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## Structural Investigation of a *B*-Ferrocenyl-Substituted Tetracarbon Carborane, 4-[( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)]-2,3,7,8-(CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>7</sub>

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The title compound was isolated as a product of the reaction of (CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>8</sub> with sodium naphthalenide, FeCl<sub>2</sub>, and NaC<sub>5</sub>H<sub>5</sub> in tetrahydrofuran and was structurally characterized from its <sup>11</sup>B and <sup>1</sup>H NMR spectra, its mass spectra, and a single-crystal X-ray diffraction study. The molecule consists of a C<sub>4</sub>B<sub>8</sub> distorted-icosahedral cage which essentially corresponds to that of the previously reported (CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>8</sub> species, with a ferrocenyl group attached to B(4). The present structure represents a significant improvement in precision over that of the earlier unsubstituted carborane. There are no marked structural effects in the polyhedron that can be attributed to the ferrocenyl group, but the C<sub>5</sub>H<sub>4</sub> ring attached to boron is itself significantly perturbed; electron delocalization between the C<sub>5</sub>H<sub>4</sub> ring and the carborane is suggested as a possible cause. The molecule crystallizes in the monoclinic space group *P*2<sub>1</sub>/*n* with *a* = 11.044 (2) Å, *b* = 7.999 (1) Å, *c* = 23.697 (11) Å,  $\beta$  = 94.58 (3)°, *V* = 2087 Å<sup>3</sup>, and  $\rho$ (calcd) = 1.23 g cm<sup>-3</sup> for *Z* = 4. Full-matrix least-squares refinement of the positional and anisotropic thermal parameters for all nonhydrogen atoms, with varying isotropic thermal parameters for hydrogen atoms included for several cycles and thereafter held invariant, converged at *R* = 0.054 for the 2217 independent reflections for which *F*<sub>o</sub><sup>2</sup> > 3σ(*F*<sub>o</sub><sup>2</sup>).

### Introduction

The four-carbon carborane (CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>8</sub>, a colorless, volatile, air-stable solid, has played a major role in studies of the chemistry and structure of electron-rich boron clusters.<sup>1</sup> The facile formation of this species from [(CH<sub>3</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]<sub>2</sub>MH<sub>x</sub> sandwich complexes (M = Co or Fe; *x* = 1 or 2) under mild conditions provided the first example of concerted metal-promoted face-to-face linkage of carborane cages (oxidative fusion).<sup>2</sup> The structure of (CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>8</sub> itself is of some interest since it has two electrons in excess of the required number of an icosahedral system and has an oddly distorted geometry in which two edges of the icosahedron have been stretched to nonbonding distances;<sup>3</sup> moreover, it is fluxional in solution, undergoing reversible cage isomerization but reverting to a single isomeric form in the solid state. Beyond this, the insertion of transition metals into neutral (CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>8</sub> and the (CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>8</sub><sup>2-</sup> ion has generated a variety of structurally novel metallocarboranes,<sup>4</sup> which in turn have helped to develop some understanding of how cage geometry is dictated by electron distribution within the framework.

Current knowledge of the solid-state structure of (CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>8</sub> is based on an X-ray crystallographic study in this laboratory,<sup>3</sup> which of necessity employed crystals of marginal quality. Although the molecular geometry and atomic connectives were established, those data yielded only approximate values for bond distances and angles. Recently we obtained high-quality crystals of a *B*-ferrocenyl derivative of (CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>8</sub>, a previously unreported compound which is formed as a minor product in the reaction of the (CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>8</sub><sup>2-</sup> ion with FeCl<sub>2</sub> and NaC<sub>5</sub>H<sub>5</sub> in tetrahydrofuran (THF) (the major products, described in an earlier publication,<sup>4a</sup> are mono- and diferracarboranes). A crystal structure analysis was conducted on this species with three objectives in mind: to determine whether the C<sub>4</sub>B<sub>8</sub> isomer in this complex is the same as that of the parent carborane, to determine more accurate molecular parameters for the C<sub>4</sub>B<sub>8</sub> system than those previously available,

and to examine the structural consequences of ferrocenyl substitution on the cage.

### Experimental Section

**Materials.** Tetramethyltetracarbadodecaborane(12) [(CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>8</sub>] was prepared as described elsewhere.<sup>2a</sup> Tetrahydrofuran (THF) was dried over lithium aluminum hydride before use. All other materials were commercially obtained and used as received.

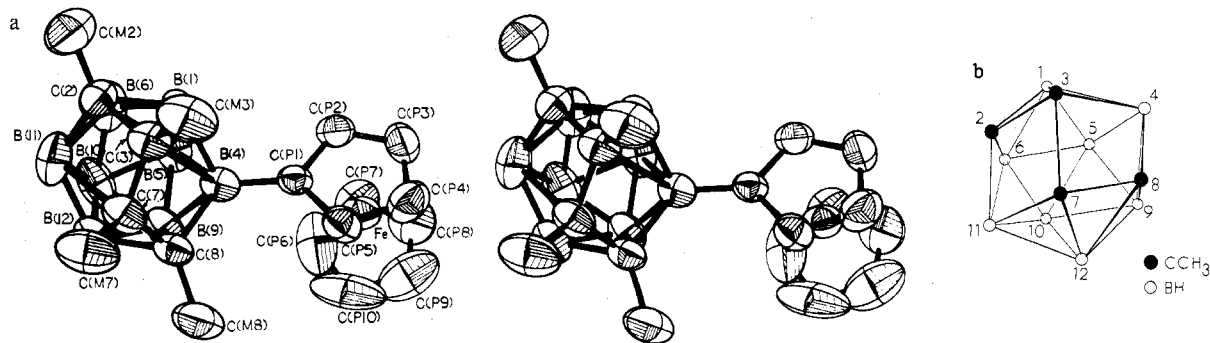
**Spectra.** Boron-11 and proton pulse Fourier transform (FT) NMR, infrared, and unit- and high-resolution mass spectra were obtained on instruments specified in other publications.<sup>2b</sup>

