fiber, en-

closed in a borosilicate capillary and mounted on a Syntex P1 automated diffractometer equipped with scintillation counter, pulse height analyzer, and a locally constructed low-temperature attachment⁸ which maintained the crystal temperature at $-160 \pm 5^\circ$ with a temperature stability of $\pm 0.5^\circ$. A graphite crystal was used to produce monochromatic Mo $K\alpha$ radiation (λ 0.71069 Å). Fifteen strong, high angle reflections observed on a rotation photograph were automatically centered and indexed. A least-squares fit of these reflections determined the lattice parameters to be $a = 8.999(7)$ Å, $b = 12.860(10)$ Å, $c = 11.989(4)$ Å, and $\beta = 92.00(5)^\circ$. The sample density was found to be 1.58(3) by flotation in iodobutane-iodohexane at 25°, while the calculated density was 1.623 g cm⁻³ (assuming $Z = 4$) at -160° .

Intensity data were collected on the same crystal used for preliminary examinations. The shape of the crystal could be approximated by a hexagonal plate with dimensions $0.046 \times 0.160 \times 0.120$ mm. Data were collected with a θ - 2θ scan technique to a limit of $2\theta = 50^\circ$ and with a takeoff angle of 4° . The scintillation counter was 19.5 cm from the crystal and equipped with a 1-mm collimator. Reflections were scanned at a constant rate of $2^\circ/\text{min}$ from 1° below the $K\alpha_1$ reflection to 1° above the $K\alpha_2$ reflection. Background was measured at each end of the scan. The total time spent counting background radiation was 0.8 of the scan time for each reflection.

The intensities of three standard reflections were remeasured every 97 reflections to monitor the tube efficiency and possible crystal deterioration. No significant deviations were observed. As data collection progressed, the systematic absences $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, were observed, which indicated that the space group was $P2_1/n$, an alternate setting of $P2_1/c$ (C_{2h}^5 , No. 14).⁹

The reflections were corrected for Lorentz and polarization effects. The intensity of a reflection, $I(hkl)$, and $\sigma[I(hkl)]$, its estimated standard deviation, were calculated according to the equations $I = CT - (t_c/t_b)(B1 + B2)/2$ and $\sigma = \{\sigma_s^2 + [(0.04)^2]\}^{1/2}$, where I is the net integrated intensity, CT is the total integrated count, t_c and t_b are the times employed for counting the scan and background, respectively, $B1$ and $B2$ are the background counts on the low and high sides of the reflection, and σ_s is the standard deviation in the intensity due to counting statistics. Reflections having intensities less than three times their standard deviations were defined as unobserved and not included in subsequent calculations.

Solution and Refinement of the Structure

The coordinates of the two iron atoms were determined by solution of a three-dimensional Patterson map,¹⁰ and a Fourier synthesis based on these input parameters ($R = 30.9\%$, $R_w = 36.1\%$)¹¹ showed the positions of the ten carbon atoms of the two cyclopentadienyl rings. Full-matrix least-squares refinement of the positional and isotropic temperature factors of these 12 atoms resulted in $R = 18.0\%$, $R_w = 22.5\%$. Another Fourier map revealed the positions of four additional atoms in the polyhedral cage. Further least-squares refinement, with anisotropic temperature factors assigned to the iron atoms, was followed by another electron density map which revealed the positions of three more cage atoms. The one remaining atom in the polyhedron was located in the electron density map following two more least-squares cycles. To this stage of the refinement, all of the light atoms in the polyhedron were treated as boron atoms, and refined with isotropic temperature factors. Least-squares refinement of the positional and thermal parameters of all the nonhydrogen atoms resulted in the identification of the polyhedral carbon atoms; these atoms showed isotropic temperature factors smaller than those of the other atoms, and their bond distances were also shorter than those of other cage atoms. In all calculations these atoms were given carbon scattering factors. Another cycle of least-squares refinement, followed by a difference Fourier map ($R = 5.5\%$, $R_w = 6.4\%$) resulted in the location of all 18 hydrogen atoms.

Isotropic temperature factors of 3.0 \AA^2 were assigned to all hydrogen atoms but were not refined at this stage. An absorption correction applied to the diffraction data gave maximum and minimum transmission factors of 0.9533 for (0,5,-1) and (0,6,0) and 0.8926 for (0,7,-11). The geometry of the crystal was approximated as a hexagonal plate bounded by (1,0,0), (0,1,0), (0,1,-2), (0,0,1), and centrosymmetrically related faces. Two least-squares

