development of these ideas will depend on continuing synthetic and structural investigations in the metalloboron cluster field.

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Registry No. $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$, 59370-82-0.

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

References and Notes

(1) (a) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **98**, 1600 (1976); (b) V. R. Miller, R. Weiss, and R. N. Grimes, *ibid.*, **99**, 5646 (1977).

(2) J. R. Bowser and R. N. Grimes, *J. Am. Chem. Soc.*, **100**, 4623 (1978).

(3) J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, **16**, 3255 (1977).

(4) C. G. Salentine, C. E. Strouse, and M. F. Hawthorne, *Inorg. Chem.*, **15**, 1832 (1976).

(5) R. Weiss, J. R. Bowser, and R. N. Grimes, *Inorg. Chem.*, **17**, 1522 (1978).

(6) L. J. Guggenberger, *Inorg. Chem.*, **8**, 2771 (1969).

(7) (a) K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976); (b) R. W. Rudolph, *Acc. Chem. Res.*, **9**, 446 (1976); (c) D. M. F. Mingos, *Nature (London), Phys. Sci.*, **236**, 99 (1972).

(8) W. M. Maxwell, E. Sinn, and R. N. Grimes, *J. Am. Chem. Soc.*, **98**, 3490 (1976).

(9) R. Mason, K. M. Thomas, and D. M. P. Mingos, *J. Am. Chem. Soc.*, **95**, 3802 (1973).

(10) C. R. Eady, B. F. G. Johnson, J. Lewis, R. Mason, P. B. Hitchcock, and K. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 385 (1977).

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

(12) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

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

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

(15) D. T. Cromer and J. A. Ibers, ref 13.

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

(17) J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, preceding paper in this issue.

(18) B. R. Penfold and B. H. Robinson, *Acc. Chem. Res.*, **6**, 73 (1973).

(19) V. Albano, P. L. Bellon, P. Chini, and V. Scatturin, *J. Organomet. Chem.*, **16**, 461 (1969).

(20) V. G. Albano, G. Ciani, and P. Chini, *J. Chem. Soc., Dalton Trans.*, 423 (1974).

(21) L. F. Dahl and D. L. Smith, *J. Am. Chem. Soc.*, **84**, 2450 (1962).

(22) H. Hart and W. N. Lipscomb, *Inorg. Chem.*, **7**, 1070 (1968).

(23) (a) G. S. Pawley, *Acta Crystallogr.*, **20**, 631 (1966); (b) R. A. Jacobson and W. N. Lipscomb, *J. Chem. Phys.*, **31**, 605 (1959); (c) R. A. Jacobson and W. N. Lipscomb, *J. Am. Chem. Soc.*, **80**, 5571 (1958).

(24) Each BH and $Co(C_5H_5)$ unit is a formal two-electron donor to framework bonding, while CH, $C(CH_3)$, and $Ni(C_5H_5)$ are three-electron donors.[7]

(25) (a) A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 2270 (1975); 962 (1977); (b) W. E. Carroll, M. Green, F. G. A. Stone, and A. J. Welch, *ibid.*, 2263 (1975); (c) G. K. Barker, M. Green, J. L. Spencer, F. G. A. Stone, B. F. Taylor, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 804 (1975); (d) D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 602 (1977).

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

(27) J. R. Pipal and R. N. Grimes, to be submitted for publication.

(28) The persistence of the same polyhedral shape among eight-vertex cages with different skeletal electron populations can be contrasted with the family of 12-vertex, 28-electron carborane species we have described elsewhere.[29] In this latter group, the number of skeletal electrons is the same, but the cage structures are dissimilar!

(29) J. R. Pipal and R. N. Grimes, *J. Am. Chem. Soc.*, **100**, 3083 (1978).

(30) (a) R. E. Enrione, F. P. Boer, and W. N. Lipscomb, *Inorg. Chem.*, **3**, 1659 (1964); (b) R. R. Rietz, R. Schaeffer, and L. G. Sneddon, *ibid.*, **11**, 1242 (1972).

(31) R. E. Williams, *Adv. Inorg. Chem. Radiochem.*, **18**, 67 (1976).

(32) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 2830 (1973).

(33) L. G. Sneddon, D. C. Beer, and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 6623 (1973).

(34) M. L. Thompson and R. N. Grimes, *J. Am. Chem. Soc.*, **93**, 6677 (1971).

(35) K.-S. Wong and R. N. Grimes, *Inorg. Chem.*, **16**, 2053 (1977).

(36) D. C. Moody and R. Schaeffer, *Inorg. Chem.*, **15**, 233 (1976).

(37) A. J. Gotcher, J. F. Ditter, and R. E. Williams, *J. Am. Chem. Soc.*, **95**, 7514 (1973).

(38) T. P. Fehlner, *J. Am. Chem. Soc.*, **99**, 8355 (1977).

(39) J. Dobson, R. Maruca, and R. Schaeffer, *Inorg. Chem.*, **9**, 2161 (1970).