**Synthesis of 4-[( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)]-2,3,7,8-(CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>7</sub>.** The reaction of (CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>8</sub> with sodium naphthalenide, FeCl<sub>2</sub>, and NaC<sub>5</sub>H<sub>5</sub> in THF at room temperature has been described in an earlier paper.<sup>4a</sup> Following exposure of the reaction mixture to the air and removal of solvent, the products were extracted with dichloromethane and chromatographed on silica gel plates by using *n*-hexane initially, followed by a 10%/90% mixture of benzene/hexane. The major bands consisted of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>7</sub>H<sub>8</sub> and several isomers of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe<sub>2</sub>(CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>8</sub>, as previously reported.<sup>4a</sup> A minor yellow-orange band was further chromatographed in cyclohexane and then in 10%/90% benzene/hexane to afford 3-4 mg of the yellow title compound. The mass spectrum of this material exhibits a parent grouping having a major cutoff at *m/e* 388, corresponding to the <sup>56</sup>Fe<sup>11</sup>B<sub>8</sub><sup>12</sup>C<sub>18</sub><sup>1</sup>H<sub>28</sub><sup>+</sup> ion, with major fragments at *m/e* 334 and 280, and a C<sub>5</sub>H<sub>5</sub>Fe<sup>+</sup> peak at *m/e* 121; the intensity pattern of the parent grouping corresponds to an eight-boron species, in agreement with the assigned formula. The 32.1-MHz <sup>11</sup>B FT NMR spectrum in CDCl<sub>3</sub> contains doublets at  $\delta$  -4.8 relative to BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (*J* = 150 Hz), -9.4 (140), -22.4 (180), and -28.8 (180) and a singlet at  $\delta$  7.1, with approximate relative areas of 3:2:1:1:1, respectively.<sup>5</sup> On <sup>1</sup>H decoupling, the doublets collapsed to singlets, and the singlet resonance at  $\delta$  +7.1 (assigned to the substituted boron) was unchanged. The spectrum also contained several small peaks in the range  $\delta$  +10 to -10 which may have arisen from other isomeric forms of the title compound (analogous to the reversible isomerization of (CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>8</sub> itself in solution, mentioned in the Introduction). The above range of chemical shifts corresponds closely to that of the parent species, (CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>8</sub>, whose spectrum<sup>4a</sup> (isomer A) in CDCl<sub>3</sub> contains four equal area resonances<sup>5</sup> at  $\delta$  +9.2, +8.4, -22.4, and -29.5; isomer B has signals at  $\delta$  -2.4 and -11.0 in a 3:1 area ratio.

The 100-MHz <sup>1</sup>H NMR spectrum of the ferrocenyl derivative in CDCl<sub>3</sub> contains four CH<sub>3</sub> resonances of area 3 at  $\delta$  2.11, 2.06, 2.03, and 1.98, a C<sub>5</sub>H<sub>5</sub> peak at  $\delta$  4.15 (area 5), and a complex pattern of signals with major peaks at  $\delta$  4.24 and 4.22 arising from the *B*-substituted C<sub>5</sub>H<sub>4</sub> ring (total area 4). The H-B protons were not observed in the uncoupled spectrum, and <sup>11</sup>B decoupling disclosed only three small H-B resonances at  $\delta$  ~3.96, ~3.55, and ~2.54; the remaining

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- (5) Chemical shifts downfield of BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> are reported with positive signs.



**Figure 1.** (a) Stereoview of the molecular structure showing nonhydrogen atoms. (b)  $C_4B_8$  cage geometry and numbering system.

H-B peaks (all of unit area owing to the total asymmetry of the molecule) are presumably hidden under the methyl and cyclopentadienyl signals.

**X-ray Crystallographic Study of  $4\{(\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)\}-2,3,7,8-(CH_3)_4C_4B_8H_7$ .** Yellow-orange plates of the compound were grown from hexane at 0 °C, and a crystal was mounted on a glass fiber in an arbitrary orientation. Crystal data:  $FeB_8C_{18}H_{28}$ ; mol wt 388; space group  $P2_1/n$ ;  $Z = 4$ ;  $a = 11.044$  (2),  $b = 7.999$  (1),  $c = 23.697$  (11) Å;  $\beta = 94.58$  (3)°;  $V = 2087$  Å<sup>3</sup>;  $\mu(Mo K\alpha) = 7.4$  cm<sup>-1</sup>;  $\rho(\text{calcd}) = 1.23$  g cm<sup>-3</sup>. Crystal dimensions (distance of faces from centroid in mm): (100) 0.02, (100) 0.02, (010) 0.25, (010) 0.25, (001) 0.11, (001) 0.11, (013) 0.19, (013) 0.19. 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 25 accurately centered reflections. The mosaicity of the crystal was examined by the  $\omega$ -scan technique and found to be satisfactory. Systematic absences for  $k = 2n + 1$  on  $0k0$  and  $h + l = 2n + 1$  on  $h0l$  uniquely determine the space group to be  $P2_1/n$ . This is a nonstandard setting of  $P2_1/c$  (No. 14) but can be converted to it by the transformation  $a' = a$ ,  $b' = b$ , and  $c' = -a + c$ , where  $a$ ,  $b$ , and  $c$  are axes in  $P2_1/n$  and  $a'$ ,  $b'$ , and  $c'$  are the axes in  $P2_1/c$ . All data collection and refinement were conducted in the  $P2_1/n$  setting.