Table I. Final Atomic Positions^a

Atom	X	Y	Z	Atom	X	Y	Z
I. Heavy Atoms							
Fe1	-0.01987 (8)	0.13151 (6)	0.77916 (6)	Cp1	0.0386 (6)	0.0584 (4)	0.6315 (4)
C2	-0.1498 (6)	0.2322 (4)	0.8506 (5)	Cp2	0.0416 (6)	-0.0141 (4)	0.7213 (4)
C3	0.0834 (6)	0.1164 (4)	0.9281 (4)	Cp3	-0.1016 (6)	-0.0211 (4)	0.7626 (4)
B4	0.1243 (7)	0.2535 (5)	0.7411 (5)	Cp4	-0.1942 (6)	0.0472 (5)	0.6994 (4)
B5	-0.0789 (7)	0.1676 (5)	0.9510 (5)	Cp5	-0.1083 (6)	0.0954 (5)	0.6187 (4)
Fe6	0.23912 (8)	0.18358 (6)	0.85759 (6)	Cp6	0.3960 (6)	0.0996 (4)	0.7660 (5)
B7	-0.0475 (7)	0.3030 (5)	0.7808 (5)	Cp7	0.3959 (6)	0.0620 (4)	0.8759 (5)
B8	-0.0548 (7)	0.3095 (5)	0.9327 (5)	Cp8	0.4353 (6)	0.1458 (5)	0.9481 (5)
B9	0.1035 (6)	0.2347 (5)	0.9844 (5)	Cp9	0.4585 (6)	0.2340 (5)	0.8820 (5)
B10	0.1218 (6)	0.3225 (5)	0.8702 (5)	Cp10	0.4331 (5)	0.2053 (4)	0.7688 (4)
II. Hydrogen Atoms							
C2H	-0.257 (7)	0.236 (4)	0.848 (5)	Cp2H	0.134 (7)	-0.053 (5)	0.749 (5)
C3H	0.104 (6)	0.048 (4)	0.972 (5)	Cp3H	-0.135 (7)	-0.062 (5)	0.826 (5)
B4H	0.161 (6)	0.290 (4)	0.654 (5)	Cp4H	-0.298 (7)	0.059 (5)	0.711 (5)
B5H	-0.148 (6)	0.126 (5)	1.015 (5)	Cp5H	-0.138 (7)	0.148 (5)	0.564 (5)
B7H	-0.099 (6)	0.367 (4)	0.727 (4)	Cp6H	0.377 (6)	0.064 (5)	0.696 (5)
B8H	-0.107 (6)	0.377 (4)	0.979 (5)	Cp7H	0.382 (7)	-0.007 (5)	0.897 (5)
B9H	0.135 (6)	0.246 (4)	1.071 (5)	Cp8H	0.444 (6)	0.138 (5)	1.028 (5)
B10H	0.178 (6)	0.402 (5)	0.884 (4)	Cp9H	0.492 (7)	0.304 (5)	0.905 (5)
Cp1H	0.124 (7)	0.084 (5)	0.585 (5)	Cp10H	0.448 (7)	0.247 (5)	0.703 (5)

^a Estimated standard deviations, shown in parentheses, refer to the last digit of the preceding number.

Table II. Thermal Parameters^a

Atom	A. Anisotropic Temperature Factors of Nonhydrogen Atoms					
	10 ⁴ β ₁₁	10 ⁴ β ₂₂	10 ⁴ β ₃₃	10 ⁴ β ₁₂	10 ⁴ β ₁₃	10 ⁴ β ₂₃
Fe1	22.5 (9)	19.7 (5)	19.7 (5)	1.8 (6)	1.0 (5)	0.3 (5)
C2	32 (6)	26 (4)	44 (4)	4 (4)	9 (4)	-4 (3)
C3	49 (7)	25 (4)	25 (4)	0 (4)	-1 (4)	4 (3)
B4	53 (8)	17 (4)	24 (4)	-2 (5)	0 (5)	4 (3)
B5	47 (8)	37 (5)	31 (4)	-2 (5)	14 (5)	-8 (4)
Fe6	22.7 (9)	17.0 (5)	17.8 (5)	2.2 (6)	1.0 (5)	0.8 (4)
B7	36 (7)	27 (4)	33 (4)	2 (5)	-2 (5)	0 (4)
B8	48 (8)	27 (4)	28 (4)	8 (5)	-1 (5)	-6 (4)
B9	30 (7)	27 (4)	18 (4)	0 (4)	7 (4)	0 (3)
B10	37 (7)	17 (3)	27 (4)	1 (5)	9 (4)	-1 (3)
Cp1	41 (7)	28 (4)	29 (4)	-6 (4)	1 (4)	-11 (3)
Cp2	52 (7)	23 (3)	35 (4)	-3 (4)	-3 (4)	-9 (3)
Cp3	58 (7)	23 (4)	32 (4)	-18 (4)	-5 (4)	-2 (3)
Cp4	48 (7)	32 (4)	34 (4)	-8 (4)	-8 (4)	-9 (3)
Cp5	63 (8)	37 (4)	20 (4)	-4 (4)	-8 (4)	-2 (3)
Cp6	30 (7)	34 (4)	40 (4)	8 (4)	4 (4)	-8 (3)
Cp7	32 (7)	24 (4)	60 (5)	11 (4)	6 (4)	5 (4)
Cp8	36 (7)	45 (5)	30 (4)	15 (4)	-3 (4)	6 (3)
Cp9	17 (6)	38 (4)	40 (4)	-5 (4)	-5 (4)	-6 (3)
Cp10	24 (6)	33 (4)	33 (4)	2 (4)	8 (4)	0 (3)
Atom	B. Isotropic Temperature Factors of Hydrogen Atoms					
	β	Atom	β	Atom	β	
C2H	0.5 (1.3)	B9H	0.9 (1.4)	Cp5H	1.1 (1.4)	
C3H	3.1 (1.4)	B10H	0.7 (1.4)	Cp6H	3.2 (1.4)	
B4H	1.8 (1.3)	Cp1H	0.7 (1.4)	Cp7H	1.1 (1.4)	
B5H	1.4 (1.3)	Cp2H	1.4 (1.4)	Cp8H	3.6 (1.4)	
B7H	1.1 (1.3)	Cp3H	0.6 (1.4)	Cp9H	1.0 (1.4)	
B8H	1.6 (1.3)	Cp4H	2.6 (1.4)	Cp10H	2.0 (1.4)	

^a See footnote *a* of Table I. The anisotropic temperature factor *T* is defined as $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Thermal ellipsoids are depicted in the figures.

cycles reduced *R* to 3.6% and *R_w* to 3.8%. One final cycle allowed variation of the isotropic temperature factors of the hydrogen atoms and included correction for the anomalous scattering of the iron atoms. The standard deviation of an observation of unit weight was 1.09.

