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Tetracarbon Metallocarboranes. 3. Crystal Structure of a Closo 14-Vertex Cage, 1,14,2,5,9,12-(η^5-C_5H_5)$_2Fe_2(CH_3)_4C_4B_8H_8$, a Bicapped Hexagonal Antiprism[1]

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The structure of the title compound was determined by single-crystal x-ray diffraction and found to consist of a 14-vertex $Fe_2C_4B_8$ closo cage with the geometry of a bicapped hexagonal antiprism of idealized D_{2d} symmetry. The iron atoms occupy the two high-coordinate vertices at opposite ends of the molecule, and the four cage carbon atoms are arranged in staggered fashion in the two equatorial rings such that the mutual C–C separations are maximized; there are no carbon–carbon bonds in the polyhedron. The structure is in agreement with that proposed earlier from NMR data and represents the thermodynamically favored geometry for this system. The two C_5H_5 rings are planar but the two $(CH_3)_2C_2B_4H_4$ rings are not quite planar, with the carbon atoms in each case drawn slightly out-of-plane in the direction of the other ring. All four rings are parallel within 1°. The molecule crystallizes in space group *Pbca* with $a = 18.595$ (4) Å, $b = 13.826$ (5) Å, $c = 16.139$ (6) Å, $V = 4149$ (2) Å^3, and $d_{\text{calcd}} = 1.437$ g cm^{-3} for $Z = 8$. The structure was refined by full-matrix least-squares methods to a final R value of 0.059 for the 2226 reflections for which $F_o^2 > 3\sigma(F_o^2)$.

Introduction

In earlier papers[1,2] it was reported that four isomers of a diiron 14-vertex metallocarborane, (η^5-C_5H_5)$_2Fe_2(CH_3)_4C_4B_8H_8$, are formed on reaction of the $(CH_3)_4C_4B_8H_8^{2-}$ dianion with $FeCl_2$ and NaC_5H_5 in THF below 25 °C. X-ray diffraction studies[1] of two of these isomers (I and II) and of a third isomer (V), which is formed on thermal rearrangement of I and II, revealed that all of these species have irregular open-cage (nido) structures with four- or five-membered open faces. These molecules contain 30 skeletal valence electrons and thus violate the skeletal electron-counting theory[3] which predicts closo structures (polyhedra with all sides triangular) for n-vertex cages with $2n + 2$ framework electrons. However, at 300 °C V is converted to a new isomer VII, which in turn yields the final rearrangement product VIII. From ^{11}B and ^{1}H NMR spectra both VII and VIII were assigned closo structures based on a bicapped hexagonal antiprism with the iron atoms occupying the apex positions and the boron and carbon atoms distributed among the two six-membered equatorial rings.[1] Since isomer VIII exhibited only one ^{11}B NMR resonance, as well as one C_5H_5 peak and one CH_3 signal in the ^{1}H NMR spectrum, the D_{2d} geometry with cage carbons in staggered, nonadjacent locations appeared to be uniquely established. However, no previous examples of a bicapped hexagonal-antiprismatic cluster of any type had been crystallographically characterized. Consequently, it was deemed worthwhile to conduct an x-ray investigation of VIII, both to confirm the assigned structure and to provide distances and angles in this prototypal 14-vertex closo system.

Experimental Section

One crystal of 1,14,2,5,9,12-$(C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$ (isomer VIII) was grown by rapid evaporation at room temperature from a methylene chloride–nonane solution. The multifaceted diamond-shaped green crystal had maximum dimensions of 0.19 × 0.44 × 0.74 mm and was mounted along the long dimension which subsequently proved to be the a axis of the chosen unit cell. Since only one crystal was available, a density measurement was not made. Crystal data: $Fe_2C_{18}B_8H_{30}$; mol wt 444.6; space group *Pbca* (No. 61); $Z = 8$; $a = 18.595$ (4), $b = 13.826$ (5), $c = 16.139$ (6) Å; $V = 4149$ (2) Å^3; μ(Mo Kα) = 14.48 cm^{-1}; ρ(calcd) = 1.437 g/cm^3; $F(000) = 1840$. For this crystal 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 18.5 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 monochromator. The θ–2θ scan technique was used to record the intensities for all reflections for which $1° \leq 2\theta \leq 48°$. 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 0.85 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 2577 intensities of which 2226 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.[4] These latter reflections were used in the final refinement of the structural parameters.