(40) (a) R. A. Schunn, C. J. Fritchie, Jr., and C. T. Prewitt, *Inorg. Chem.*, **5**, 892 (1966); (b) C. H. Wei, G. R. Wilkes, P. M. Treichel, and L. F. Dahl, *ibid.*, **5**, 900 (1966).

(41) E. B. Fleischer, *J. Am. Chem. Soc.*, **86**, 3889 (1964).

(42) L. D. Lower and L. F. Dahl, *J. Am. Chem. Soc.*, **98**, 5046 (1976).

(43) M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, **13**, 1065 (1974).

(44) (a) M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, **13**, 1427 (1974); (b) M. R. Churchill, B. G. DeBoer, and D. J. Donovan, *ibid.*, **14**, 617 (1975).

(45) R. S. Nyholm, M. R. Truter, and C. W. Bradford, *Nature (London), Phys. Sci.*, **228**, 648 (1970).

(46) B.-K. Teo and J. C. Calabrese, *Inorg. Chem.*, **15**, 2474 (1976).

(47) B.-K. Teo and J. C. Calabrese, *Inorg. Chem.*, **15**, 2467 (1976).

(48) Trinh-Toan, W. P. Fehlammer, and L. F. Dahl, *J. Am. Chem. Soc.*, **99**, 402 (1977).

(49) R. N. Grimes, *Ann. N.Y. Acad. Sci.*, **239**, 180 (1974).

(50) R. B. King and D. H. Rouvray, *J. Am. Chem. Soc.*, **99**, 7834 (1977).

(51) E. L. Muetterties and B. F. Beier, *Bull. Soc. Chim. Belg.*, **84**, 397 (1975).

(52) J. Evans, *J. Chem. Soc., Dalton Trans.*, 18 (1978).

(53) E. L. Muetterties, R. J. Wiersema, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **95**, 7520 (1973).

(54) R. Weiss and R. N. Grimes, *J. Organomet. Chem.*, **113**, 29 (1976).

(55) (a) D. C. Beer, V. R. Miller, L. G. Sneddon, R. N. Grimes, M. Mathew, and G. J. Palenik, *J. Am. Chem. Soc.*, **95**, 3046 (1973); (b) W. T. Robinson and R. N. Grimes, *Inorg. Chem.*, **14**, 3056 (1975); (c) J. R. Pipal and R. N. Grimes, *ibid.*, **17**, 10 (1978).

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Crystal and Molecular Structure of an Iron Dihydrogen Metallocarborane, $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2FeH_2$. Steric Aspects of the Oxidative Fusion Process

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A single-crystal X-ray diffraction investigation of the title compound established the structure as a sandwich composed of two pentagonal-pyramidal carborane ligands face bonded to iron, in accord with the geometry proposed earlier from NMR data. The "extra" hydrogen atoms were not directly located, but strong evidence that they occupy bridging locations on the FeB_2 polyhedral faces is given by the orientation of the C_2B_3 bonding faces on the ligands. The C_2B_3 planes are inclined at an angle of 7.80° such that the methyl groups are forced close together, an effect attributed to the presence of the FeH_2 hydrogens wedged between the polyhedra on the side of the complex opposite the methyl groups. The relationship of this structure to that of $(CH_3)_4C_4B_8H_8$, which is produced from the title compound by oxidative fusion of the $[(CH_3)_2C_2B_4H_4]^{2-}$ ligands, is discussed. Crystal data: space group *Aba*2; $a = 12.861\ (4)$ Å, $b = 10.144\ (4)$ Å, $c = 11.257\ (5)$ Å; $V = 1469\ (2)$ Å^3; $\mu(\text{Mo K}\alpha) = 10.2\ \text{cm}^{-1}$; $\rho(\text{calcd}) = 1.178\ \text{g cm}^{-3}$ for $Z = 4$. The structure was refined by full-matrix least-squares methods to a final R value of 0.039 for the 662 reflections for which $F_o^2 > 3\sigma(F_o^2)$.

Introduction

The bis(2,3-dimethyl-2,3-dicarbahexaboranyl)iron(II) dihydrogen complex $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2FeH_2$, a deep red solid, has played an important role in the recent development of some novel metallocarborane and carborane chemistry.[1] A number of singular kinds of reactions involving this compound and its cobalt monohydrogen analogue, $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2CoH$, have been described elsewhere;[2] particularly significant is the air oxidation of both complexes to produce the tetracarbon carborane $(CH_3)_4C_4B_8H_8$. This type of process has been labeled "oxidative cage fusion"[2c] since it involves joining two formal $(CH_3)_2C_2B_4H_4^{2-}$ ligands face-to-face with loss of four electrons and elimination of the metal. Recent work has shown that oxidative fusion occurs in other reaction systems as well[2c,3] and can be exploited to generate dimetallic, tetracarbon cages directly from monometallic, dicarbon precursors.