Scattering factors for neutral iron, carbon, and boron were taken from Hanson, *et al.*¹² hydrogen scattering factors were obtained from Stewart, Davidson, and Simpson,¹³ and the real and imaginary corrections for anomalous scattering of iron were taken from Cromer.¹⁴ The function $\sum w|F_o| - |F_c|^2$ was minimized during least-squares refinement.

The final observed and calculated structure factors are available.¹⁵ Atomic fractional coordinates are collected in Table I. Anisotropic thermal parameters of the heavy atoms and isotropic tem-

perature factors of the hydrogen atoms are listed in Table II.

The Molecular Structure

Intramolecular distances and their estimated standard deviations (esd's) are listed in Table III. Average bond distances, with their root-mean-square deviations, are collected in Table IV. The individual bond angles and their associated esd's are presented in Table V. The structure of 1,6-(η -C₅H₅)₂-1,6,2,3-Fe₂C₂B₆H₈ is shown in Figure 1, which also illustrates the numbering system employed.¹⁶ It should be noted that the crystal is composed of a mixture of *dl* isomers. A unit cell packing diagram is presented in Figure 2.

The two iron atoms in the compound are in distinctly dif-

Table III. Interatomic Distances^a

Atoms	Distance, Å	Atoms	Distance, Å
I. Distances around Iron Atoms			
Fe1-Cp1	2.088 (5)	Fe1-C2	1.962 (5)
Fe1-Cp2	2.079 (5)	Fe1-C3	1.993 (5)
Fe1-Cp3	2.103 (5)	Fe1-B4	2.096 (6)
Fe1-Cp4	2.109 (5)	Fe1-B5	2.196 (6)
Fe1-Cp5	2.107 (5)	Fe1-B7	2.219 (6)
Fe6-Cp6	2.115 (5)	Fe6-C3	1.873 (5)
Fe6-Cp7	2.113 (5)	Fe6-B4	1.930 (6)
Fe6-Cp8	2.097 (5)	Fe6-B9	2.089 (6)
Fe6-Cp9	2.089 (5)	Fe6-B10	2.083 (6)
Fe6-Cp10	2.095 (5)	Fe1-Fe6	2.571 (1)
II. Distances in Cyclopentadienyl Rings			
Cp1-Cp2	1.424 (7)	Cp6-Cp7	1.404 (8)
Cp1-Cp5	1.408 (8)	Cp6-Cp10	1.399 (8)
Cp2-Cp3	1.399 (7)	Cp7-Cp8	1.420 (8)
Cp3-Cp4	1.413 (8)	Cp8-Cp9	1.404 (8)
Cp4-Cp5	1.403 (8)	Cp9-Cp10	1.417 (7)
III. Boron-Boron Distances			
B4-B7	1.753 (8)	B7-B10	1.849 (8)
B4-B10	1.785 (8)	B8-B9	1.811 (8)
B5-B8	1.852 (9)	B8-B10	1.788 (8)
B5-B9	1.885 (9)	B9-B10	1.786 (8)
B7-B8	1.826 (8)		
IV. Carbon-Boron Distances			
C2-B5	1.579 (9)	C3-B5	1.634 (8)
C2-B7	1.559 (8)	C3-B9	1.671 (8)
C2-B8	1.621 (8)		
V. Boron-Hydrogen and Carbon-Hydrogen Distances			
B4-B4H	1.21 (6)	Cp2-Cp2H	1.02 (6)
B5-B5H	1.14 (6)	Cp3-Cp3H	0.98 (6)
B7-B7H	1.14 (6)	Cp4-Cp4H	0.96 (6)
B8-B8H	1.14 (6)	Cp5-Cp5H	0.97 (6)
B9-B9H	1.07 (5)	Cp6-Cp6H	0.96 (6)
B10-B10H	1.15 (6)	Cp7-Cp7H	0.94 (6)
C2-C2H	0.96 (6)	Cp8-Cp8H	0.97 (6)
C3-C3H	1.04 (6)	Cp9-Cp9H	0.98 (6)
Cp1-Cp1H	1.02 (6)	Cp10-Cp10H	0.96 (6)

^a See footnote *a* of Table I.

Table IV. Average Bond Lengths

Atoms	No.	Range, ^a Å	Av, ^b Å
Fe-C	13	1.873 (5)-2.115 (5)	2.06 (7)
Fe-B	6	1.930 (6)-2.219 (6)	2.10 (10)
C-C	10	1.399 (7)-1.424 (7)	1.409 (9)
B-B	9	1.753 (8)-1.885 (9)	1.82 (4)
C-B	5	1.559 (8)-1.671 (8)	1.61 (4)
B-H	6	1.07 (5)-1.21 (6)	1.14 (4)
C-H	12	0.94 (6)-1.04 (6)	0.98 (3)

^a See footnote *a* of Table I. ^b Esd's for average bond lengths were calculated using the internal routine of an HP-45 calculator.

ferent environments. Although both iron atoms are coordinated to π -bonded cyclopentadienyl rings at equal distances within experimental error (2.097 (13) vs. 2.102 (12) Å), Fe1 is bonded to six polyhedral atoms while Fe6 is bonded to only five atoms in the polyhedron, including the Fe-Fe bond. As might be expected, this difference in coordination number is reflected in differences in the bond lengths exhibited by the two iron atoms. Each iron atom forms three bonds to polyhedral boron atoms; the average Fe1-B distance is 2.17 (7) Å, while the average Fe6-B distance is 2.03 (9) Å. These distances, however, involve bonds to boron atoms of differing coordination numbers. More relevant distances for comparison are as follows: Fe1 to six-coordinate boron = 2.219 (6), 2.196 (6), Fe6 to six-coordinate boron = 2.089 (6), 2.083 (6), Fe1 to five-coordinate boron = 2.096 (6), Fe6 to five-coordinate boron = 1.930 (6) Å. This tabulation indicates that the Fe-B distances differ