Solution and Refinement of the Structure. The coordinates of the two iron atoms were determined from a somewhat vague three-dimensional Patterson map. An electron density map phased on the refined coordinates of the Fe atoms yielded 20 of the 26 remaining nonhydrogen atoms. A second map phased on 22 atoms revealed the remaining six carbon and boron atoms. At this point an absorption correction was made (maximum and minimum transmission coefficients were 0.873 and 0.762, respectively). Several cycles of least-squares refinement with all atoms anisotropic reduced R to 0.074 and R_w to 0.088. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum(|F_o| - |F_c|)^2/\sum|F_o|^2)^{1/2}$. Another electron density map was calculated and from it the positions of four of the eight B–H cage hydrogen atoms were determined. Further refinement which included these cage hydrogens with fixed thermal parameters ($B = 5.0$ Å^2) and also the methyl hydrogens (fixed at calculated positions of 0.95 Å from the carbon, $B = 5.0$ Å^2) reduced R to 0.063. Another map yielded two additional cage hydrogen atoms, but the positions of the remaining two had to be calculated. Further refinement, following recalculation of the positions of the methyl hydrogens to reset them to 0.95 Å, resulted in a final $R = 0.059$ and $R_w = 0.066$. The error in an observation of unit weight was 2.9, and the largest parameter shift in the final cycle of refinement was 0.16 times its estimated standard deviation. The data to parameter ratio was 2226/277 = 8.0, and the value of R including reflections for which $F_o^2 < 3\sigma(F_o^2)$ was 0.067.

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[5] and those for hydrogen from Stewart.[6] The effects of anomalous dispersion were included in F_c using Cromer and Ibers'[7] values of $\Delta f'$ and $\Delta f''$. The

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}
Fe1	−0.00621 (4)	0.21483 (6)	0.19164 (5)	0.00098 (2)	0.00518 (4)	0.00351 (3)	0.00084 (5)	−0.00047 (5)	0.00028 (8)
Fe14	−0.19646 (4)	0.23699 (7)	0.06110 (5)	0.00086 (2)	0.00742 (6)	0.00319 (3)	0.00080 (6)	−0.00021 (5)	−0.00033 (8)
C2	−0.0329 (3)	0.3049 (4)	0.0856 (3)	0.0013 (2)	0.0049 (3)	0.0030 (2)	−0.0008 (4)	−0.0000 (3)	0.0013 (5)
C5	−0.1083 (3)	0.1403 (4)	0.2093 (3)	0.0016 (2)	0.0052 (3)	0.0035 (2)	−0.0001 (4)	−0.0001 (4)	0.0015 (5)
C9	−0.1595 (3)	0.3163 (5)	0.1697 (3)	0.0014 (2)	0.0062 (4)	0.0034 (3)	0.0023 (4)	−0.0008 (3)	−0.0014 (5)
C12	−0.1040 (3)	0.1424 (4)	0.0410 (3)	0.0014 (2)	0.0055 (4)	0.0033 (2)	0.0004 (4)	0.0006 (4)	−0.0012 (5)
CM2	0.0231 (4)	0.3736 (5)	0.0482 (4)	0.0023 (2)	0.0075 (4)	0.0061 (4)	−0.0025 (5)	0.0005 (5)	0.0014 (7)
CM5	−0.1158 (4)	0.0659 (5)	0.2790 (4)	0.0028 (2)	0.0086 (5)	0.0053 (3)	−0.0010 (6)	0.0012 (5)	0.0039 (7)
CM9	−0.2062 (4)	0.3952 (5)	0.2091 (4)	0.0026 (2)	0.0082 (5)	0.0057 (3)	0.0049 (5)	−0.0005 (5)	−0.0022 (7)
CM12	−0.1044 (4)	0.0696 (5)	−0.0306 (4)	0.0025 (2)	0.0075 (5)	0.0052 (3)	0.0002 (5)	0.0007 (5)	−0.0037 (6)
CP11	0.1036 (3)	0.1915 (7)	0.1836 (5)	0.0012 (2)	0.0164 (8)	0.0067 (4)	0.0015 (7)	−0.0016 (5)	0.0017 (10)
CP12	0.0894 (4)	0.2795 (6)	0.2181 (6)	0.0045 (3)	0.0079 (5)	0.0144 (6)	−0.0031 (7)	−0.0119 (6)	0.0065 (10)
CP13	0.0530 (4)	0.2661 (8)	0.2919 (5)	0.0045 (3)	0.0233 (8)	0.0103 (4)	0.0140 (7)	−0.0109 (5)	−0.0212 (9)
CP14	0.0423 (4)	0.1677 (10)	0.2983 (4)	0.0021 (2)	0.0337 (14)	0.0036 (3)	0.0013 (10)	−0.0024 (5)	0.0099 (11)
CP15	0.0731 (4)	0.1225 (6)	0.2326 (6)	0.0028 (2)	0.0080 (5)	0.0119 (5)	0.0002 (6)	−0.0076 (6)	0.0064 (9)
CP141	−0.2422 (4)	0.2337 (9)	−0.0547 (4)	0.0019 (2)	0.0263 (11)	0.0039 (3)	0.0052 (8)	−0.0024 (5)	−0.0040 (10)
CP142	−0.2561 (4)	0.3217 (7)	−0.0189 (6)	0.0024 (2)	0.0182 (8)	0.0106 (4)	−0.0021 (8)	−0.0069 (5)	0.0143 (11)
CP143	−0.2949 (4)	0.3045 (7)	0.0543 (6)	0.0032 (2)	0.0155 (7)	0.0107 (5)	0.0083 (7)	−0.0082 (5)	−0.0083 (11)
CP144	−0.3053 (4)	0.2057 (8)	0.0607 (5)	0.0011 (2)	0.0220 (10)	0.0059 (4)	−0.0014 (8)	−0.0024 (5)	0.0044 (11)
CP145	−0.2717 (4)	0.1603 (7)	−0.0064 (6)	0.0024 (2)	0.0140 (7)	0.0102 (5)	0.0019 (7)	−0.0062 (6)	−0.0074 (11)
B3	−0.0681 (4)	0.3402 (5)	0.1749 (4)	0.0017 (2)	0.0042 (4)	0.0044 (3)	0.0008 (5)	−0.0009 (4)	0.0000 (6)
B4	−0.1076 (3)	0.2535 (5)	0.2396 (4)	0.0014 (2)	0.0061 (4)	0.0032 (3)	0.0012 (5)	0.0005 (4)	0.0002 (6)
B6	−0.0595 (4)	0.1020 (5)	0.1281 (4)	0.0017 (2)	0.0042 (4)	0.0041 (3)	0.0010 (5)	0.0009 (4)	−0.0002 (6)
B7	−0.0208 (3)	0.1889 (5)	0.0643 (4)	0.0010 (2)	0.0063 (4)	0.0032 (3)	0.0003 (5)	0.0006 (4)	−0.0004 (6)
B8	−0.1202 (4)	0.3469 (5)	0.0814 (4)	0.0015 (2)	0.0052 (4)	0.0039 (3)	0.0017 (5)	−0.0000 (4)	0.0011 (6)
B10	−0.1841 (3)	0.2046 (6)	0.1875 (4)	0.0012 (2)	0.0081 (5)	0.0029 (3)	−0.0004 (5)	0.0001 (4)	0.0005 (7)
B11	−0.1562 (4)	0.1135 (5)	0.1214 (4)	0.0016 (2)	0.0050 (4)	0.0041 (3)	−0.0013 (5)	−0.0001 (4)	0.0000 (6)
B13	−0.0909 (4)	0.2567 (5)	0.0143 (4)	0.0015 (2)	0.0063 (4)	0.0027 (3)	0.0001 (5)	0.0000 (4)	0.0006 (6)