The nature of the cage-fusion process has been a subject of continuing structural and chemical investigation in our laboratory. An X-ray diffraction study of $(CH_3)_4C_4B_8H_8$[4] disclosed that it has a distorted icosahedral shape in which two "edges" are stretched to nonbonding distances; other crystallographic investigations[3,5,6] have been conducted on various metallocarboranes which form via ligand-fusion reactions. However, the structure of the iron dihydrogen complex itself was assigned only from ^{11}B and ^{1}H NMR data and other spectroscopic evidence.[2a] This compound was therefore a high-priority candidate for crystallographic study, but a search for suitable crystals (which was complicated by extreme sensitivity to air) was fruitless until they happened to be fortuitously obtained as described below.

Experimental Section

Crystals of the title compound of satisfactory quality for crystallographic study were unexpectedly formed by sublimation at 0 °C in vacuo from an impure sample of the tin–iron species[2c] $SnFe(CH_3)_4C_4B_8H_8$, which contained $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2FeH_2$ (the two compounds are somewhat similar in color but the latter complex is the more volatile). Several of these red acicular crystals were mounted in Pyrex capillaries under nitrogen and examined by precession photography. One of them with maximum dimensions 0.15 × 0.16 × 0.60 mm was selected for data collection. Crystal data: $FeC_8B_8H_{22}$; space group *Aba*2 (No. 41); $Z = 4$; $a = 12.861$ (4) Å, $b = 10.144$ (4) Å, $c = 11.257$ (5) Å; $V = 1469$ (2) Å^3; $\mu(\text{Mo K}\alpha) = 10.2$ cm^{-1}; $\rho(\text{calcd}) = 1.178$ g/cm^3; $F(000) = 544$. 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 $h + l = 2n + 1$ for hkl, $h = 2n + 1$ (or $l = 2n + 1$) for $h0l$, and $k = 2n + 1$ for $0kl$ indicate the space group to be either *Bba*2 or its centrosymmetric analogue *Bbcm*. Both can be easily transformed to standard settings, *Aba*2 (No. 41) and *Cmca* (No. 64), respectively. *Aba*2 was taken as the initial choice since *Cmca* would require the molecule either to be disordered or to $2/m$ symmetry. Although $2/m$ symmetry is possible, it is not consistent with available physical and chemical information[2a] concerning the molecule. The correctness of *Aba*2 as the space group was demonstrated by the successful solution and refinement of the structure. The transformation from *Bba*2 to *Aba*2 was achieved by setting $a' = b$, $b' = a$, and $c' = -c$, where a', b', and c' are the axes in *Aba*2 and a, b, and c are the axes in *Bba*2.

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 $\text{SW} = A + B \tan\theta$ 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 0.70 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 eight 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 760 intensities of which 662 had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics using an ignorance factor of 0.03.[7] These latter reflections were used in the final refinement of the structural parameters. The 662 reflections included 213 Friedel pairs (hkl and $hk\bar{l}$), but symmetry-related data were not averaged.

Solution and Refinement of the Structure. A three-dimensional Patterson map easily yielded the coordinates of five of the nine independent nonhydrogen atoms. (In space group *Aba*2 with $Z = 4$, the molecule must have a twofold axis passing through the iron atom at 0, 0, 0. Consequently the most prominent features in the Patterson map, aside from Fe–Fe vectors, are Fe–C and Fe–B vectors of which five were readily identified.) The coordinates of the three remaining nonhydrogen atoms were determined from an electron density difference map. Isotropic refinement of all nonhydrogen atoms followed by anisotropic refinement reduced the conventional residual (R) to 0.053. The residuals are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Additional electron density difference maps yielded the positions of the terminal hydrogens bonded to boron plus possible positions for the methyl hydrogens and the two hydrogens bonded to Fe. The terminal B–H hydrogen atoms refined very successfully. The methyl hydrogens initially refined, but several of them eventually moved to chemically unreasonable positions. Consequently, they were reset to calculated positions 0.95 Å from their respective carbon atoms and were held fixed at this distance.

The iron-bonded hydrogen atoms proved elusive. The initial electron density difference map yielded two peaks which are probably artifacts, located on the twofold axis on opposite sides of the iron atom and approximately 1.1 Å from iron. Of these two peaks, one failed to refine and the other remained unacceptably close (1.1 Å) to the iron atom. Various measures were taken in an effort to produce refinement of one or both of these peaks or to locate the actual positions of the iron-bound hydrogens. An absorption correction was made (minimum transmission factor 0.861, maximum 0.920), and an attempt was made to determine the absolute configuration of the molecule since *Aba*2 is an acentric space group. However, R and R_w converged to the same value for both configurations and there were no meaningful differences in bond distances and angles; this result is not unexpected since the iron atom is the only significant anomalous scatterer in the molecule.

A new electron density difference map was calculated using only the data for which $(\sin\theta)/\lambda < 0.40$ Å^{-1}, in an effort to increase the height of hydrogen atom peaks relative to background noise.[8] However, there were no significant differences between this map and one based on all of the observed reflections. Accordingly, it was concluded that the data were not sufficiently precise to locate the iron-bound hydrogen atoms, despite the low final residual values of 0.039 for R and 0.040 for R_w. The final value for the estimated standard deviation of an observation of unit weight is 1.93 and the ratio of data to parameters is 7.1. During the last cycle of refinement, the largest parameter shift was 0.02 times its estimated error.