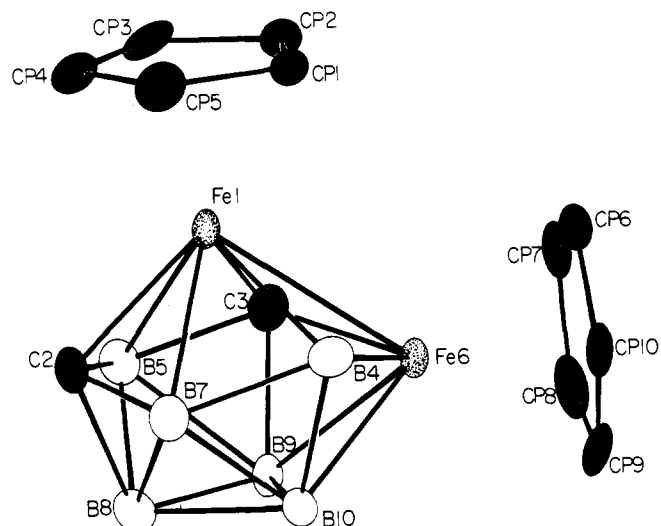


Figure 1. Structure of 1,6-(η -C₅H₅)₂-1,6,2,3-Fe₂C₂B₆H₈, showing the numbering system employed. Atoms shown as 50% probability ellipsoids. Hydrogen atoms have been removed for clarity.

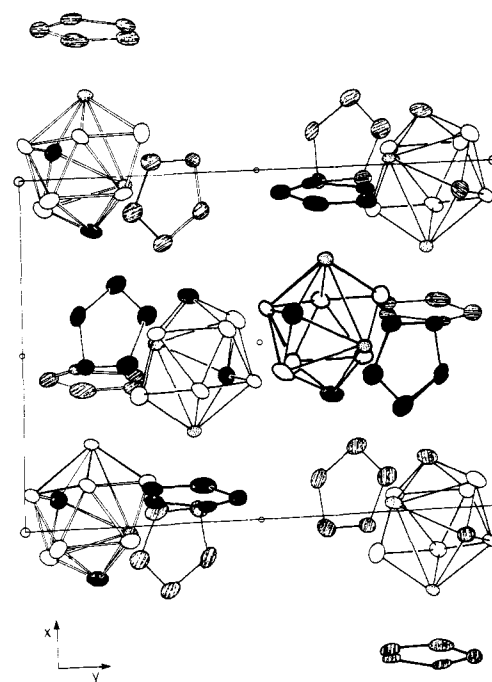


Figure 2. Unit cell packing diagram projected down *c*. Hydrogen atoms are not shown.

by ca. $\pm 9\sigma$ and $\pm 14\sigma$ for Fe to six-coordinate boron and five-coordinate boron, respectively, and reflects the change in Fe-B bond length due to change in coordination number of the metal.

The polyhedral carbon atoms occupy nonadjacent positions in this compound, the synthetically expected result when carbon atoms are nonadjacent in the carborane precursor.² Both carbon atoms are found in low-coordinate positions, *i.e.*, they bond to only four other polyhedral atoms. This is commonly observed in metallocarboranes²⁻⁴ although a ferracarborane exception has been described.² The iron-iron distance is 2.571 (7) Å, which is similar to iron-iron distances previously determined in other compounds.¹⁷ Boron atom 4 occupies a low-coordinate polyhedral position adjacent to both iron atoms. On the basis of previous observations,^{2,3,5} we feel confident in assigning the extremely low-field ¹¹B nmr resonance to this atom.

The boron-boron and boron-carbon bond distances within the polyhedron reflect the coordination of the various