Atom[b]	x	y	z	Atom[b]	x	y	z
HB3	−0.056 (3)	0.416 (4)	0.198 (3)	HC23	0.063 (0)	0.337 (0)	0.030 (0)
HB4	−0.128 (3)	0.267 (4)	0.308 (3)	HC51	−0.163 (0)	0.040 (0)	0.279 (0)
HB6	−0.044 (3)	0.028 (4)	0.121 (3)	HC52	−0.082 (0)	0.015 (0)	0.271 (0)
HB7	0.019 (3)	0.168 (4)	0.022 (3)	HC53	−0.107 (0)	0.097 (0)	0.331 (0)
HB8	−0.126 (3)	0.425 (4)	0.056 (3)	HC91	−0.182 (0)	0.422 (0)	0.255 (0)
HB10	−0.229 (3)	0.189 (4)	0.234 (3)	HC92	−0.215 (0)	0.445 (0)	0.169 (0)
HB11	−0.176 (3)	0.047 (4)	0.121 (3)	HC93	−0.251 (0)	0.368 (0)	0.226 (0)
HB13	−0.078 (3)	0.277 (4)	−0.048 (3)	HC121	−0.060 (0)	0.034 (0)	−0.031 (8)
HC21	0.003 (0)	0.407 (0)	0.003 (0)	HC122	−0.143 (0)	0.026 (0)	−0.024 (0)
HC22	0.038 (0)	0.419 (0)	0.089 (0)	HC123	−0.109 (0)	0.103 (0)	−0.082 (0)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] $B = 5.000\ (0)\ \text{Å}^2$.

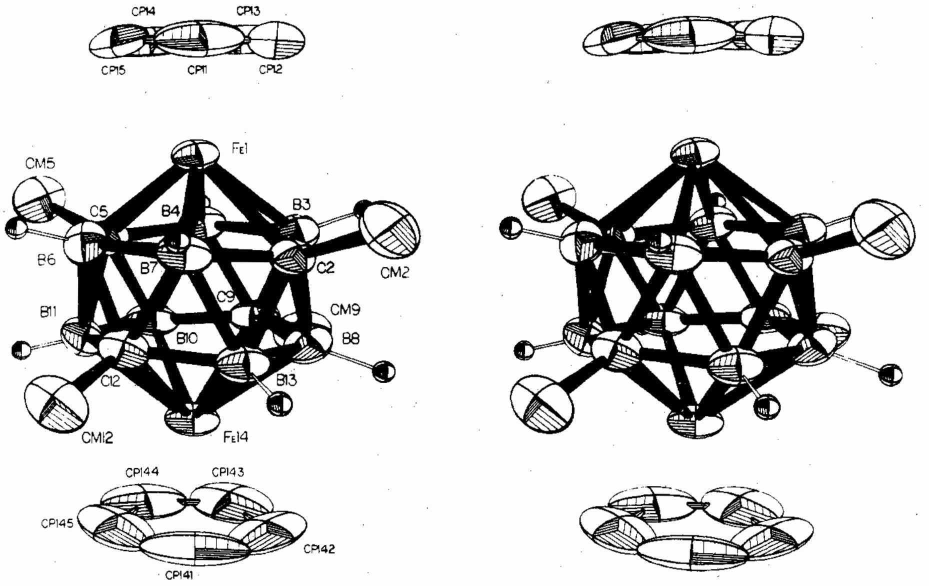

Figure 1. Stereoview of the molecule showing numbering system.

