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Crystal and Molecular Structure of Dicarbacyclopentaboranyliron Tricarbonyl

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The crystal and molecular structure of $B_3C_2H_7Fe(CO)_3$ has been determined by low-temperature, single-crystal X-ray techniques. The crystals are monoclinic, space group $P2_1/m$, with $a = 6.327$ (3) Å, $b = 10.279$ (6) Å, $c = 6.607$ (3) Å, and $\beta = 99.64$ (4)°. The calculated density is 1.60 g/cm³ for $Z = 2$. The structure was refined using full-matrix least-squares techniques using 1012 observed relfections to a conventional R value of 0.024. The dicarbacyclopentaboranyl(2−) ring is planar and the molecule possesses a mirror plane.

Introduction

The metallocarborane $B_3C_2H_7Fe(CO)_3$, a pale yellow liquid, was originally prepared[2] in the gas-phase thermal reaction of dicarba-*nido*-hexaborane(8), $B_4C_2H_8$, with iron pentacarbonyl, and was later obtained[3] in the reaction of dicarba-*nido*-pentaborane(7), $B_3C_2H_7$, with iron pentacarbonyl under ultraviolet light. From nmr and infrared data and bonding considerations, this species was assigned[2] a novel structure containing a planar B_3C_2 ring symmetrically π bonded to the iron atom, with two B-H-B bridges directed away from the metal. This structure, which may be regarded as an analog of the isoelectric metallocene cation $(\pi\text{-}C_5H_5)Fe(CO)_3^+$, has been confirmed in a single-crystal X-ray diffraction study which we now report.

Experimental Section

A sample[2] of $B_3C_2H_7Fe(CO)_3$ was transferred into a Pyrex capillary (0.55-mm diameter) using standard high-vacuum techniques. A crystal was then grown from the liquid (estimated melting point was +15 to 0°) in a nitrogen vapor cold stream,[4] mounted directly on a Picker FACS 1 diffractometer.

The crystal thus obtained was about 1 mm long and 0.55 mm in diameter and grew with the $\langle\bar{3}04\rangle$ reciprocal lattice vector coincident with the goniostat ϕ axis. A standard orientation procedure[5] determined a monoclinic unit cell with systematic extinctions only in the $\langle 0k0\rangle$ zone for odd reflections. Possible space groups are thus $P2_1/m$ ($C_{2h}{}^2$) and $P2_1$ ($C_2{}^2$).

Statistical tests for space group distinction proved ambiguous, so both space groups were used concurrently, and ultimately each produced the same R factor. The space group $P2_1/m$ was judged to provide a better model, using the magnitudes of the uncertainties of the bonded distances and angles as the criterion.

Alignment and data collection were accomplished using a Picker FACS I diffractometer, equipped with a highly oriented graphite monochromator ($\langle 002\rangle$ reflection) at a 2° takeoff angle and Mo Kα radiation.

The cell constants were determined by a least-squares fit of 12 centered reflections to be[6] $a = 6.327$ (3) Å, $b = 10.279$ (6) Å, $c = 6.607$ (3) Å, and $\beta = 99.64$ (4)°, at about −160°.

Owing to the low melting point and air sensitivity of this material, no attempt was made to measure the density of the crystal; however, the calculated density of 1.609 g/cm³ for $Z = 2$ is a reasonable value for compounds of this type.

The intensity data were collected at a temperature estimated to be −160° using a continuous θ-2θ scan over a range of $2\theta = 2.5°$ plus dispersion correction at 2°/min. Ten-second background counts were taken at the limits of each scan. Reflections with a count rate of greater than 10,000 cps were retaken with an aluminum filter. The filter factor, q, was 10.79 and the σ of the filter was 0.4.

Counting statistics ($\sigma(x) = x^{1/2}$) were assumed valid. By standard propagation of errors

$$\sigma(I) = (Lp)q[p^2C^2 + N + k^2(B_1 + B_2)]^{1/2}$$

where p is a correction term to allow for nonrandom counting errors, $C = N - k(B_1 + B_2)$, k is a factor to scale each of the background counts to half the scan time, B_1 and B_2 are background counts, N is the total scan count, and q is the filter factor ($q = 1$, for unfiltered data).

There were 3222 reflections collected of which 392 were standards. At 98% probability of being significant ($I \geqslant 2.33\sigma(I)$), 1012 of the 1309 unique intensities were considered observed. The intensities of three reflections were monitored after each interval of 25 data collected. The average standard deviation of each was less than 5% with no significant trends.