**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  $Mo K\alpha$  radiation from a highly oriented graphite-crystal monochromator. The  $\theta$ - $2\theta$  scan technique was used to record the intensities for all reflections for which  $1.4^\circ \leq 2\theta \leq 44^\circ$ . 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  $K\alpha_1$ - $K\alpha_2$  splitting. The values of  $A$  and  $B$  respectively were 0.60 and 0.35°. 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. 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 ( $p = 0.03$ ).<sup>6</sup> This resulted in 4346 reflections of which 2217 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 Structure.** The iron atom was located from a three-dimensional Patterson synthesis. Difference Fourier syntheses then revealed the locations of all nonhydrogen atoms, after which the thermal parameters for those atoms were allowed to refine anisotropically, with all cyclopentadienyl hydrogens inserted into calculated positions. All nonmethyl hydrogen atoms, and some methyl hydrogens, were then found from difference Fourier maps, and the remaining methyl hydrogens were placed in calculated locations. In subsequent refinement, all hydrogen parameters were allowed to vary for three cycles and thereafter held fixed. Following absorption

corrections (maximum and minimum transmission coefficients, 0.98 and 0.95, respectively), refinement was continued to convergence, final values of  $R$  and  $R_w$  being 0.054 and 0.057, respectively, 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 in the final cycle was 0.10, and the error in an observation of unit weight was 1.9.

There are no unusually close intermolecular contacts, the shortest being 3.563 (7) Å between C(M3) and C(P3) (symmetry operation  $-x, 1 - y, -z$ ).

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<sup>7</sup> and those for hydrogen from Stewart.<sup>8</sup> The effects of anomalous dispersion were included in  $F_c$  by using Cromer and Ibers<sup>9</sup> values of  $\Delta f'$  and  $\Delta f''$ . The computing system and programs are described elsewhere.<sup>10</sup> Tables of observed and calculated structure factors are available (see paragraph at end of paper regarding supplementary material).

## Results and Discussion

Tables I-III list positional and thermal parameters, interatomic distances, and selected bond angles, respectively. 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. Table IV contains selected mean planes for the molecule, and Figures 1 and 2 present the molecular structure and a diagram of the unit cell packing.

**The Carborane Cage.** The geometry of the  $C_4B_8$  framework is in all major respects identical with that previously found<sup>3</sup> for unsubstituted  $(CH_3)_4C_4B_8H_8$  and consists of a distorted icosahedron in which the four cage carbon atoms occupy vicinal locations at vertices 2, 3, 7, and 8. The C(2)-C(7) and C(3)-C(8) edges are stretched to nonbonding distances of 2.415 (6) and 2.438 (6) Å, respectively, thereby forming two four-sided open faces; in addition, the C(7)-B(11) and C(3)-B(4) bond lengths are quite long, with respective values of 2.197 (7) and 2.251 (6) Å. The unsubstituted molecule<sup>3</sup> has pseudo twofold symmetry generated by an axis through the midpoints of the C(3)-C(7) and B(5)-B(10) vectors, which is reflected in the 2:2:2:2 pattern of signals in the <sup>11</sup>B NMR spectrum and the appearance of two equal methyl resonances in the <sup>1</sup>H NMR spectrum.<sup>2a</sup> In the present B(4)-ferrocenyl derivative there is no rigorous molecular symmetry, but the shape of the cage is affected very little by the substituent group. This is shown in two ways: (1) bond distances and angles for the two halves of the molecule related by the pseudo- $C_2$  axis are essentially statistically identical, and (2) a comparison of the molecular parameters in the present structure with those

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for  $(C_5H_5)Fe(C_2H_4)(CH_3)_4C_4B_8H_7^a$ 