computing system and programs are described elsewhere.[8]

Results and Discussion

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. Figure 1 is a stereoscopic view of the molecule, and Figure 2 shows the relative orientation of the four rings as viewed along the

Table II. Interatomic·Distances (A)

Fe1–Fe14	4.129 (1)	B7–B13	1.796 (6)
Fe1–C2	2.174 (3)	C2–CM2	1.534 (5)
Fe1–C5	2.178 (4)	C5–CM5	1.531 (5)
Fe14–C9	2.179 (4)	C9–CM9	1.533 (5)
Fe14–C12	2.184 (4)	C12–CM12	1.533 (5)
Fe1–B3	2.098 (4)	Fe1–CP11	2.071 (4)
Fe1–B4	2.108 (4)	Fe1–CP12	2.035 (5)
Fe1–B6	2.113 (5)	Fe1–CP13	2.082 (6)
Fe1–B7	2.105 (4)	Fe1–CP14	2.049 (5)
Fe14–B8	2.103 (5)	Fe1–CP15	2.060 (4)
Fe14–B10	2.101 (4)	Fe14–CP141	2.053 (5)
Fe14–B11	2.102 (5)	Fe14–CP142	2.066 (5)
Fe14–B13	2.121 (4)	Fe14–CP143	2.058 (5)
C2–B3	1.656 (6)	Fe14–CP144	2.070 (5)
B3–B4	1.751 (6)	Fe14–CP145	2.066 (5)
B4–C5	1.639 (6)	CP11–CP12	1.36 (1)
C5–B6	1.679 (5)	CP12–CP13	1.38 (1)
B6–B7	1.738 (6)	CP13–CP14	1.38 (1)
B7–C2	1.656 (6)	CP14–CP15	1.36 (1)
B8–C9	1.656 (6)	CP11–CP15	1.36 (1)
C9–B10	1.635 (6)	CP141–CP142	1.37 (1)
B10–B11	1.730 (7)	CP142–CP143	1.40 (1)
B11–C12	1.669 (5)	CP143–CP144	1.38 (1)
C12–B13	1.656 (6)	CP144–CP145	1.40 (1)
B13–B8	1.740 (6)	CP141–CP145	1.39 (1)
C2–B8	1.725 (5)	B3–H3	1.14 (4)
C2–B13	1.712 (5)	B4–H4	1.19 (4)
B3–B8	1.796 (6)	B6–H6	1.07 (4)
B3–C9	1.734 (5)	B7–H7	1.05 (4)
B4–C9	1.719 (5)	B8–H8	1.16 (4)
B4–B10	1.785 (6)	B10–H10	1.15 (4)
C5–B10	1.704 (5)	B11–H11	0.99 (4)
C5–B11	1.717 (5)	B13–H13	1.07 (4)
B6–B11	1.809 (6)	⟨B–H⟩	1.10
B6–C12	1.724 (5)	⟨B–B⟩	1.769
B7–C12	1.716 (5)	⟨B–C⟩	1.687

Table III. Bond Angles (deg)