Lorentz and polarization corrections were applied in the usual way. The linear absorption coefficient is 72 cm⁻¹, indicating absorption correction factors varying from 11 to 14, assuming a cylindrical sample approximation.[7] However no correction was made on the data because of the uncertainty about the thickness of the wall of the glass capillary and its absorption.

The form factors used were those of Cromer and Mann[8] for the neutral iron, oxygen, carbon, boron, and hydrogen atoms with appropriate[9] anomalous dispersion corrections for iron.

Solution and Refinement of Structure

Analysis of a standard Patterson map showed a unique peak in the Harker plane at $y = 0.25$ corresponding to the iron atom. The corresponding peak at $2x$, $2y$, $2z$ placed the iron atoms on the mirror plane in special position 2e at 0.39, 0.25, 0.35. Least-squares refinement[10] based on iron alone produced a value of the conventional R index of 0.355 where $R = \Sigma(|F_o| - |F_c{}^*|)/\Sigma|F_o|$. A difference Fourier map phased on the iron position showed seven peaks corresponding to the remaining heavy atoms in the molecule. Least-squares refinement of these positions led to a value of $R = 0.053$. A second difference synthesis based on all of the heavy atoms produced four unique peaks which were reasonably assigned as the hydrogen atoms. Refining all parameters, assuming isothermal motion of all atoms except hydrogen, which were fixed at $B = 2.0$ (the average isothermal

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(1) (a) Indiana University. (b) University of Virginia.

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(9) See ref 7, p 215. $\Delta f' = 0.350$ and $\Delta f'' = 0.90$.

(10) See paragraph at end of paper regarding supplementary material.

Table I. Fractional Coordinates and Thermal Parameters ($\times 10^4$)[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0.38923 (5)	0.25	0.35230 (5)	58.2 (5)	26.2 (3)	66.7 (8)	0.0	2 (1)	0.0
O_1	0.6276 (3)	0.25	0.7764 (3)	150 (5)	64 (2)	99 (5)	0.0	−53 (8)	0.0
O_2	0.6325 (2)	0.0393 (1)	0.2013 (2)	114 (3)	46 (2)	175 (3)	31 (4)	23 (5)	−52 (3)
C_1	0.5368 (3)	0.25	0.6129 (4)	88 (5)	33 (2)	106 (5)	0.0	13 (9)	0.0
C_2	0.5370 (3)	0.1194 (2)	0.2633 (3)	75 (4)	38 (2)	102 (4)	−8 (4)	−8 (6)	1 (4)
C_3	0.1062 (3)	0.1814 (2)	0.4507 (3)	64 (3)	53 (2)	99 (4)	−15 (4)	30 (6)	25 (4)
B_1	0.1666 (5)	0.25	0.766 (4)	81 (6)	60 (3)	96 (6)	0.0	−1 (1)	0.0
B_2	0.1366 (3)	0.1132 (2)	0.2531 (3)	75 (4)	40 (2)	126 (5)	−28 (5)	10 (7)	−13 (5)
H_1	0.208 (6)	0.25	0.936 (6)	All thermal parameters isotropic, fixed at $B = 2.0$					
H_2	0.156 (4)	0.009 (2)	0.230 (4)						
H_3	0.113 (4)	0.141 (3)	0.552 (4)						
H_4	0.003 (4)	0.163 (3)	0.093 (3)						

[a] Thermal parameters are defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

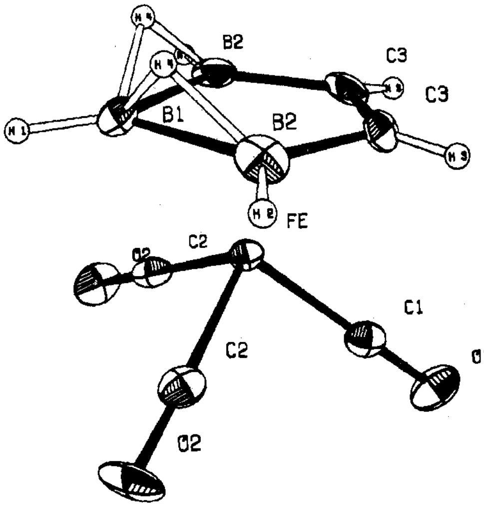

Figure 1. Molecular structure of $B_3C_2H_7Fe(CO)_3$.

value of the atoms to which they are bonded), produced a conventional R of 0.043 and a weighted R_w of 0.044 where $R_w = (\Sigma w_i |F_o| - |F_c^*| / \Sigma w_i |F_o|^2)^{1/2}$ and w_i is defined as $w_i = 1/\sigma^2(F_o)$. Finally the nonhydrogen atoms were allowed to vary anisotropically along with all positional parameters and scale factors. Refinement was allowed to continue until the maximum shift per error ratio was less than 0.8 for positional and 0.1 for thermal parameters. At this point $R = 0.024$ and $R_w = 0.023$.