atom	x	y	z	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Fe	0.17335 (9)	0.0908 (1)	0.14994 (4)	5.76 (4)	5.28 (4)	3.92 (4)	0.93 (5)	0.01 (3)	0.09 (5)
C(2)	-0.3299 (5)	0.2895 (9)	0.0346 (3)	4.2 (3)	6.6 (4)	4.6 (3)	0.7 (3)	-0.5 (3)	-0.9 (3)
C(3)	-0.2303 (5)	0.3876 (8)	0.0653 (2)	5.8 (3)	3.3 (3)	4.0 (3)	0.7 (3)	0.7 (2)	1.0 (3)
C(7)	-0.2642 (5)	0.4079 (8)	0.1257 (2)	5.8 (3)	3.2 (3)	4.8 (3)	0.9 (3)	1.5 (2)	-0.4 (3)
C(8)	-0.1758 (5)	0.3113 (7)	0.1637 (2)	5.1 (3)	4.2 (3)	3.4 (3)	0.5 (3)	0.9 (2)	-0.6 (3)
C(M2)	-0.3841 (7)	0.3401 (11)	-0.0238 (3)	7.6 (4)	13.8 (7)	6.6 (4)	3.0 (4)	-1.6 (4)	-1.6 (5)
C(M3)	-0.1678 (7)	0.5350 (8)	0.0398 (3)	9.7 (5)	5.2 (4)	5.7 (4)	0.5 (4)	1.8 (3)	1.6 (3)
C(M7)	-0.3120 (7)	0.5773 (8)	0.1423 (3)	10.6 (5)	4.3 (3)	5.8 (4)	0.9 (4)	1.5 (3)	-1.7 (3)
C(M8)	-0.1220 (6)	0.3777 (10)	0.2190 (3)	8.1 (4)	8.8 (5)	4.5 (3)	1.4 (4)	1.3 (3)	-1.6 (3)
C(P1)	0.0346 (5)	0.2308 (7)	0.1094 (2)	4.0 (3)	3.4 (3)	3.0 (3)	-0.6 (3)	0.5 (2)	-0.5 (2)
C(P2)	0.1069 (5)	0.1493 (7)	0.0704 (2)	5.0 (3)	5.1 (4)	3.6 (3)	-0.3 (3)	0.2 (3)	-0.2 (3)
C(P3)	0.2280 (5)	0.1958 (9)	0.0789 (3)	3.9 (3)	7.0 (4)	5.4 (3)	0.4 (3)	1.1 (3)	0.6 (3)
C(P4)	0.2360 (6)	0.3129 (9)	0.1234 (3)	5.6 (4)	6.1 (4)	5.9 (4)	-1.4 (3)	-0.6 (3)	-0.9 (3)
C(P5)	0.1196 (5)	0.3326 (7)	0.1412 (2)	4.7 (3)	4.7 (4)	4.1 (3)	-0.2 (3)	1.1 (3)	0.1 (3)
C(P6)	0.1093 (7)	-0.0994 (11)	0.1941 (3)	6.7 (4)	11.3 (5)	12.8 (5)	1.8 (4)	1.0 (4)	8.5 (4)
C(P7)	0.1889 (7)	-0.1608 (9)	0.1571 (3)	7.6 (4)	6.4 (4)	7.8 (4)	0.4 (4)	-0.6 (4)	0.7 (4)
C(P8)	0.2969 (7)	-0.0897 (10)	0.1710 (3)	8.0 (4)	7.9 (5)	9.3 (5)	3.6 (4)	0.0 (4)	1.2 (4)
C(P9)	0.2869 (9)	0.0152 (11)	0.2156 (4)	13.0 (6)	9.5 (6)	9.7 (5)	1.2 (5)	-4.6 (5)	0.7 (5)
C(P10)	0.1708 (9)	0.0124 (11)	0.2307 (3)	20.6 (8)	9.7 (5)	3.7 (4)	7.2 (5)	1.3 (5)	1.8 (4)
B(1)	-0.1880 (7)	0.2000 (10)	0.0435 (3)	4.4 (4)	4.9 (4)	4.3 (4)	0.8 (3)	0.6 (3)	-1.1 (3)
B(4)	-0.1009 (6)	0.2130 (8)	0.1141 (3)	5.1 (4)	2.3 (3)	3.7 (3)	1.2 (3)	0.4 (3)	0.7 (3)
B(5)	-0.1934 (7)	0.0389 (8)	0.0921 (4)	4.9 (4)	1.9 (4)	8.5 (5)	0.1 (3)	1.5 (4)	-0.3 (3)
B(6)	-0.3220 (7)	0.0884 (11)	0.0506 (4)	4.8 (4)	4.6 (4)	10.0 (5)	-0.7 (4)	0.1 (4)	-3.1 (5)
B(9)	-0.1983 (7)	0.1040 (11)	0.1610 (3)	5.5 (4)	4.8 (4)	5.5 (4)	0.2 (4)	2.0 (3)	0.6 (4)
B(10)	-0.3354 (7)	0.0591 (10)	0.1223 (4)	5.8 (4)	5.3 (5)	9.4 (5)	-0.7 (4)	3.6 (4)	0.5 (4)
B(11)	-0.4042 (7)	0.2357 (11)	0.0891 (4)	3.7 (4)	5.7 (5)	9.5 (6)	-0.5 (4)	-0.3 (4)	-0.1 (5)
B(12)	-0.3221 (7)	0.2452 (10)	0.1587 (3)	5.3 (4)	6.2 (5)	6.0 (4)	0.2 (4)	2.1 (3)	0.0 (4)