C2–Fe1–B3	45.6 (2)	Fe14–C9–B8	64.9 (2)
B3–Fe1–B4	49.2 (2)	Fe14–C9–B10	65.0 (2)
B4–Fe1–C5	44.9 (2)	B8–C9–B3	63.9 (2)
C5–Fe1–B6	46.0 (1)	B10–C9–B4	64.2 (2)
B6–Fe1–B7	48.7 (2)	B3–C9–B4	61.0 (2)
C2–Fe1–B7	45.5 (2)	B8–C9–B10	121.0 (3)
B8–Fe14–C9	45.5 (2)	Fe14–C9–CM9	120.9 (2)
C9–Fe14–B10	44.9 (2)	B8–C9–CM9	115.1 (3)
B10–Fe14–B11	48.6 (2)	B10–C9–CM9	116.2 (3)
B11–Fe14–C12	45.8 (2)	B3–C9–CM9	113.5 (3)
C12–Fe14–B13	45.2 (2)	B4–C9–CM9	113.9 (3)
B8–Fe14–B13	48.6 (2)	Fe14–B10–C9	70.1 (2)
Fe1–C2–B3	64.8 (2)	Fe14–B10–B11	65.7 (2)
Fe1–C2–B7	65.0 (2)	B4–B10–C9	60.1 (2)
B3–C2–B8	64.1 (2)	C5–B10–B11	60.0 (2)
B7–C2–B13	64.4 (2)	B4–B10–C5	56.0 (2)
B8–C2–B13	60.8 (2)	C9–B10–B11	119.7 (3)
B3–C2–B7	121.3 (2)	Fe14–B11–B10	65.6 (2)
Fe1–C2–CM2	120.6 (3)	Fe14–B11–C12	69.7 (2)
B3–C2–CM2	115.4 (3)	C5–B11–B10	59.2 (2)
B7–C2–CM2	115.2 (3)	B6–B11–C12	59.2 (2)
B8–C2–CM2	114.6 (3)	C5–B11–B6	56.8 (2)
B13–C2–CM2	113.8 (3)	B10–B11–C12	118.6 (3)
Fe–B3–C2	69.7 (2)	Fe14–C12–B11	64.5 (2)
Fe–B3–B4	65.7 (2)	Fe14–C12–B13	65.4 (2)
B4–B3–C9	59.1 (2)	B6–C12–B11	64.4 (2)
C2–B3–B8	59.8 (2)	B6–C12–B7	60.7 (2)
B8–B3–C9	55.9 (2)	B11–C12–B13	121.1 (3)
C2–B3–B4	118.9 (3)	Fe14–C12–CM12	120.1 (3)
Fe1–B4–C5	69.8 (2)	B11–C12–CM12	115.2 (3)
Fe1–B4–B3	65.1 (2)	B13–C12–CM12	115.5 (3)
C5–B4–B10	59.5 (2)	B6–C12–CM12	113.8 (3)
B3–B4–C9	59.9 (2)	B7–C12–CM12	114.5 (3)
C9–B4–B10	55.6 (2)	Fe14–B13–C12	69.4 (2)
B3–B4–C5	118.6 (3)	Fe14–B13–B8	65.1 (2)
Fe1–C5–B6	65.0 (2)	C2–B13–B8	60.0 (2)
Fe1–C5–B4	65.3 (2)	B7–B13–C12	59.4 (2)
B6–C5–B11	64.4 (2)	B7–B13–C2	56.3 (2)
B4–C5–B10	64.5 (2)	C12–B13–B8	118.4 (3)
B10–C5–B11	60.8 (2)	CP11–Fe1–CP12	38.8 (3)
B4–C5–B6	122.0 (3)	CP12–Fe1–CP13	39.2 (3)
Fe1–C5–CM5	119.6 (3)	CP13–Fe1–CP14	39.0 (3)
B4–C5–CM5	115.0 (3)	CP14–Fe1–CP15	38.6 (3)
B6–C5–CM5	114.3 (3)	CP11–Fe1–CP15	38.5 (2)
B10–C5–CM5	115.3 (3)	CP141–Fe14–CP142	38.9 (3)
B11–C5–CM5	114.5 (3)	CP142–Fe14–CP143	39.8 (3)
Fe1–B6–B7	65.4 (2)	CP143–Fe14–CP144	39.2 (3)
Fe1–B6–C5	69.0 (2)	CP144–Fe14–CP145	39.5 (2)
B7–B6–C12	59.4 (2)	CP141–Fe14–CP145	39.5 (3)
C5–B6–B11	58.8 (2)	CP12–CP11–CP15	107.9 (6)
B11–B6–C12	56.3 (2)	CP11–CP12–CP13	109.1 (7)
C5–B6–B7	117.9 (3)	CP12–CP13–CP14	105.4 (6)
Fe1–B7–C2	69.5 (2)	CP13–CP14–CP15	109.6 (7)
Fe1–B7–B6	65.9 (2)	CP14–CP15–CP11	107.8 (6)
C2–B7–B13	59.3 (2)	CP142–CP141–CP145	109.7 (7)
B6–B7–C12	59.9 (2)	CP141–CP142–CP143	107.5 (7)
C12–B7–B13	56.2 (2)	CP142–CP143–CP144	107.5 (7)
B6–B7–C2	119.3 (3)	CP143–CP144–CP145	108.9 (6)
Fe14–B8–C9	69.7 (2)	CP144–CP145–CP141	106.4 (6)
Fe14–B8–B13	66.2 (2)	⟨Fe–B–H⟩	127 (2)
C9–B8–B3	60.1 (2)	⟨B–B–H⟩^{a}	121 (2)
B13–B8–C2	59.2 (3)	⟨B–B–H⟩^{b}	110 (2)
C2–B8–B3	56.0 (2)	⟨C–B–H⟩^{a}	119 (2)
C9–B8–B13	119.4 (3)	⟨C–B–H⟩^{b}	112 (2)

[a] Boron (or carbon) atoms in the same C_2B_4 ring. [b] Boron (or carbon) atoms in different C_2B_4 rings.