Refinements were carried out using GENLES, Larson's[11] full-matrix least-squares program. The function minimized was $\Sigma w_i^{1/2} \cdot (|F_o| - |F_c^*|)$, where

$$F_c^* = kF_c \left\{ 1 + gLp \left[\frac{2\,(1 + \cos^4 2\theta)}{(1 + (\cos^2 2\theta)^2} \right] F_c^{\,2} \right\}^{1/2}$$

in which k is a scale factor, Lp is the Lorentz-polarization factor, g is the extinction coefficient,[12] and F_c is the structure factor calculated in the usual way.

A final difference Fourier was featureless with the largest residuals being 0.6 e/Å^3 in the vicinity of the iron atoms and 0.2^{-3} e/Å^3 elsewhere compared to 0.88 e/Å^3 for the average density at the hydrogen positions in a difference map where these were omitted.

A value was obtained for the extinction coefficient, $g = 7 \times 10^{-6}$; however this was judged to produce no significant[13] improvement in the R index or in the uncertainities of the calculated bond distances.

In a test of disorder between the boron and carbon atoms in the ring, the quantity $1 - P(\text{atom A}) + P(\text{atom B})$, where P is a population parameter, was included early in the refinement. The values of P were insignificant; examination of the thermal parameters and the B-H *vs.* C-H bonds uniquely determined the ring carbon positions, and the parameter, P, was deleted from subsequent refinements.

Results and Discussion

In order to verify the choice of $P2_1/m$ instead of the corresponding acentric space group ($P2_1$), we carried out simultaneous refinements in each. Displacement of the atom positions from the centric structure were only of the order of the uncertainties in the positions themselves and there was not sufficient improvement of the R index to justify[13] the number of parameters added by refining the acentric case.

The molecular structure of $B_3C_2H_7Fe(CO)_3$ is given in Figure 1[14] and the corresponding positional and thermal parameters are given in Table I. A reasonable qualitative description of the bonding utilizes the commonly invoked analogy between the metallocarboranes and the metallocenes, in which the carborane ligand is assigned a formal dinegative charge and is assumed to contain six delocalized electrons in bonding molecular orbitals extending about the open face of the ligand.[15] These electrons are, of course, available for donation to metal orbitals of appropriate symmetry, as in the π-cyclopentadienyl transition metal compounds. Application of this approach to the present case suggests a six-electron donation from delocalized[16] ring MO's on the formal $B_3C_2H_7^{2-}$ cyclo carboranyl group to the $Fe(CO)_3^{2+}$ moiety, as in the analogous $(\pi\text{-}C_5H_5)Fe(CO)_3^+$ species cited earlier. This ring-delocalized model emphasizes the close structural, electronic, and chemical relationship between the metallocarboranes and the metallocenes, for which a substantial body of evidence exists.[15] Finally, we note that the formal $B_3C_2H_7^{2-}$ ligand is a diprotonated derivative of formal planar $B_3C_2H_5^{4-}$ (a $C_5H_5^-$ analog) of which several complexes have been prepared[17] and is also closely related to the pyramidal $B_4C_2H_6^{2-}$ ligand which exists in a number of metallocarboranes, *e.g.*, $B_4C_2H_6Fe(CO)_3$,[2] $B_4C_2H_6FeC_5H_5$,[18] and $B_4C_2H_6GaCH_3$.[19]

Other compounds containing the formal $B_3C_2H_7^{2-}$ ligand have recently been prepared[20] and are assumed to have sand-

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(11) A. C. Larson, unpublished programs.

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(15) Recent metallocarborane reviews, including discussions of the bonding: M. F. Hawthorne, *Pure Appl. Chem.*, 29, 547 (1972); L. J. Todd, *Advan. Organometal. Chem.*, 8, 87 (1970); R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970, Chapter 9.