Table V. Interatomic Angles^a

Atoms 1,2,3	Angle, deg	Atoms 1,2,3	Angle, deg	Atoms 1,2,3	Angle, deg	Atoms 1,2,3	Angle, deg
I. Angles around Iron Atoms							
A. C ₅ H ₅ -Fe-C ₅ H ₅							
Cp1-Fe1-Cp2	40.0 (2)	Cp1-Fe1-Cp3	66.2 (2)	Cp4-Cp5-Cp1	108.3 (5)	Cp9-Cp10-Cp6	107.8 (5)
Cp1-Fe1-Cp5	39.2 (2)	Cp1-Fe1-Cp4	65.8 (2)	Cp5-Cp1-Cp2	107.2 (5)	Cp10-Cp6-Cp7	108.7 (5)
Cp2-Fe1-Cp3	39.1 (2)	Cp2-Fe1-Cp4	65.7 (2)	B. C-C-Fe Angles			
Cp3-Fe1-Cp4	39.2 (2)	Cp2-Fe1-Cp5	66.0 (2)	Cp1-Cp2-Fe1	70.4 (3)	Cp6-Cp7-Fe6	70.7 (3)
Cp4-Fe1-Cp5	38.9 (2)	Cp3-Fe1-Cp5	65.7 (2)	Cp1-Cp5-Fe1	69.7 (3)	Cp6-Cp10-Fe6	71.4 (3)
Cp6-Fe6-Cp7	38.8 (2)	Cp6-Fe6-Cp8	65.5 (2)	Cp2-Cp1-Fe1	69.7 (3)	Cp7-Cp6-Fe6	70.5 (3)
Cp6-Fe6-Cp10	38.8 (2)	Cp6-Fe6-Cp9	65.5 (2)	Cp2-Cp3-Fe1	69.5 (3)	Cp7-Cp8-Fe6	70.9 (3)
Cp7-Fe6-Cp8	39.4 (2)	Cp7-Fe6-Cp9	65.8 (2)	Cp3-Cp2-Fe1	71.4 (3)	Cp8-Cp7-Fe6	69.7 (3)
Cp8-Fe6-Cp9	39.2 (2)	Cp7-Fe6-Cp10	65.5 (2)	Cp3-Cp4-Fe1	70.2 (3)	Cp8-Cp9-Fe6	70.7 (3)
Cp9-Fe6-Cp10	39.6 (2)	Cp8-Fe6-Cp10	65.9 (2)	Cp4-Cp3-Fe1	70.6 (3)	Cp9-Cp8-Fe6	70.1 (3)
B. C ₂ B ₆ H ₈ -Fe-C ₂ B ₆ H ₈				Cp4-Cp5-Fe1	70.6 (3)	Cp9-Cp10-Fe6	70.0 (3)
C2-Fe1-C3	86.5 (2)	B4-Fe1-B7	47.8 (2)	Cp5-Cp1-Fe1	71.1 (3)	Cp10-Cp6-Fe6	69.8 (3)
C2-Fe1-B4	89.1 (2)	B5-Fe1-B7	75.6 (2)	Cp5-Cp4-Fe1	70.5 (3)	Cp10-Cp9-Fe6	70.4 (3)
C2-Fe1-B5	44.2 (2)	C3-Fe6-B4	98.7 (2)	III. C ₂ B ₆ H ₈ Cage Angles			
C2-Fe1-B7	43.3 (2)	C3-Fe6-B10	88.5 (2)	A. B-B-B Angles			
C3-Fe1-B4	89.7 (2)	C3-Fe6-B9	49.5 (2)	B7-B4-B10	63.0 (3)	B9-B8-B10	59.5 (3)
C3-Fe1-B5	45.6 (2)	B4-Fe6-B10	52.6 (2)	B8-B5-B9	58.0 (3)	B5-B9-B8	60.1 (3)
C3-Fe1-B7	97.9 (2)	B4-Fe6-B9	93.9 (2)	B4-B7-B8	110.5 (4)	B5-B9-B10	103.3 (4)
B4-Fe1-B5	102.6 (2)	B9-Fe6-B10	50.7 (2)	B4-B7-B10	59.3 (3)	B8-B9-B10	59.6 (3)
C. Fe-Fe-C ₂ B ₆ H ₈				B8-B7-B10	58.2 (3)	B4-B10-B7	57.6 (3)
Fe6-Fe1-C2	102.4 (2)	Fe1-Fe6-C3	50.3 (2)	B5-B8-B7	94.7 (4)	B4-B10-B8	110.8 (4)
Fe6-Fe1-C3	46.3 (2)	Fe1-Fe6-B4	53.2 (2)	B5-B8-B9	61.9 (4)	B4-B10-B9	110.8 (4)
Fe6-Fe1-B4	47.5 (2)	Fe1-Fe6-B9	78.6 (2)	B5-B8-B10	104.5 (3)	B7-B10-B8	60.2 (3)
Fe6-Fe1-B5	81.2 (2)	Fe1-Fe6-B10	78.2 (2)	B7-B8-B9	105.2 (4)	B7-B10-B9	105.2 (4)
Fe6-Fe1-B7	80.7 (2)					B7-B8-B10	61.5 (3)
D. Fe-Fe-C ₅ H ₅				B. C-B-B Angles			
Fe6-Fe1-Cp1	100.1 (1)	Fe1-Fe6-Cp6	106.9 (2)	C2-B5-B8	55.7 (3)	C2-B8-B9	105.9 (5)
Fe6-Fe1-Cp2	96.2 (1)	Fe1-Fe6-Cp7	116.0 (2)	C2-B5-B9	104.3 (4)	C2-B8-B10	105.1 (4)
Fe6-Fe1-Cp3	125.9 (2)	Fe1-Fe6-Cp8	149.9 (2)	C2-B7-B4	118.5 (5)	C3-B5-B8	105.5 (4)
Fe6-Fe1-Cp4	161.9 (2)	Fe1-Fe6-Cp9	166.5 (2)	C2-B7-B8	56.6 (3)	C3-B5-B9	56.2 (3)
Fe6-Fe1-Cp5	134.4 (2)	Fe1-Fe6-Cp10	127.6 (1)	C2-B7-B10	104.9 (4)	C3-B9-B5	54.3 (3)
E. C ₅ H ₅ -Fe-C ₂ B ₆ H ₈				C2-B8-B5	53.6 (3)	C3-B9-B8	105.8 (4)
Cp1-Fe1-C2	147.1 (2)	Cp5-Fe1-B5	143.8 (2)	C2-B8-B7	53.4 (3)	C3-B9-B10	106.1 (4)
Cp1-Fe1-C3	126.3 (2)	Cp5-Fe1-B7	100.8 (2)	C. B-C-B Angles			
Cp1-Fe1-B4	88.6 (2)	Cp6-Fe6-C3	121.5 (2)	B5-C2-B7	119.1 (5)	B7-C2-B8	70.1 (4)
Cp1-Fe1-B5	165.3 (2)	Cp6-Fe6-B4	102.3 (2)	B5-C2-B8	70.7 (4)	B5-C3-B9	69.5 (4)
Cp1-Fe1-B7	119.1 (2)	Cp6-Fe6-B9	163.0 (2)	D. B-B-Fe Angles			
Cp2-Fe1-C2	155.5 (2)	Cp6-Fe6-B10	145.6 (2)	B7-B4-Fe1	69.8 (3)	B10-B7-Fe1	92.8 (3)
Cp2-Fe1-C3	95.2 (2)	Cp7-Fe6-C3	96.9 (2)	B7-B4-Fe6	115.3 (4)	B5-B9-Fe6	103.2 (3)
Cp2-Fe1-B4	115.3 (2)	Cp7-Fe6-B4	139.4 (2)	B10-B4-Fe1	99.0 (3)	B8-B9-Fe6	113.0 (3)
Cp2-Fe1-B5	125.4 (2)	Cp7-Fe6-B9	124.2 (2)	B10-B4-Fe6	68.1 (3)	B10-B9-Fe6	64.5 (3)
Cp2-Fe1-B7	158.3 (2)	Cp7-Fe6-B10	164.9 (2)	B8-B5-Fe1	93.6 (3)	B4-B10-Fe6	59.3 (3)
Cp3-Fe1-C2	116.5 (2)	Cp8-Fe6-C3	106.8 (2)	B9-B5-Fe1	93.4 (3)	B7-B10-Fe6	104.5 (3)
Cp3-Fe1-C3	98.3 (2)	Cp8-Fe6-B4	154.5 (2)	B4-B7-Fe1	62.4 (3)	B8-B10-Fe6	114.3 (4)
Cp3-Fe1-B4	153.5 (2)	Cp8-Fe6-B9	101.5 (2)	B8-B7-Fe1	93.6 (3)	B9-B10-Fe6	64.8 (3)
Cp3-Fe1-B5	101.0 (2)	Cp8-Fe6-B10	125.5 (2)	E. C-B-C Angle			
Cp3-Fe1-B7	152.8 (2)	Cp9-Fe6-C3	143.0 (2)	C2-B5-C3	115.0 (4)		
Cp4-Fe1-C2	95.3 (2)	Cp9-Fe6-B4	115.9 (2)	F. C-B-Fe Angles			
Cp4-Fe1-C3	132.3 (2)	Cp9-Fe6-B9	112.0 (2)	C2-B5-Fe1	60.0 (3)	C2-B7-Fe1	59.5 (3)
Cp4-Fe1-B4	137.9 (2)	Cp9-Fe6-B10	101.7 (2)	C3-B5-Fe1	60.6 (3)	C3-B9-Fe6	58.5 (2)
Cp4-Fe1-B5	109.5 (2)	Cp10-Fe6-C3	160.2 (2)	G. B-C-Fe Angles			
Cp4-Fe1-B7	115.7 (2)	Cp10-Fe6-B4	90.3 (2)	B5-C2-Fe1	75.8 (3)	B5-C3-Fe6	125.3 (4)
Cp5-Fe1-C2	109.4 (2)	Cp10-Fe6-B9	147.8 (2)	B7-C2-Fe1	77.2 (3)	B9-C3-Fe1	108.3 (3)
Cp5-Fe1-C3	161.0 (2)	Cp10-Fe6-B10	110.9 (2)	B8-C2-Fe1	111.1 (4)	B9-C3-Fe6	72.0 (3)
Cp5-Fe1-B4	100.6 (2)					B5-C3-Fe1	73.8 (3)
II. Cyclopentadienyl Ring Angles							
A. C-C-C Angles							
Cp1-Cp2-Cp3	108.4 (5)	Cp6-Cp7-Cp8	107.6 (5)	Fe1-B4-Fe6	79.3 (2)	H. Fe-B-Fe Angle	
Cp2-Cp3-Cp4	107.7 (5)	Cp7-Cp8-Cp9	107.9 (5)	I. Fe-C-Fe Angle			
Cp3-Cp4-Cp5	108.4 (5)	Cp8-Cp9-Cp10	108.0 (5)	Fe1-C3-Fe6	83.3 (2)		