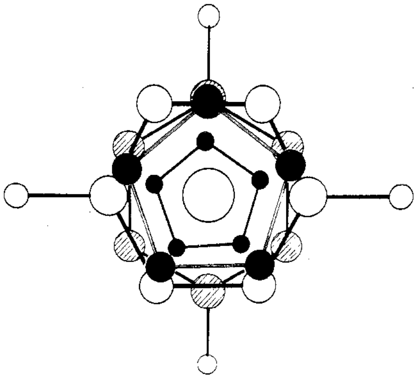

Figure 2. View down the Fe–Fe axis showing the relative orientation of the four rings. Atoms in the cyclopentadienyl rings are shown as solid black, those in the upper (nearer) C_2B_4 ring are white, and those in the lower C_2B_4 ring are shaded.

Fe–Fe vector. A diagram of the unit-cell packing is given in Figure 3.

The molecular geometry is in agreement with the structure originally deduced from ^{11}B and ^1H NMR observations.[1] The 14-vertex central cage has idealized D_{2d} symmetry with the cage carbon atoms achieving maximum mutual separation, in accordance with the experimental observation[1] that this is the most thermodynamically stable arrangement for the $(C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$ system. Although there is no crystallographically imposed symmetry, the bond distances and angles exhibit remarkable regularity. The two cyclopentadienyl rings are planar and parallel and are in an eclipsed configuration relative to each other. The two equatorial C_2B_4 rings are not quite planar; in each case the carbon atoms are ~0.14 Å out of the plane formed by the four boron atoms, due to the fact that the inter-ring B–C bonds are necessarily shorter than the inter-ring B–B links. The four rings—two C_5H_5 and two C_2B_4—are all parallel within 1°, and these together with the two iron atoms form a kind of quadridecker sandwich[9] which is 7.518 Å from end to end. The average Fe–C_2B_4 and Fe–C_5H_5 distances (vectors normal to the planes of the rings) are respectively 1.309 and 1.695 Å, reflecting the fact that the metal atoms must approach the six-membered ring planes more closely in order to achieve reasonable Fe–cage bond distances.[10] The Fe–Fe distance is 4.129 (1) Å, interestingly only ~0.3 Å greater than the metal–metal

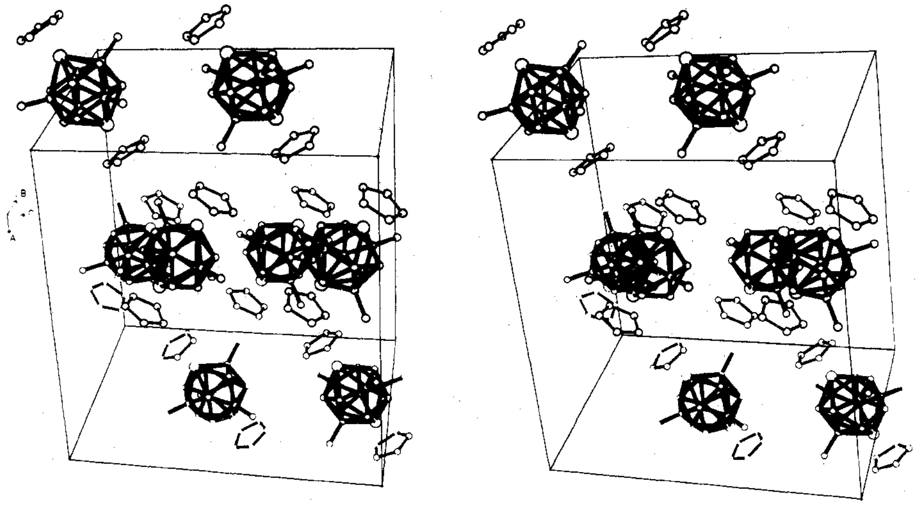

Figure 3. Stereoview of unit cell contents.

Table IV. Selected Intramolecular Planes

Atom	Dev, Å	Atom	Dev, Å
Plane 1: B3, B4, B6, B7			
$-0.8555x + 0.0760y - 0.5121z = -0.0030$			
B3	−0.002	C2	0.140
B4	0.002	C5	0.143
B6	−0.002	Fe1	−1.26
B7	0.002	Fe14	2.87
Plane 2: B8, B10, B11, B13			
$-0.8559x + 0.0754y - 0.5115z = 1.5997$			
B8	0.004	C9	−0.133
B10	−0.004	C12	−0.135
B11	0.004	Fe14	1.27
B13	−0.004	Fe1	−2.86
Plane 3: CP11, CP12, CP13, CP14, CP15			
$0.8600x - 0.0719y + 0.5052z = 2.9486$			
CP11	−0.014	CP14	0.006
CP12	0.018	CP15	0.005
CP13	−0.015	Fe1	1.70
Plane 4: CP141, CP142, CP143, CP144, CP145			
$-0.8524x + 0.0687y - 0.5183z = 4.5184$			
CP141	0.000	CP144	0.009
CP142	0.005	CP145	−0.006
CP143	−0.009	Fe14	−1.69
Plane 5: Fe1, Fe14, C2, C5, CM2, CM5			
$-0.3043x + 0.7257y + 0.6170z = 4.0987$			
Fe1	0.000	C5	−0.006
Fe14	0.001	CM2	0.001
C2	0.000	CM5	0.004
Plane 6: Fe1, Fe14, C9, C12, CM9, CM12			
$0.4147x + 0.6879y - 0.5956z = 0.1533$			
Fe1	0.000	C12	0.005
Fe14	−0.002	CM9	0.005
C9	−0.007	CM12	−0.001