	x	y	z	$B, \text{Å}^2$	x	y	z	$B, \text{Å}^2$	
H(P2) <sup>b</sup>	0.301 (4)	0.177 (6)	0.059 (2)	4 (1)	H(11)	-0.498 (4)	0.260 (6)	0.086 (2)	4 (1)
H(P3)	0.075 (4)	0.073 (5)	0.048 (2)	3 (1)	H(12)	-0.381 (4)	0.267 (6)	0.195 (2)	5 (1)
H(P4)	0.308 (5)	0.362 (7)	0.141 (2)	7 (2)	H(21)	-0.353 (5)	0.401 (8)	-0.038 (2)	10 (2)
H(P5)	0.103 (4)	0.398 (6)	0.170 (2)	3 (1)	H(22)	-0.386 (5)	0.238 (8)	-0.049 (2)	8 (2)
H(P6)	0.038 (4)	-0.109 (6)	0.196 (2)	4 (1)	H(23)	-0.464 (5)	0.360 (7)	-0.022 (2)	9 (2)
H(P7)	0.141 (5)	-0.236 (7)	0.132 (2)	7 (2)	H(31)	-0.094 (4)	0.556 (6)	0.063 (2)	6 (1)
H(P8)	0.370 (5)	-0.119 (8)	0.155 (3)	9 (2)	H(32)	-0.150 (5)	0.510 (6)	0.002 (2)	6 (2)
H(P9)	0.336 (5)	0.093 (7)	0.225 (2)	7 (2)	H(33)	-0.218 (5)	0.627 (7)	0.040 (2)	6 (1)
H(P10)	0.155 (5)	0.100 (7)	0.258 (2)	7 (2)	H(71)	-0.378 (4)	0.597 (7)	0.104 (2)	6 (1)
H(1)	-0.138 (3)	0.210 (5)	0.007 (2)	2 (1)	H(72)	-0.350 (4)	0.584 (6)	0.178 (2)	5 (1)
H(5)	-0.154 (4)	-0.071 (6)	0.087 (2)	5 (1)	H(73)	-0.254 (5)	0.661 (7)	0.149 (2)	7 (2)
H(6)	-0.368 (5)	0.017 (6)	0.027 (2)	5 (1)	H(81)	-0.044 (4)	0.317 (6)	0.232 (2)	5 (1)
H(9)	-0.152 (4)	0.050 (6)	0.205 (2)	4 (1)	H(82)	-0.175 (4)	0.373 (6)	0.249 (2)	5 (1)
H(10)	0.400 (4)	0.037 (6)	0.860 (2)	5 (1)	H(83)	-0.101 (5)	0.498 (8)	0.215 (3)	9 (2)

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

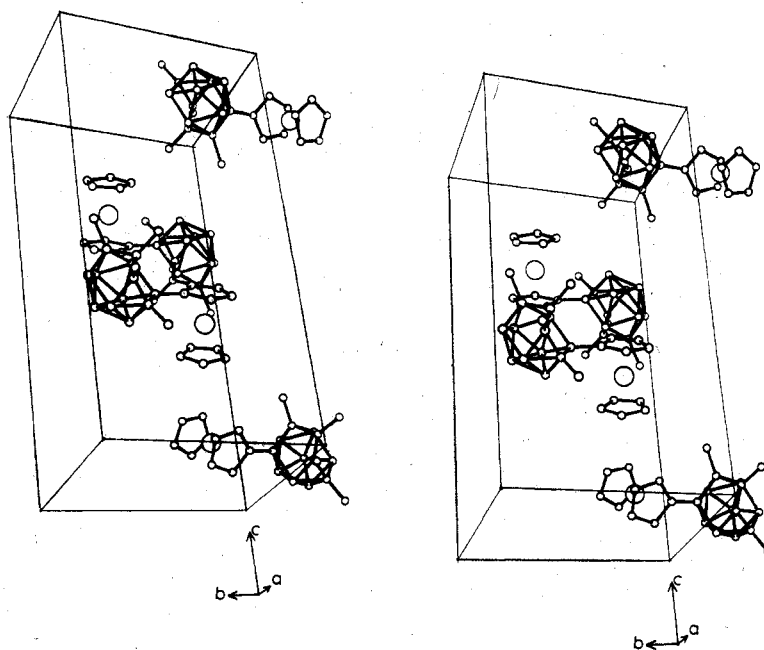


Figure 2. Stereoview of the unit cell contents.

Table II. Interatomic Distances (Å)

Bonded Distances			
C(2)-C(M2)	1.519 (6)	B(9)-B(10)	1.744 (8)
C(2)-C(3)	1.493 (6)	B(9)-B(12)	1.771 (8)
C(2)-B(1)	1.720 (6)	B(10)-B(11)	1.759 (9)
C(2)-B(6)	1.653 (8)	B(10)-B(12)	1.721 (8)
C(2)-B(11)	1.641 (7)	B(11)-B(12)	1.819 (9)
C(3)-C(M3)	1.516 (6)	C(P1)-C(P2)	1.427 (5)
C(3)-C(7)	1.515 (5)	C(P2)-C(P3)	1.387 (6)
C(3)-B(1)	1.666 (7)	C(P3)-C(P4)	1.409 (6)
C(3)-B(4)	2.251 (6)	C(P4)-C(P5)	1.393 (6)
C(7)-C(M7)	1.518 (6)	C(P5)-C(P1)	1.414 (5)
C(7)-C(8)	1.490 (6)	C(P6)-C(P7)	1.38 (1)
C(7)-B(11)	2.197 (7)	C(P7)-C(P8)	1.338 (8)
C(7)-B(12)	1.673 (7)	C(P8)-C(P9)	1.36 (1)
C(8)-C(M8)	1.493 (6)	C(P9)-C(P10)	1.36 (1)
C(8)-B(4)	1.684 (6)	C(P10)-C(P6)	1.39 (1)
C(8)-B(9)	1.677 (7)	Fe-C(P1)	2.071 (4)
C(8)-B(12)	1.695 (7)	Fe-C(P2)	2.022 (4)
B(1)-B(4)	1.866 (7)	Fe-C(P3)	2.016 (5)
B(1)-B(5)	1.732 (7)	Fe-C(P4)	2.025 (5)
B(1)-B(6)	1.748 (8)	Fe-C(P5)	2.029 (4)
B(4)-B(5)	1.780 (7)	Fe-C(P6)	2.007 (6)
B(4)-B(9)	1.828 (7)	Fe-C(P7)	2.026 (6)
B(4)-C(P1)	1.516 (6)	Fe-C(P8)	2.021 (6)
B(5)-B(6)	1.708 (8)	Fe-C(P9)	2.012 (7)
B(5)-B(9)	1.719 (8)	Fe-C(P10)	2.017 (7)
B(5)-B(10)	1.784 (8)	<B-H>	1.061
B(6)-B(10)	1.733 (9)	<C(CH <sub>3</sub> ) <sub>3</sub> -H>	0.953
B(6)-B(11)	1.782 (8)	<C(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> -H>	0.914
Nonbonded Distances			
C(2)-C(7)	2.415 (6)	C(3)-C(8)	2.438 (6)
C(3)-B(11)	2.378 (7)	B(4)-C(7)	2.416 (7)