^a See footnote a of Table I.

atoms, longer internuclear distances being observed between atoms which have a greater number of bonding interactions. It is of some interest that C2 forms uniformly shorter bonds than does C3, although both atoms are formally five-coordinate; this may be a result of the fact that C3 occupies a position between the two iron atoms, while C2 is bonded to only one iron atom.

The two independent cyclopentadienyl rings are planar

within experimental error (Table VI). The dihedral angle between these two rings is 88.4°. The carbon-carbon bond distances average 1.409 (10) and 1.409 (9) Å, in good agreement with previously observed values.¹⁸

Overall Geometry

The polyhedral geometry of (C₅H₅)₂Fe₂C₂B₆H₈ is significantly different from a biccapped square antiprism, the ide-

Table VI. Important Planes in the Molecule^a

Atom	Dev, Å	Atom	Dev, Å
Cyclopentadienyl Ring Cp1, Cp2, Cp3, Cp4, Cp5			
$0.1955x + 0.7398y + 0.6438z = 5.4380$			
Cp1	+0.001	Cp4	+0.003
Cp2	+0.001	Cp5	-0.002
Cp3	-0.002		
Cyclopentadienyl Ring Cp6, Cp7, Cp8, Cp9, Cp10			
$-0.9687x + 0.2410y + 0.0595z = -2.2844$			
Cp6	-0.004	Cp9	-0.002
Cp7	+0.003	Cp10	+0.004
Cp8	0.000		
Polyhedral Plane C3, B4, B9, B10			
$-0.9889x + 0.1173y - 0.0914z = -1.2141$			
C3	+0.015	B9	-0.024
B4	-0.015	B10	+0.024
Polyhedral Plane C3, B4, B5, B7			
$0.4337x + 0.6558y + 0.6179z = 7.9873$			
C3	+0.017	B5	-0.018
B4	-0.016	B7	+0.017

^a Planes are defined as $C_1x + C_2y + C_3z = d$, where z, y, x are orthogonal coordinates (in Ångströms) and the axes parallel a, b , and c^* .

alized structure found for other ten-vertex closo borane species such as $B_{10}H_{10}^{2-}$,¹⁹ $(CH_3)_2C_2B_8H_8$,²⁰ and $(C_5H_5)_2Co_2C_2B_6H_8$.²¹ Despite its unusual structure, $(C_5H_5)_2Fe_2C_2B_6H_8$ is still classified as a closo metallocarborane, for it adopts a fully triangulated closed polyhedral structure.²² The polyhedral framework can be viewed in several ways.