Planes	Dihedral angle, deg	Planes	Dihedral angle, deg
1,2	0.06	2,6	89.91
1,3	0.53	3,4	0.88
1,4	0.57	3,5	90.12
1,5	89.97	3,6	90.36
1,6	89.86	4,5	89.40
2,3	0.47	4,6	89.86
2,4	0.58	5,6	90.31
2,5	89.97		

Table V. Intermolecular Contacts ≤3.8 Å

Atoms	Distance, Å	Relation
CP13-CP144	3.65	$^1/_2 + x, y, ^1/_2 - z$
CP14-CP144	3.67	$^1/_2 + x, y, ^1/_2 - z$
CP11-CP141	3.69	$^1/_2 + x, ^1/_2 - y, -z$
CP11-CP142	3.73	$^1/_2 + x, ^1/_2 - y, -z$
CP13-CP143	3.80	$^1/_2 + x, y, ^1/_2 - z$
CM2-CP144	3.80	$^1/_2 + x, ^1/_2 - y, -z$

distances[1] in isomers I and V in which the iron atoms have a meta, rather than para, relationship to each other.

The B–B and B–C distances are within the normal range, but we note that with respect to the two equatorial C_2B_4 rings, the inter-ring bond lengths are significantly longer than the intra-ring distances; thus, the average B–B and B–C distances *within* the rings are 1.740 and 1.656 Å, respectively, while the corresponding average distances *between* the rings are 1.797 and 1.719 Å. The differences of 0.06 Å correspond to about 10 standard deviations and thus are unquestionably real. This phenomenon is probably a consequence of the metal atoms' drawing of the atoms in each C_2B_4 ring closer together in order to maximize the overlap of the carbon and boron bonding orbitals with those of iron; this is, of course, directly related to the close approach of the metal atoms to the six-membered carborane faces as mentioned above. It is debatable whether one might expect this effect in other metalloboron polyhedra having metals in para positions, such as the icosahedral 2,9,1,12-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_8H_{10}$ system;[13] x-ray data on species of this type have not been reported, and a perusal of structures of monometallocarborane icosahedra reveals no such pattern. Certainly the 14-vertex system $(\eta^5\text{-}C_5H_5)_2Co_2C_2B_{10}H_{12}$,[14] whose central cage is proposed to be isostructural with the diiron species discussed here, can be expected to exhibit a similar contraction in the rings bonded to the metals.

Finally, the coordination of each iron atom to a nearly planar six-membered ring suggests an analogy to arene–metal complexes. Assigning the iron atoms a formal oxidation state of 2+, the carborane ligand is formulated as $[(CH_3)_4C_4B_8H_8]^{2-}$, the parent species of which would be $C_4B_8H_{12}^{2-}$. Such a dianion would be isoelectronic with the hypothetical $C_{12}H_{12}^{6+}$ ion which can be imagined to form by face-to-face fusion of two benzene rings in staggered fusion, with concomitant loss of six electrons. Both $C_{12}H_{12}^{6+}$ and its hypothetical borane analogue $B_{12}H_{12}^{6-}$ would have 30 skeletal electrons and thus constitute $2n + 6$ (arachno)[3] systems, in accordance with their postulated geometry having two open faces. The high charge on these ions makes their existence unlikely, but their neutral counterpart, $C_6B_6H_{12}$, might well be stable. A number of isomers are theoretically possible, but the one which is perhaps structurally most intriguing would consist of planar hexagonal B_6H_6 and C_6H_6 rings fused face to face, again, of course, staggered. The two open hexagonal faces on $C_6B_6H_{12}$ could then be closed by insertion of two zero-electron donors such as $Cr(CO)_3$ or $(\eta^5\text{-}C_5H_5)Mn$ to create a closo 14-vertex cage analogous to $(\eta^5\text{-}C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$.

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Registry No. 1,14,2,5,9,12-$(C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$ (isomer VIII), 64201-89-4.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part 2: W. M. Maxwell, R. Weiss, E. Sinn, and R. N. Grimes, *J. Am. Chem. Soc.*, **99**, 4016 (1977).

(2) W. M. Maxwell, R. F. Bryan, and R. N. Grimes, *J. Am. Chem. Soc.*, **99**, 4008 (1977).

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

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

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

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

(7) D. T. Cromer and J. A. Ibers, ref 5.

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

(9) A true quadridecker sandwich, of course, would have a third metal atom between the two central rings.

(10) Similar effects have been noted in $(\eta^5\text{-}C_5H_5)CoB_9H_{13}$[11] and in organometallics such as $(\eta^5\text{-}C_5H_5)Co[\eta^4\text{-}C_5H_5(C_6H_5)]$.[12]

(11) J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, **16**, 10 (1977).