in the unsubstituted species reveals few significant differences. Corresponding bond distances differing by more than 0.05 Å in the two species are as follows (present values given first in each case, in angstroms): C(2)-C(3), 1.493 (6) vs. 1.43 (1); C(2)-B(1), 1.720 (6) vs. 1.66 (1); C(2)-B(11), 1.641 (7) vs. 1.73 (1); C(3)-B(4), 2.251 (6) vs. 2.15 (1); C(8)-C(M8), 1.493 (6) vs. 1.57 (1); B(1)-B(5), 1.732 (7) vs. 1.84 (2); B(1)-B(6), 1.748 (8) vs. 1.83 (2); B(5)-B(6), 1.708 (8) vs. 1.78 (2); B(10)-B(11), 1.759 (9) vs. 1.68 (1). There is no apparent pattern to these differences, and notably absent are effects in the region of B(4) (the substituted atom) which could be attributed to the ferrocenyl group. Thus, we conclude that the ferrocenyl substituent exerts no clearly detectable influence on the geometry of the carborane framework. Moreover, given the higher quality of the present data compared to our earlier study, the structure reported here provides a significantly more accurate and precise definition of the (CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>8</sub> geometry than was previously available.

Earlier discussion of the structure of the C<sub>4</sub>B<sub>8</sub> cluster and its deviation from icosahedral geometry<sup>3</sup> is substantiated in every qualitative way by the present data. It will be noted that the three framework C-C bond distances are statistically identical (~1.50 Å) and that the polyhedron has opened in such a way as to allow all four carbon atoms to reduce their cage coordination to 4, in line with previous observations that carbon prefers low coordination sites.<sup>11</sup> This trend is further underlined by the fact that the (CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>5</sub><sup>-</sup> dianion, which has two more framework electrons than neutral (CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>8</sub>, adopts an even more open geometry in which one of the carbons is lifted out of the cage and assumes a methylene-like bridging role.<sup>12</sup> One would also predict that, when electrons are removed from (CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>8</sub> to generate the dication, the cage reverts to closo (icosahedral) geometry analogous to its isoelectronic analogue C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>; this has not yet been experimentally verified.

Table III. Selected Bond Angles (Deg)