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[9] and those for hydrogen from Stewart.[10] The effects of anomalous dispersion were included in F_c using Cromer and Ibers'[11] values of $\Delta f'$ and $\Delta f''$. The computing system and programs are described elsewhere.[12] A table of structure factors is available.

Results and Discussion

Table I contains the final positional and thermal parameters, Tables II and III present intramolecular distances and angles, and Table IV lists selected mean planes. 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. Figure 1 is a general view of the molecule, and Figure 2 depicts the relative orientation of the two C_2B_3 rings as viewed along the B(7)–B(7′) vector. There are no intermolecular contacts of any significance.

The complex contains two pyramidal carborane ligands face bonded to the iron atom and can also be described as two pentagonal bipyramids fused at a common vertex. This

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2FeH_2$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	0.0000	0.0000	0.0000	2.73 (3)	4.30 (3)	3.48 (3)	−0.95 (4)	0.0000	0.0000
C(2)	0.0877 (3)	0.1669 (5)	0.0246 (7)	2.4 (2)	3.5 (2)	6.8 (4)	−0.4 (2)	−0.6 (3)	0.1 (2)
C(3)	0.1082 (4)	0.0707 (6)	0.1211 (5)	2.8 (2)	3.9 (2)	4.2 (3)	0.2 (2)	−0.4 (2)	−0.2 (2)
CM(2)	0.0623 (5)	0.3095 (6)	0.0581 (8)	4.4 (3)	3.6 (2)	10.7 (6)	0.1 (2)	−0.1 (4)	0.3 (3)
CM(3)	0.1066 (4)	0.1095 (6)	0.2473 (7)	4.9 (3)	6.2 (3)	4.8 (3)	0.3 (3)	−0.4 (3)	−1.0 (3)
B(4)	0.1505 (6)	−0.0622 (7)	0.0714 (7)	4.5 (3)	3.8 (2)	5.0 (4)	0.6 (3)	1.6 (3)	−0.1 (3)
B(5)	0.1548 (6)	−0.0419 (7)	−0.0800 (8)	4.0 (3)	5.1 (3)	6.3 (4)	−1.0 (2)	1.8 (3)	−1.9 (3)
B(6)	0.1095 (6)	0.1136 (7)	−0.1011 (7)	3.5 (3)	6.4 (3)	4.3 (4)	−0.5 (3)	−0.0 (3)	1.2 (3)
B(7)	0.2052 (4)	0.0823 (5)	0.0117 (11)	3.1 (2)	4.2 (2)	6.0 (4)	−0.4 (2)	0.4 (4)	−0.9 (4)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
HB(4)	0.172 (5)	−0.144 (5)	0.139 (5)	5 (1)[b]	HC(22)	0.001	0.311	0.106	6
HB(5)	0.194 (5)	−0.105 (6)	−0.142 (7)	7 (2)	HC(23)	0.119	0.346	0.101	6
HB(6)	0.107 (4)	0.174 (4)	−0.178 (5)	4 (1)	HC(31)	0.121	0.035	0.295	6
HB(7)	0.279 (3)	0.124 (5)	0.023 (6)	5 (1)	HC(32)	0.158	0.175	0.261	6
HC(21)	0.051	0.360	−0.012	6	HC(33)	0.040	0.143	0.267	6

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

Table II. Bond Distances (Å)

Fe–C(2)	2.053 (4)	C(3)–B(7)	1.76 (1)
Fe–C(3)	2.076 (6)	B(4)–B(5)	1.72 (1)
Fe–B(4)	2.19 (1)	B(4)–B(7)	1.76 (1)
Fe–B(5)	2.23 (1)	B(5)–B(6)	1.70 (2)
Fe–B(6)	2.146 (8)	B(5)–B(7)	1.75 (1)
C(2)–C(3)	1.484 (4)	B(6)–B(7)	1.80 (1)
C(2)–CM(2)	1.530 (7)	B(4)–HB(4)	1.16 (5)
C(2)–B(6)	1.54 (1)	B(5)–HB(5)	1.06 (6)
C(2)–B(7)	1.744 (6)	B(6)–HB(6)	1.06 (5)
C(3)–CM(3)	1.474 (9)	B(7)–HB(7)	1.04 (4)
C(3)–B(4)	1.56 (1)		

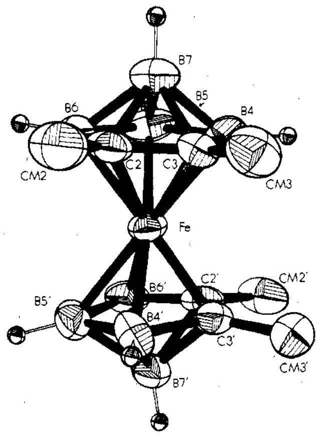

Figure 1. View of the molecule showing nonhydrogen atoms as 50% probability ellipsoids and B–H hydrogen atoms as spheres of arbitrary radius.