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

(13) W. J. Evans and M. F. Hawthorne, *J. Am. Chem. Soc.*, **96**, 301 (1974).

(14) W. J. Evans and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 38 (1974).

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Crystal Structure of a Novel Triple-Decked Sandwich Metallocarborane, $\mu(2,3)$-1,3-C_3H_4-1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_3$, a Complex Containing a Bicyclic Planar Carborane Ligand Related to Pentalene. Partial Incorporation of a Cyclopentadienyl Ring into a Polyhedral Borane Cage

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The structure of the title compound was determined from a single-crystal x-ray diffraction study and was found to consist of a seven-vertex $Co_2C_2B_3$ pentagonal bipyramid with the two cage carbon atoms bridged by an exo-polyhedral propenylene group. The exo-polyhedral ring together with the equatorial ring of the polyhedron forms a planar bicyclic $C_5B_3H_7^{4-}$ ligand which is isoelectronic with the pentalenide monoanion $C_8H_7^-$. This complex consists of a metalloborane polyhedron into which a cyclopentadienyl group has been partially inserted and represents the first example of such insertion. The molecule is also a *C,C′*-1,3-propenylene-substituted derivative of the known triple-decked complex 1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ but has a slightly longer cage C–C bond than the latter species. Crystal data: mol wt 347.60; space group $P2_1/n$; $a = 8.672$ (2), $b = 16.441$ (4), $c = 10.873$ (3) Å; $\beta = 108.95$ (2)°; $V = 1466.3$ (9) Å^3; $d_{\text{calcd}} = 1.58$ g cm^{-3} for $Z = 4$. The structure was refined by full-matrix least-squares methods to a final R value of 5.9% for the 2012 reflections for which $F_o^2 > 3\sigma(F_o^2)$.

Introduction

The reaction between $Na^+B_5H_8^-$, $CoCl_2$, and $Na^+C_5H_5^-$ in tetrahydrofuran (THF) yields a family of structurally varied cobaltaboranes which can be isolated as air-stable crystalline solids.[1] These molecules consist of open and closed polyhedral cages containing one to four $(\eta^5\text{-}C_5H_5)Co$ groups, whose structures were deduced from NMR spectra and supported in several cases by x-ray structural studies [2-$(C_5H_5)CoB_4H_8$,[2] $(C_5H_5)CoB_9H_{13}$,[3a] $(C_5H_5)_3Co_3B_3H_5$,[3a] $(C_5H_5)_3Co_3B_4H_4$,[3a] and $(C_5H_5)_4Co_4B_4H_4$[3b]].

One product, obtained in very low yield,[1c] was characterized tentatively as σ-$C_5H_5(\eta^5\text{-}C_5H_5)_2Co_2B_3H_2$, i.e., a σ-cyclopentadienyl-, B-substituted cobaltaborane whose (unknown) parent species would be trigonal-bipyramidal $(\eta^5\text{-}C_5H_5)_2Co_2B_3H_3$. In one respect this formulation seemed reasonable, since several σ-C_5H_9- and σ-C_5H_7-substituted cobaltaboranes had been isolated from the same reaction;[1] it was clear that the $C_5H_5^-$ ion can function as an attacking reagent and is not restricted merely to the role of a capping ligand for cobalt. However, we were uncomfortable with the postulated Co_2B_3 cage which would have only 10 skeletal valence electrons instead of the 12 expected[4] for a five-vertex closo polyhedron. Accordingly, an x-ray investigation was undertaken and disclosed the altogether surprising result that the extra cyclopentadienyl ring is fused into the polyhedral cage, which thereby becomes not a five-vertex Co_2B_3 cobaltaborane, but a seven-vertex $Co_2C_2B_3$ cobaltacarborane having triple-decked sandwich geometry. This finding has been briefly described in an earlier paper,[1c] and we present here the details of the structural investigation.

Experimental Section

From a very large red single crystal,[5] grown by the vapor diffusion of pentane into a dichloromethane solution of the title compound, a cone-shaped fragment of maximum dimensions 0.65 × 0.4 mm was cut and mounted on a glass fiber. After preliminary precession photographs indicated good crystal quality, this crystal was used for data collection. Crystal data: $Co_2C_{15}B_3H_{17}$; mol wt 347.60; space group $P2_1/n$; $Z = 4$; $a = 8.672$ (2), $b = 16.441$ (4), $c = 10.873$ (3) Å; $\beta = 108.95$ (2)°; $V = 1466.3$ (9) Å^3; μ(Mo Kα) = 23.4 cm^{-1}; $d_{\text{calcd}} = 1.58$ g cm^{-3}; $F(000) = 704$. For this crystal, the Enraf-Nonius program SEARCH was used to obtain 15 accurately centered reflections which were then employed in the program INDEX to obtain an orientation matrix for data collection and also to provide approximate cell constants. Refined cell dimensions and their estimated standard deviations were obtained from least-squares refinement of 28 accurately

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