C(M2)-C(2)-C(3)	121.7 (5)	C(3)-B(4)-B(5)	90.5 (3)
C(M2)-C(2)-B(1)	120.7 (4)	C(3)-B(4)-B(1)	46.6 (2)
C(M2)-C(2)-B(6)	118.6 (5)	C(3)-B(4)-C(8)	75.0 (3)
C(M2)-C(2)-B(11)	127.0 (4)	B(5)-B(4)-B(1)	56.6 (3)
C(3)-C(2)-B(1)	62.0 (3)	C(8)-B(4)-B(9)	56.9 (3)
C(3)-C(2)-B(6)	112.1 (4)	B(1)-B(4)-C(P1)	112.4 (4)
C(3)-C(2)-B(11)	98.6 (4)	C(3)-B(4)-C(P1)	119.6 (3)
B(1)-C(2)-B(6)	62.4 (3)	B(5)-B(4)-C(P1)	126.7 (4)
B(1)-C(2)-B(11)	107.6 (4)	C(8)-B(4)-C(P1)	123.4 (4)
B(6)-C(2)-B(11)	65.5 (4)	B(9)-B(4)-C(P1)	136.2 (4)
C(M3)-C(3)-C(2)	123.8 (4)	B(1)-B(5)-B(4)	64.2 (3)
C(M3)-C(3)-C(7)	116.6 (4)	B(1)-B(5)-B(6)	61.1 (3)
C(M3)-C(3)-B(1)	115.4 (4)	B(4)-B(5)-B(6)	114.8 (4)
C(M3)-C(3)-B(4)	113.4 (3)	C(2)-B(6)-B(1)	60.7 (3)
C(2)-C(3)-C(7)	106.8 (4)	C(2)-B(6)-B(5)	112.6 (4)
C(2)-C(3)-B(1)	65.7 (3)	B(1)-B(6)-B(5)	60.1 (3)
C(2)-C(3)-B(4)	109.7 (3)	C(8)-B(9)-B(10)	110.1 (4)
C(7)-C(3)-B(1)	119.1 (4)	C(8)-B(9)-B(12)	58.8 (3)
C(7)-C(3)-B(4)	77.1 (3)	B(10)-B(9)-B(12)	58.6 (3)
B(1)-C(3)-B(4)	54.4 (2)	B(9)-B(10)-B(11)	113.3 (4)
C(M7)-C(7)-C(3)	117.2 (4)	B(9)-B(10)-B(12)	61.5 (4)
C(M7)-C(7)-C(8)	122.1 (4)	B(11)-B(10)-B(12)	63.0 (4)
C(M7)-C(7)-B(11)	114.4 (3)	C(2)-B(11)-B(6)	57.6 (3)
C(M7)-C(7)-B(12)	114.8 (4)	C(2)-B(11)-C(7)	76.4 (3)
C(3)-C(7)-C(8)	108.4 (3)	C(7)-B(11)-B(10)	93.6 (4)
C(3)-C(7)-B(11)	77.3 (3)	C(7)-B(11)-B(12)	48.1 (3)
C(3)-C(7)-B(12)	119.4 (4)	B(10)-B(11)-B(12)	57.5 (4)
C(8)-C(7)-B(11)	108.6 (4)	C(7)-B(12)-C(8)	52.5 (3)
C(8)-C(7)-B(12)	64.5 (3)	C(7)-B(12)-B(11)	77.8 (4)
B(11)-C(7)-B(12)	54.1 (3)	C(8)-B(12)-B(9)	57.8 (3)
C(M8)-C(8)-C(7)	122.8 (4)	B(9)-B(12)-B(10)	59.9 (4)
C(M8)-C(8)-B(4)	109.0 (4)	B(10)-B(12)-B(11)	59.5 (4)
C(M8)-C(8)-B(9)	115.7 (4)	B(4)-C(P1)-C(P2)	127.7 (4)
C(M8)-C(8)-B(12)	118.8 (4)	B(4)-C(P1)-C(P5)	129.2 (4)
C(7)-C(8)-B(4)	98.9 (3)	C(P2)-C(P1)-C(P5)	103.1 (4)
C(7)-C(8)-B(9)	113.7 (4)	C(P1)-C(P2)-C(P3)	111.5 (4)
C(7)-C(8)-B(12)	63.0 (3)	C(P2)-C(P3)-C(P4)	106.8 (4)
B(4)-C(8)-B(9)	65.9 (3)	C(P3)-C(P4)-C(P5)	107.3 (4)
B(4)-C(8)-B(12)	109.0 (4)	C(P4)-C(P5)-C(P1)	111.3 (4)
B(9)-C(8)-B(12)	63.4 (3)	C(P7)-C(P6)-C(P10)	108.8 (8)
C(2)-B(1)-C(3)	52.3 (2)	C(P6)-C(P7)-C(P8)	107.0 (7)
C(3)-B(1)-B(4)	79.0 (3)	C(P7)-C(P8)-C(P9)	109.2 (7)
C(2)-B(1)-B(6)	56.9 (3)	C(P8)-C(P9)-C(P10)	109.3 (9)
B(4)-B(1)-B(5)	59.2 (3)	C(P9)-C(P10)-C(P6)	105.7 (8)
B(5)-B(1)-B(6)	58.8 (3)		

Table IV. Selected Mean Planes<sup>a</sup>

atom	dev, Å	atom	dev, Å
Plane 1: C(P1), C(P2), C(P3), C(P4), C(P5)			
-0.1203x + 0.7451y - 0.6560z = -0.3352			
C(P1)	-0.006	C(P5)	0.003
C(P2)	0.008	Fe	-1.643
C(P3)	-0.006	B(4)	-0.004
C(P4)	0.002	C(8)	-0.075
Plane 2: C(P6), C(P7), C(P8), C(P9), C(P10)			
-0.1895x + 0.7500y - 0.6337z = -3.6574			
C(P6)	-0.003	C(P9)	-0.002
C(P7)	0.002	C(P10)	0.003
C(P8)	0.000	Fe	1.649

<sup>a</sup> Angle between planes 1 and 2 is 4.18°.

**The Ferrocenyl Group.** Both cyclopentadienyl rings are planar within experimental error, all deviations from the calculated least-squares plane being less than 0.01 Å (Table IV). The iron atom is equidistant (~1.64 Å) from the two rings, and the conformation of the rings is nearly eclipsed as can be seen in Figure 1a; also clearly evident is the much greater thermal libration of the carbon atoms in the unsubstituted ring in comparison to those in the C(P1)-C(P5) ring, to which the carboranyl cage is attached. The substituted ring exhibits significant distortion at C(P1), the atom bonded to the carborane, an effect which has been observed in cobaltocenium-substituted carboranes<sup>13</sup> and metallacarboranes.<sup>12,14</sup>

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viz., C(P1) is further from its ring neighbors, and from iron, than are the other cyclopentadienyl carbon atoms. Thus, the C(P1)-C(P2) and C(P1)-C(P5) distances of 1.427 (5) and 1.414 (5) Å can be compared with an average value of 1.377 Å for the remaining C-C distances. The Fe-C(P1) bond length of 2.071 (4) Å is substantially larger than the average distance for the other Fe-C bonds, 2.019 (7) Å. Moreover, the C(P2)-C(P1)-C(P5) angle is only 103.1 (4)°, which is significantly smaller than all other C-C-C angles and can be compared with the average value of 108° in these planar C<sub>5</sub> rings. Since the same effect has been observed in four different metallocene-substituted boron cage species but not, in general, in organo-substituted metallocenes,<sup>15</sup> this perturbation of the

C<sub>5</sub>H<sub>4</sub> ring can reasonably be attributed to the electron-delocalized borane framework and may involve a shift of electron density from the substituted carbon toward the cage. It will be noted that the boron atom bonded to the ferrocenyl moiety in the present structure [B(4)] is coplanar with the C<sub>5</sub>H<sub>4</sub> ring (Table IV); this would permit a p orbital of suitable symmetry on B(4) to engage in a π interaction with the cyclopentadienyl system and thus facilitate ring-to-cage electron delocalization. Moreover, the B(4)-C(P1) distance of 1.516 (6) Å is relatively short for a B-C bond (sum of covalent radii is 1.59 Å), consistent with a bond-order intermediate between 1 and 2.