Table III. Selected Bond Angles (deg)

C(2)–Fe–C(3)	42.1 (2)	B(5)–B(4)–HB(4)	137 (3)
C(3)–Fe–B(4)	42.7 (3)	B(7)–B(4)–HB(4)	138 (3)
B(4)–Fe–B(5)	45.8 (3)	Fe–B(5)–B(4)	66.0 (6)
B(5)–Fe–B(6)	45.7 (4)	Fe–B(5)–B(6)	64.7 (4)
B(6)–Fe–C(2)	43.0 (3)	B(4)–B(5)–B(7)	60.9 (7)
Fe–C(2)–C(3)	69.8 (3)	B(6)–B(5)–B(7)	62.8 (6)
Fe–C(2)–B(6)	71.7 (4)	B(4)–B(5)–B(6)	103.8 (9)
C(3)–C(2)–B(7)	65.4 (5)	Fe–B(5)–HB(5)	143 (3)
B(6)–C(2)–B(7)	66.0 (6)	B(4)–B(5)–HB(5)	126 (4)
B(6)–C(2)–C(3)	114.1 (4)	B(6)–B(5)–HB(5)	129 (4)
Fe–C(2)–CM(2)	134.1 (3)	B(7)–B(5)–HB(5)	130 (3)
C(3)–C(2)–CM(2)	118.6 (5)	Fe–B(6)–B(5)	69.7 (4)
B(6)–C(2)–CM(2)	126.7 (6)	Fe–B(6)–C(2)	65.3 (4)
B(7)–C(2)–CM(2)	132.1 (4)	B(5)–B(6)–B(7)	60.1 (5)
Fe–C(3)–C(2)	68.1 (3)	C(2)–B(6)–B(7)	62.4 (5)
Fe–C(3)–B(4)	72.5 (4)	B(5)–B(6)–C(2)	105.1 (7)
C(2)–C(3)–B(7)	64.5 (4)	Fe–B(6)–HB(6)	136 (3)
B(4)–C(3)–B(7)	63.8 (5)	B(5)–B(6)–HB(6)	131 (3)
C(2)–C(3)–B(4)	111.6 (6)	C(2)–B(6)–HB(6)	123 (3)
Fe–C(3)–CM(3)	135.7 (5)	B(7)–B(6)–HB(6)	134 (3)
C(2)–C(3)–CM(3)	121.8 (5)	C(2)–B(7)–C(3)	50.2 (4)
B(4)–C(3)–CM(3)	125.6 (6)	C(3)–B(7)–B(4)	52.6 (5)
B(7)–C(3)–CM(3)	131.9 (6)	B(4)–B(7)–B(5)	58.6 (4)
Fe–B(4)–C(3)	64.8 (4)	B(5)–B(7)–B(6)	57.2 (7)
Fe–B(4)–B(5)	68.3 (6)	B(6)–B(7)–C(2)	51.6 (4)
C(3)–B(4)–B(7)	63.6 (6)	C(2)–B(7)–HB(7)	125 (2)
B(5)–B(4)–B(7)	60.6 (7)	C(3)–B(7)–HB(7)	126 (4)
C(3)–B(4)–B(5)	105 (1)	B(4)–B(7)–HB(7)	131 (3)
Fe–B(4)–HB(4)	131 (3)	B(5)–B(7)–HB(7)	134 (3)
C(3)–B(4)–HB(4)	118 (3)	B(6)–B(7)–HB(7)	129 (3)

Table IV. Selected Mean Planes[a]

atom	deviation, Å	atom	deviation, Å
Plane 1: C(2), C(3), B(4), B(5), B(6)			
$0.9359x + 0.3458y + 0.0680z = 1.6488$			
C(2)	−0.011	Fe	1.649
C(3)	0.006	B(7)	−1.118
B(4)	0.001	CM(2)	−0.231
B(5)	−0.006	CM(3)	−0.208
B(6)	0.010		
Plane 2: C(2′), C(3′), B(4′), B(5′), B(6′)			
$-0.9359x - 0.3458y + 0.0680z = 1.6488$			
C(2′)	−0.011	B(5′)	−0.006
C(3′)	0.006	B(6′)	0.010
B(4′)	0.001		

[a] Angle between plane 1 and plane 2 is 7.80°.

molecule is the first clear example of fused 7-vertex polyhedra to be crystallographically characterized, although $(\eta^5\text{-}C_5H_5)CoFe(CH_3)_4C_4B_8H_8$[13] (vide infra) is closely related. X-ray studies have also been carried out on several triple-decked complexes and other small metallocarboranes involving pyramidal or pentagonal-bipyramidal cage systems.[14]