The geometry may be described in terms of a rearranged bicapped square antiprism in which an equatorial bond has been broken and replaced by a new bond between one apex and an atom in the second equatorial belt from this apex. With reference to Figure 1, the broken bond would be C3–B4, and the new bond would be Fe1–Fe6.

An alternate geometrical description relates this compound to the next larger polyhedron, the 11-vertex octadecahedral geometry exhibited by compounds such as 2,3- $C_2B_9H_{11}$,²³ and $(C_5H_5)CoC_2B_8H_{10}$.¹⁰ The structure of the iron compound is related to these species by the formal removal of one of the two low-coordinate vertices of the octadecahedron and creation of a new bond between the unique high-coordinate atom and the coordinatively unsaturated basal boron atom.

A third approach to the geometrical description of this compound involves the next lower coordination polyhedron, the nine-vertex tricapped trigonal prism observed in $C_2B_7H_9$.²⁴ Several groups of six atoms in $(C_5H_5)_2Fe_2C_2B_6H_8$ adopt geometries close to that of a trigonal prism, and the remaining four atoms are located in positions describable as caps around this geometry, one of the caps having additional connectivity to a trigonal face of the prism.

Structural Comparisons

The crystal and molecular structure of the analogous bicobaltacarborane, $(C_5H_5)_2Co_2C_2B_6H_8$, has recently been reported.²¹ This compound has two more electrons than does $(C_5H_5)_2Fe_2C_2B_6H_8$, and consistent with the $2n + 2$ rule²⁵ it adopts a distorted, but still recognizable, bicapped square antiprismatic geometry. The cobalt–cobalt bond is a rather short 2.489 (1) Å, and the polyhedral carbon atoms occupy low-coordinate apical vertices, while the two cobalt

atoms are located in adjacent equatorial high-coordinate polyhedral positions.

In $(C_5H_5)_2Fe_2C_2B_6H_8$, severe distortions from the idealized bicapped square antiprismatic geometry are found. These distortions, however, permit the polyhedral atoms to attain their preferred coordination numbers. If bicapped square antiprismatic geometry were adopted in $(C_5H_5)_2Fe_2C_2B_6H_8$, in which the Fe–Fe bond is broken and a new bond created between C3 and B4, Fe6 would reside in an undesirable low-coordinate apical position, while C3 would be located at an equally unfavorable six-coordinate equatorial vertex. The distortions from this idealized symmetry observed in this structure permit C3 to occupy a five-coordinate position, while Fe6 is bonded to five other polyhedral atoms.

Other ten-vertex closed polyhedral species have been crystallographically studied including $B_{10}H_{10}^{2-}$ as its Cu(I) salt,¹⁹ $(CH_3)_2C_2B_8H_8$,²⁰ and $[Co(C_2B_7H_9)_2]^-$.²⁶ In each of these species, which are isoelectronic with each other and with the previously discussed $(C_5H_5)_2Co_2C_2B_6H_8$, a bicapped square antiprismatic geometry is observed. Bond distances in these compounds and in $(C_5H_5)_2Fe_2C_2B_6H_8$, which are comparable in terms of types of elements and coordination numbers of the atoms, show no major differences.

Discussion

It is attractive to extrapolate from the structure back to a possible geometry for the paramagnetic isomer. The easiest way to produce a paramagnetic compound from this geometry would be to break the bond between the two metals, producing a nido structure containing an "open" four-membered face as postulated for $B_{10}H_{10}^{2-}$ in the presence of electrophilic cations.²⁷ Interestingly, such a structure would resemble the octadecahedral $C_2B_9H_{11}$ after a low-coordinate vertex had been removed, which was one description of the geometry of this diamagnetic compound (*vide supra*). Such a geometry is inconsistent with the ¹¹B nmr spectrum of the paramagnetic isomer, however, which indicates that all of the polyhedral boron atoms are bonded to iron atoms.

Another possible way to explain the paramagnetic to diamagnetic isomerization of this compound would involve the rearrangement of a bicapped square antiprismatic structure, as discussed previously. Such a rearrangement, to produce the disrupted geometry observed here, would be favored by the changes in coordination numbers of the carbon and iron atoms. Again, however, the structure of the paramagnetic isomer thus derived would have one boron atom not bonded to an iron vertex, in conflict with ¹¹B nmr data. It is quite conceivable that the paramagnetic to diamagnetic isomerization may also involve rearrangements of the heteroatoms, as observed in other metallocarboranes,²⁸ from a paramagnetic isomer in which all boron atoms are bonded to iron atoms to the structure of the diamagnetic isomer observed here. Consequently, only a crystallographic study of the paramagnetic isomer will permit complete elucidation of this unusual system. This work is now in progress.