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**Registry No.** (C<sub>5</sub>H<sub>5</sub>)Fe(C<sub>5</sub>H<sub>4</sub>)(CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>7</sub>, 74282-50-1; (C-H<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>8</sub>, 54387-54-1; FeCl<sub>2</sub>, 7758-94-3; NaC<sub>5</sub>H<sub>5</sub>, 4984-82-1.

**Supplementary Material Available:** A listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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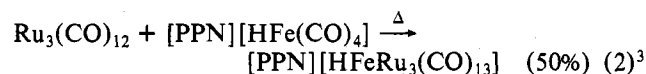
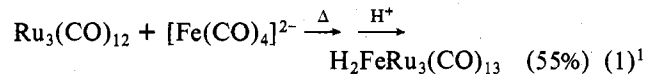
## Synthesis and Structural Characterization of [PPN][CIRu<sub>4</sub>(CO)<sub>13</sub>]: A Butterfly Cluster with a Bridging Chloride

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The new cluster [PPN][CIRu<sub>4</sub>(CO)<sub>13</sub>] (PPN = (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>) results from the reaction of Ru<sub>3</sub>(CO)<sub>12</sub> with [PPN]Cl in refluxing THF. It has been characterized by its spectroscopic properties and by a complete single-crystal X-ray diffraction study. It crystallizes in the space group P1̄ with Z = 2 and unit cell dimensions a = 14.536 (2) Å, b = 16.732 (3) Å, c = 11.508 (8) Å, α = 91.35 (3)°, β = 93.88 (3)°, γ = 64.79 (2)°, and V = 2527 (2) Å<sup>3</sup>. Diffraction data (0° < 2θ ≤ 50°) were collected with an Enraf-Nonius CAD4 automated diffractometer, using graphite-monochromatized Mo Kα radiation, and the structure was refined to R = 0.061 and R<sub>w</sub> = 0.087 for 5924 independent reflections with I ≥ 3.0σ(I). The molecule possesses a butterfly arrangement of the four Ru atoms with the chlorine bridging the two end metals of the open butterfly. Each Ru bears three terminal carbonyls, and one carbonyl ligand bridges the two Ru atoms which constitute the hinge of the butterfly.

The condensation of a carbonylmetalate with a closed metal carbonyl trimer is a valuable method for the synthesis of tetranuclear mixed-metal clusters,<sup>1-5</sup> e.g., eq 1 and 2. While



attempting to extend this synthetic procedure to prepare derivatized mixed-metal clusters by bringing the desired substituent into the cluster along with the carbonylmetalate reagent, e.g., H in eq 2, we allowed [PPN][PhC(O)Fe(CO)<sub>4</sub>] (PPN = (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>) to react with Ru<sub>3</sub>(CO)<sub>12</sub> with the aim of obtaining an acyl-substituted FeRu<sub>3</sub> cluster. However, the red crystalline product obtained from these reactions in ~25%

yield proved not to be an acyl cluster but rather a new Ru<sub>4</sub> cluster, [PPN][CIRu<sub>4</sub>(CO)<sub>13</sub>]. Herein we report the characterization of this compound by a complete single-crystal X-ray diffraction study which shows it to have an unusual butterfly structure with a bridging chloride. Significantly, we have also found that the best preparative method for the cluster is the reaction of Ru<sub>3</sub>(CO)<sub>12</sub> with [PPN]Cl in refluxing THF.

### Experimental Section

Ru<sub>3</sub>(CO)<sub>12</sub><sup>6</sup> and [PPN][PhC(O)Fe(CO)<sub>4</sub>]<sup>7</sup> were prepared according to the literature procedures. MeLi (Aldrich Chemical Corp.), Fe(CO)<sub>5</sub>, and [PPN]Cl (Alfa Ventron Corp.) were purchased and used as received. Tetrahydrofuran (THF), hexane, petroleum ether, and diethyl ether were dried by distillation from sodium benzophenone ketyl under N<sub>2</sub>. All manipulations of compounds were accomplished by using standard Schlenk techniques.<sup>8</sup> IR spectra were recorded on a Perkin-Elmer 580 grating infrared spectrophotometer using 0.5-mm NaCl solution IR cells. These were sealed with Luer-lock fittings and purged with N<sub>2</sub> to record spectra of air-sensitive solutions.

**Preparation of [PPN][CIRu<sub>4</sub>(CO)<sub>13</sub>].** In the most convenient preparation, a solution of Ru<sub>3</sub>(CO)<sub>12</sub> (210 mg, 0.337 mmol) and [PPN]Cl (188 mg, 0.337 mmol) in 40 mL of dried, deoxygenated

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