The present structure is in agreement with that assigned from ^{11}B and ^1H NMR spectra,[2a] except for the orientation of the ligands relative to each other. As shown in Figure 2, the carborane units are mutually rotated about 90° away from an eclipsed configuration in which each ring atom would be directly opposite its counterpart in the other ligand. The molecule has rigorous C_2 symmetry, with a crystallographic twofold axis passing through the iron atom and bisecting the C(3)–C(3′) vector. This conformation *appears* to conflict with the NMR data obtained in solution,[2a] which indicated equivalence of all C–CH_3 groups; from this observation one might infer that the rotamer existing in solution differs from that in the solid crystal or that there is fluxional behavior in

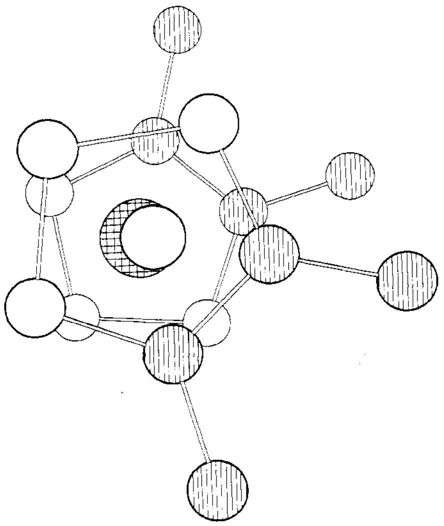

Figure 2. Perspective view down the B(7)–B(7′) axis, showing the orientations of the C_2B_3 rings. Carbon atoms are shaded, boron atoms are white, and the iron atom is crosshatched.

solution. However, given the fact that the two ligands are well separated from each other in the molecule, it is quite possible that the same rotamer exists in the solid state and in solution and that the NMR effects arising from nonequivalence of the methyl groups are simply too weak to be seen. The rotational conformation of the two ligands in solution, or in the gas phase, is thus a moot question at present. We would argue that completely free rotation of the carborane ligands is unlikely, in view of (1) the heterocyclic nature of the C_2B_3 rings face bonded to iron, (2) probable steric hindrance of rotation by the methyl groups, and (3) the presence of the two metal-bound hydrogen atoms (discussed below) which would tend to complicate any attempt at free rotation by the ligands.

The C(2)–C(3)–B(4)–B(5)–B(6) ring (and its crystallographically equivalent counterpart, designated by primes) is planar within experimental error (Table IV) and the bonding of this face to iron is not quite symmetric, with distances ranging from 2.053 (4) Å for Fe–C(2) to 2.23 (1) Å for Fe–B(5). The iron atom is a rather long 1.649 (1) Å from the plane of the C_2B_3 bonding face, reflecting the larger radius of the formal iron(II) atom in comparison with cobalt(III); in Co(III) complexes of the $C_2B_4H_6^{2-}$, $C_2B_3H_5^{4-}$, and $C_2B_3H_7^{2-}$ ligands or their C-substituted derivatives,[14b,d–g] the metal–ring distances range from 1.510 (1) to 1.570 (1) Å. In contrast, the iron(II) complexes 1,2,3-$(CO)_3FeC_2B_3H_7$[14c] and $(\eta^5\text{-}C_5H_5)CoFe(CH_3)_4C_4B_8H_8$[13] have metal–$C_2B_3$ ring vectors of 1.617 (1) and 1.63 (1) Å, respectively.

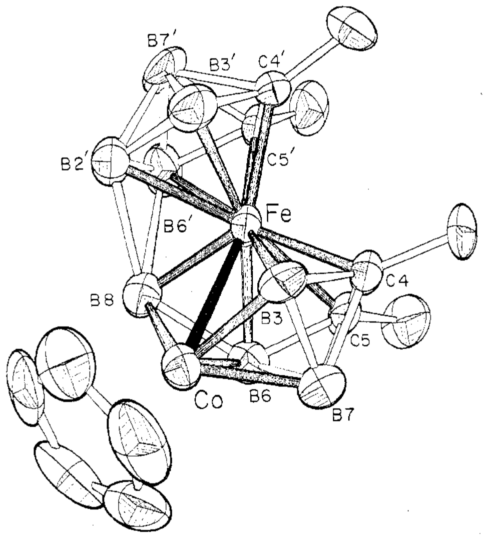

Figure 3. Structure[13] of $(\eta^5\text{-}C_5H_5)CoFe(CH_3)_4C_4B_8H_8$.