Examination of the structure of $(C_5H_5)_2Fe_2C_2B_6H_8$ as a capped tricapped trigonal prism appears significant in a chemical sense when one considers the skeletal electronic bonding requirements of closo borane polyhedra. In general, an n -vertex closo borane requires $2n + 2$ electrons for skeletal bonding.²⁵ Hence, $B_{10}H_{10}^{2-}$, $CB_9H_{10}^-$, $C_2B_8H_{10}$, $C_5H_5CoC_2B_7H_9$, and $(C_5H_5)_2Co_2C_2B_6H_8$ have 22 framework electrons, the proper number for a ten-vertex polyhedron, and these isoelectronic species have structures based on the regular ten-vertex polyhedron, the bicapped square antiprism. In $(C_5H_5)_2Fe_2C_2B_6H_8$, although it has ten vertices, there are only 20 electrons available for skele-

tal bonding, a consequence of the inclusion of two iron vertices in the polyhedron. For $2n + 2 = 20$, an $n =$ nine-vertex structure might be expected. Therefore, the fact that $(C_5H_5)_2Fe_2C_2B_6H_8$ resembles a capped tricapped trigonal prism is consistent with electronic bonding requirements for this species.

A similar approach to the structures of electron deficient polyhedral molecules, *i.e.*, employment of capped polyhedra, has been used in metal cluster chemistry.²⁹ The recently investigated $Os_6(CO)_{18}$, for example, has an insufficient number of skeletal electrons for a six-vertex octahedral structure. Consequently, this species is found to have a bicapped tetrahedral geometry, in which the skeletal bonding requirements of the basic polyhedron, here the tetrahedron, are satisfied. Similar results obtain for $Os_7(CO)_{21}$, where a capped octahedral geometry has been found. Hence the observation of capped polyhedra in metallocarborane chemistry could be another manifestation of the similarities in polyhedral boranes and transition metal clusters.

Experimental Section

Electrochemical data were obtained with an instrument previously described, equipped with a platinum button electrode. All measurements were made in acetonitrile with 0.1 *M* tetraethylammonium perchlorate as a supporting electrolyte. The visible-ultraviolet and infrared spectra were measured on a Beckman DB and a Perkin-Elmer 137 sodium chloride spectrophotometer, respectively. An instrument designed and built by Professor F. A. L. Anet and coworkers was used to measure 80.5-MHz ¹¹B nmr spectra. Mass spectra were obtained with an Associated Electrical Industries MS-9 spectrometer. Elemental analysis was carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

Anhydrous sublimed ferric chloride and hydrogen-reduced iron powder were obtained from Matheson Coleman and Bell. Preparative thick-layer chromatography was performed on ChromAR-Sheet 1000 purchased from Mallinckrodt Chemical Co. Tetrahydrofuran (THF) was freshly distilled from LiAlH₄. NaC₅H₅ was prepared from freshly distilled C₅H₆, obtained from Aldrich Chemical Co., and sodium hydride in THF; the THF solution of NaC₅H₅ was decanted into the reaction mixture. Literature methods were used to prepare 4,5-C₂B₇H₉.³⁰

Ferracarboranes from 4,5-C₂B₇H₉. The reduction of 4,5-C₂B₇H₉ (1.413 g, 12.9 mmol) in a 500-ml three-neck flask was carried out as previously described.² NaC₅H₅ (65 mmol) and a gray slurry of FeCl₂ in THF, prepared by reaction of iron powder (2.9 g, 52 mmol) and FeCl₃ (8.4 g, 52 mmol) in 100 ml of THF at reflux for 3 hr, were added to the flask. After 30 min, the nitrogen inlet was removed and the reaction mixture was stirred in air for 1 min. The solution was poured onto silica gel (30 ml) and the THF was removed on a rotary evaporator. The solids were chromatographed on deoxygenated silica gel in nitrogen-saturated solvents. Ferrocene and a brown-red band were initially eluted with hexane.

(a) **4-(η -C₅H₅)-4,1,8-FeC₂B₆H₈ (I).** A red-brown band was eluted with hexane and contained 40 mg (0.2 mmol, 1.5%) of the previously described² compound.

(b) **1-(η -C₅H₅)-1,4,6-FeC₂B₆H₈ (II).** Elution with hexane-CH₂Cl₂ (9:1 v/v) allowed the separation of another red-brown fraction containing 0.227 g (1.0 mmol, 8.1%) of 1-(η -C₅H₅)-1,4,6-FeC₂B₆H₈.² Ultimate purification of I and II required multiple-elution thick-layer chromatography in hexane.

(c) **(C₅H₅)₂Fe₂C₂B₆H₈ (III).** A green band was next eluted with hexane-CH₂Cl₂ (8:2 v/v). Purification by thick-layer chromatography followed by recrystallization from hexane-CH₂Cl₂ afforded 0.234 g (0.7 mmol, 5.4%) of III, mp 212–215° dec. *Anal.* Calcd for (C₅H₅)₂Fe₂C₂B₆H₈: B, 19.14; C, 42.54; H, 5.35; Fe, 32.96. Found: B, 19.16; C, 42.44; H, 5.47; Fe, 32.75. Uv-visible spectrum (acetonitrile solvent) [λ_{max} , nm (log ϵ)] 244 (4.24), 308 (3.82), 420 sh

(3.18), 648 (2.67); ir (cm⁻¹, Nujol mull) 2890 vs, 2500 s, 1470 vs, 1420 m, 1375 s, 1150 w, 1110 m, 1080 w, 1040 w, 1010 m, 970 w, 950 w, 930 w, 900 w, 890 w, 860 m, 840 m, 820 m, 800 w, 725 s.

(d) **1-(η -C₅H₅)-1,2,3-FeC₂B₆H₁₀ (IV).** Continued elution with hexane-CH₂Cl₂ allowed the separation of a red-brown band. Recrystallized from hexane-CH₂Cl₂ was 0.193 g (0.8 mmol, 6.2%) of the previously described² 1-(η -C₅H₅)-1,2,3-FeC₂B₆H₁₀.

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Supplementary Material Available. A listing of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-296.

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