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Table II. Distances and Angles[a]

Atoms	Bond, Å	Atoms	Angle, deg
B_1-B_2	1.852 (3)	B_2-B_1-B_2	98.2 (2)
B_2-C_3	1.520 (3)	B_1-B_2-C_3	103.7 (2)
C_3-C_3	1.410 (4)	B_2-C_3-C_3	117.2 (1)
H_1-B_1	1.01 (4)	H_1-B_1-B_2	130.6 (2)
H_2-B_2	1.10 (3)	H_2-B_2-B_1	129 (1)
H_3-C_3	0.78 (2)	H_2-B_2-C_3	127 (1)
H_4-B_1	1.25 (3)	H_3-C_3-C_3	122 (2)
H_4-B_2	1.26 (2)	H_3-C_3-B_2	120 (2)
C_1-O_1	1.136 (3)	B_1-H_4-B_2	96 (2)
C_2-O_2	1.138 (2)	H_4-B_1-B_2	42 (1)
Fe-C_1	1.816 (3)	H_4-B_2-B_1	42 (1)
Fe-C_2	1.791 (2)	C_1-Fe-C_2	95.6 (1)
Fe-B_1	2.11 (3)	C_2-Fe-C_2	97.2 (1)
Fe-B_2	2.14 (2)	Fe-C_1-O_1	179.4 (2)
Fe-C_3	2.13 (2)	Fe-C_2-O_2	177.5 (2)
H_4-H_4	1.78 (6)		
O_1-O_2	4.379 (5)		
O_2-O_2	4.331 (5)		
Intermolecular			
O_2-O_2	3.007 (3)		

[a] Calculated using A. C. Larson's program DISAGL. The numbers in parentheses are least-squares standard deviations of the least significant figure obtained using a variance-covariance matrix.

wich structures in which the metal-carborane ring bonding is analogous to that in $B_3C_2H_7Fe(CO)_3$.

Reference to Table II reveals two slight anomalies in the present structure. The angles subtended by the carbonyl carbon atoms and the iron are greater than the expected 90° and the iron-carbonyl distance in the symmetry plane is slightly elongated. These draw attention to the difference between boron and carbon atoms in forming the delocalized MO's.

In the case of the cyclopentadienide ligand it is generally accepted that carbon AO's overlap perfectly giving a system of delocalized MO's which on bonding to iron result in producing nearly orthogonal iron-carbonyl bonds. Inasmuch as boron orbitals are different from carbon and the 2,3-dicarbacyclopentaboranyl ligand has two bridge hydrogens, not present in cyclopentadienide, the resulting MO's will be different and on bonding to iron will result in slightly different iron-carbonyl orbitals as well. It is reasonable then to expect that the $B_3C_2H_5^{4-}$ mentioned above would not exhibit these anomalies since the bridge hydrogens are absent and are probably the major factor in the difference between cyclopentadienide and dicarbacyclopentaboranyl ligands.

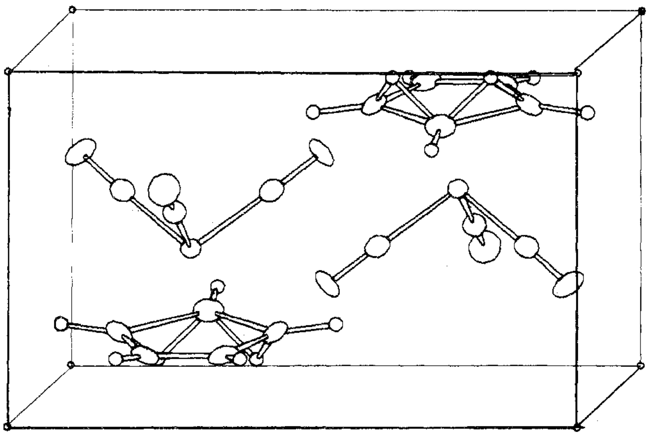

Figure 2. Cell packing diagram for $B_3C_2H_7Fe(CO)_3$.

The packing in the cell is shown in Figure 2 and the closest observed nonbonding interactions are H_4-H_4 = 1.78 (6) Å (intramolecular) and O_2-O_2 = 3.007 (3) Å (intermolecular). Finally, nonlinearity of the Fe-C_2-O_2 bond (177.5 (2)°) possibly results from the above O_2-O_2 interaction. No such proximity exists for O_1, and Fe-C_1-O_1 is found to be 179.4 (2)°.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2266.