A highly significant feature of the $[(CH_3)_2C_2B_4H_4]_2FeH_2$ molecule is the presence of two hydrogen atoms in the vicinity of the iron atom, which are believed[2c] to be directly involved in the ligand-fusion process described earlier. Although other complexes have been prepared which contain hydrogens bound to metal atoms sandwiched between two carborane ligands (e.g., $[(CH_3)_2C_2B_4H_4]_2CoH$,[2b] $[(CH_3)_2C_2B_3H_5]CoH[(CH_3)_2C_2B_4H_4]$,[2b] $[(CH_3)_2C_2B_3H_5]CoH[(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_3]$,[2b] isomers of $(\eta^5\text{-}C_5H_5)Fe^{II}H(C_2B_4H_6)$,[15] and others), in no case have these hydrogen atoms been located precisely; the primary evidence of metal–hydrogen bonding is the high-field proton NMR signal (usually >10 ppm from $(CH_3)_4Si$) which is observed in each instance. Two cobalt–boron clusters having "extra" hydrogens associated with transition metals have been crystallographically studied. The cobaltaborane 1,2-$(\eta^5\text{-}C_5H_5)_2Co_2B_4H_6$ has two triply bridging hydrogen atoms which have been located on Co_2B faces and refined,[16] and 1,2,3-$(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$ has two such hydrogens for which there is crystallographic evidence although they were not refined.[17] Face-bridging hydrogens have also been located on trimetallic faces in several metal clusters.[18]

In the present investigation the two "extra" hydrogen atoms were not directly observed. It is clear that these hydrogens are intimately associated with iron, given the characteristic high-field (δ −10.44) 100-MHz ^1H NMR resonance which appears as a moderately sharp ($w_{1/2} = 55$ Hz) peak.[2a] Since the four boron atoms B(4), B(6), B(4′), and B(6′) exhibit a single ^{11}B NMR resonance, it was assumed[2a] that the two metal-bound hydrogen atoms tautomerize rapidly through several positions, most probably over the centers of the four FeB_2 triangular faces.[19] This hypothesis is strongly supported in the present study by the following evidence: the planes of the C_2B_3 bonding faces on the two ligands are inclined at an angle of 7.80° such that *the carbon atoms C(3) and C(3′) and their attached methyl groups are moved toward each other.* The significance of this observation is heightened by the fact that the methyl carbon atoms CM(3) and CM(3′) are only 3.53 (1) Å apart, which is 0.5 Å *less* than the sum of van der Waals radii for methyl groups (2.0 Å) as given by Pauling.[20] For comparison, it is useful to note that in $[(CH_3)_2C_2B_9H_9]_2Ni^{IV}$, where the nearest interligand methyl–methyl distance is 3.414 (17) Å, the bonding faces of the ligands are tilted so as to *increase* the CH_3–CH_3 distance and thereby relieve steric crowding of these groups.[21]

The observed tilt of the ligands in $[(CH_3)_2C_2B_4H_4]_2FeH_2$, in a direction opposite to that expected if the metal-bound hydrogens were not present, indicates that these hydrogen atoms are wedged between the polyhedra on the side of the complex furthest removed from the C–CH_3 groups, i.e., in the vicinity of the Fe–B(5)–B(6) and Fe–B(5′)–B(6′) faces. Since the "extra" hydrogens on the closo systems CB_5H_7[22] and 1,2-$(\eta^5\text{-}C_5H_5)_2Co_2B_4H_6$[16] have been shown to occupy face-bridging locations, it is reasonable to assume that this is the case in the present structure also (moreover, given the geometry of the molecule it would be difficult for the iron-bound hydrogen atoms to avoid some degree of interaction with nearby borons in any case). As was previously noted, tautomeric movement over the two FeB_2 triangles mentioned, as well as the other two [Fe–B(5)–B(4) and Fe–B(5′)–B(4′)], is likely. In the crystal, disorder of the bridging hydrogens over the four FeB_2 faces, which would produce peaks averaging only 0.5 electron in intensity, could well account for the failure to locate them from the X-ray data.

The previously studied metallocarborane $(\eta^5\text{-}C_5H_5)CoFe(CH_3)_4C_4B_8H_8$[13] (Figure 3) has a structural relationship with the present complex that should be noted. In both molecules

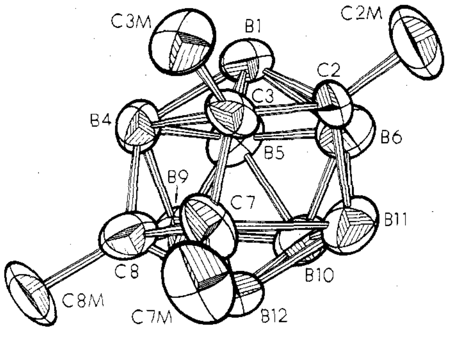

Figure 4. Structure[4] of $(CH_3)_4C_4B_8H_8$.

there are two pentagonal-bipyramidal polyhedra sharing a common iron atom; in the Fe–Co species, there is an additional BH group wedged between the polyhedra such that it caps triangular faces on both cages. In electron-counting terms,[23] the bridging BH group (a two-electron donor to the skeletal framework) is equivalent to the two "extra" hydrogens in $[(CH_3)_2C_2B_4H_4]_2FeH_2$; since $Co(\eta^5\text{-}C_5H_5)$ and BH units are also equivalent, the two complexes are electronic analogues. It is not surprising, therefore, that their structures have much in common. The similarity is further underlined by the fact that in the Fe–Co system the presence of the wedging BH group causes the equatorial rings to tilt by 9.35° such that the methyl carbons CM(4) and CM(4′) are pushed close together; the separation of only 3.52 Å is identical with the corresponding CM(3)–CM(3′) distance in $[(CH_3)_2C_2B_4H_4]_2FeH_2$.

Finally, we wish to comment on one other aspect of this structure. The relative orientation of the $(CH_3)_2C_2B_4H_4^{2-}$ ligands bears a remarkable similarity to the structure of the tetracarbon carborane $(CH_3)_4C_4B_8H_8$[4] (Figure 4), which is significant in view of the facile conversion of the iron complex to $(CH_3)_4C_4B_8H_8$ as mentioned in the Introduction. While the mechanism of the ligand-fusion process is not known, given the structure in Figure 1 it is certainly easy to visualize initial linkage of the two carborane ligands, perhaps between the B(5)–B(6) and B(5′)–B(6′) edges, followed by expulsion of 2H + Fe and completion of the face-to-face bonding to give the carborane. The present investigation, together with the earlier structure determination[4] on $(CH_3)_4C_4B_8H_8$, thus establishes the geometries of the initial and final species involved in this particular ligand-fusion reaction. The difficult tasks of determining the nature, and if possible the structure, of one or more intermediates in this process are challenges which remain to be met.

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Registry No. $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2FeH_2$, 58846-86-9.

Supplementary Material Available: A listing of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) R. N. Grimes, *Acc. Chem. Res.*, **11**, 420 (1978).
(2) (a) W. M. Maxwell, V. R. Miller, and R. N. Grimes, *Inorg. Chem.*, **15**, 1343 (1976); (b) *J. Am. Chem. Soc.*, **98**, 4818 (1976); (c) W. M. Maxwell, K.-S. Wong, and R. N. Grimes, *Inorg. Chem.*, **16**, 3094 (1977).
(3) K.-S. Wong, J. R. Bowser, J. R. Pipal, and R. N. Grimes, *J. Am. Chem. Soc.*, **100**, 5045 (1978).
(4) D. P. Freyberg, R. Weiss, E. Sinn, and R. N. Grimes, *Inorg. Chem.*, **16**, 1847 (1977).
(5) J. R. Pipal and R. N. Grimes, *J. Am. Chem. Soc.*, **100**, 3083 (1978).
(6) J. R. Pipal and R. N. Grimes, submitted for publication.
(7) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(8) M. R. Churchill and B. G. DeBoer, *J. Am. Chem. Soc.*, **96**, 6310 (1974).
(9) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.
(10) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(11) D. T. Cromer and J. A. Ibers, ref 9.
(12) D. P. Freyberg, G. M. Mockler, and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 447 (1976).
(13) W. M. Maxwell, E. Sinn, and R. N. Grimes, *J. Am. Chem. Soc.*, **98**, 3490 (1976).
(14) (a) R. N. Grimes, W. J. Rademaker, M. L. Denniston, R. F. Bryan, and P. T. Greene, *J. Am. Chem. Soc.*, **94**, 1865 (1972); (b) D. C. Beer, V. R. Miller, L. G. Sneddon, R. N. Grimes, M. Mathew, and G. J. Palenik, *ibid.*, **95**, 3046 (1973); (c) J. P. Brennan, R. N. Grimes, R. Schaeffer, and L. G. Sneddon, *Inorg. Chem.*, **12**, 2266 (1973); (d) W. T. Robinson and R. N. Grimes, *ibid.*, **14**, 3056 (1975); (e) J. R. Pipal and R. N. Grimes, *ibid.*, **17**, 10 (1978); (f) J. R. Pipal, W. M. Maxwell, and R. N. Grimes, *ibid.*, **17**, 1447 (1978); (g) R. Weiss and R. F. Bryan, *Acta Crystallogr., Sect. B*, **33**, 589 (1977).
(15) L. G. Sneddon, D. C. Beer, and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 6623 (1973).
(16) J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, in press.
(17) J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, **16**, 3255 (1977).
(18) (a) G. Huttner and M. Lorenz, *Chem. Ber.*, **108**, 973 (1975); (b) B. T. Huie, C. B. Knobler, and H. D. Kaesz, *J. Am. Chem. Soc.*, **100**, 3059 (1978); (c) R. G. Teller, R. D. Wilson, R. K. McMullan, T. F. Koetzle, and R. Bau, *ibid.*, **100**, 3071 (1978); R. D. Wilson and R. Bau, *ibid.*, **98**, 4687 (1976).
(19) In the analogous cobalt complex $[(CH_3)_2C_2B_4H_4]_2Co^{III}H$ there is direct evidence that the cobalt-bound hydrogen also interacts with neighboring boron atoms: the 100-MHz proton NMR resonance of the Co–H proton sharpens on ^{11}B decoupling.[2b]
(20) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, p 261.
(21) M. R. Churchill and K. Gold, *J. Am. Chem. Soc.*, **92**, 1180 (1970).
(22) E. A. McNeill and F. R. Scholer, *Inorg. Chem.*, **14**, 1081 (1975).
(23) K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976), and references therein.