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ADDITION OF BOROHYDRIDE ION TO COORDINATED ISOCYANIDES: THE STRUCTURE OF π-$C_5H_5Fe(CO)[(CHNCH_3)_2BH_2]$

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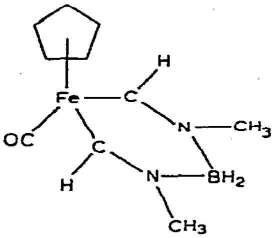
SUMMARY

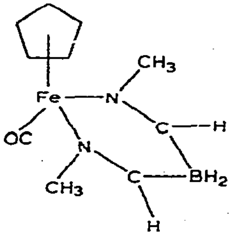
The structure of π-$C_5H_5Fe(CO)[(CHNCH_3)_2BH_2]$ has been determined from three dimensional X-ray diffractometer data collected by counter methods. The compound crystallizes in the space group $P2_1/a$ with four molecules in a cell of dimensions $a = 12.33(3)$, $b = 6.14(2)$ and $c = 16.21(7)$ Å with $\beta = 105.0(2)°$. The observed and calculated densities are 1.37(2) and 1.379(6) g/cm^3 respectively. Full-matrix least-squares refinement has resulted in $R = 0.113$ for the 1238 data with $F_o^2 \geqslant \sigma(F_o^2)$. The structure results from a BH_4^- anion adding across two coordinated isocyanide ligands to form a six-membered heterocyclic ring containing B–N bonds.

INTRODUCTION

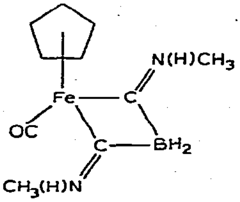
The compound π-$C_5H_5Fe(CO)[(CHNCH_3)_2BH_2]$, (I), was synthesized and characterized by Treichel and coworkers. They proposed[1] that the complex had structure (Ia), although the available data were also consistent with (Ib) and (Ic). Structure (Ic) is very similar to the structure of $[(CNCH_3)_4Fe(CHNCH_3)_2NCH_3][PF_6]_2$[2], (II); therefore we felt that an X-ray structure determination of (I) was warranted.



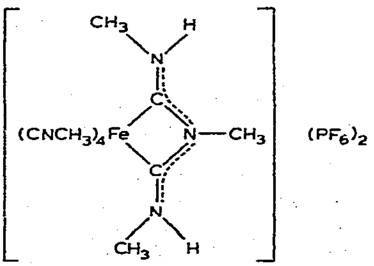
(Ia)



(Ib)



(Ic)



(II)

EXPERIMENTAL

A sample of π-$C_5H_5Fe(CO)[(CHNCH_3)_2BH_2]$ was kindly supplied by Drs. P. M. Treichel and J. P. Stenson. The sample was air- and light-sensitive, particularly in solution. Suitable crystals were obtained (with difficulty) by cooling a hexane solution slowly to $-40°$. The crystals were sealed in 0.3 mm thin-walled glass capillaries, and preliminary precession photographs (Mo-$K\alpha$) indicated the crystals were monoclinic with diffraction conditions $h0l$, $h=2n$; $0k0$, $k=2n$. These conditions are consistent with space group $P2_1/a$, (C^5_{2h}). Successful solution and refinement confirmed this choice of space group. The equivalent positions in this space group are $\pm(x, y, z)$; $\pm(\frac{1}{2}+x, \frac{1}{2}-y, z)$.

Several crystals were examined on a Picker FACS-I four-circle diffractometer before one was obtained which had acceptable ω scans (peak widths at half-height of $< 0.25°$ at a take-off angle of 0.7°). The crystal had dimensions $0.09 \times 0.15 \times 0.57$ mm. Twelve reflections with 2θ in the range 21–25° were manually centered on the Mo-$K\bar{\alpha}$ peak ($\lambda = 0.71069$ Å). A least-squares refinement of the setting angles for the twelve reflections gave unit cell parameters at $23 \pm 2°$ of $a = 12.33(3)$, $b = 6.14(2)$, and $c = 16.21(7)$ Å with $\beta = 105.0(2)°$. The density of the crystal was determined to be 1.37(2) g/cm^3 by the gradient column technique using aqueous KI solutions. The calculated density assuming four molecules per cell is 1.379(6) g/cm^3.

An incident beam monochromator equipped with a graphite crystal was used to obtain Mo-$K\alpha$ radiation. The $\theta-2\theta$ axis of the monochromator was perpendicular to the $\theta-2\theta$ axis of the diffractometer. Data were collected using the $\theta-2\theta$ scan technique and a scan range from 2θ Mo-$K\alpha_1$ $-0.85°$ to 2θ Mo-$K\alpha_2$ $+0.85°$ at a take-off angle of 1.7°. The scan rate was 2°/min and background measurements of 10 sec were taken at each end of the scan. The pulse height analyzer was set to admit $\approx 90\%$ of the Mo-$K\alpha$ peak and the scintillation counter was 24 cm from the crystal. During data collection the intensities of three reflections were monitored every 50 reflections. There was an average decrease in the intensity of the three standards of 13.7%, and a linear correction was assumed and applied to the data. A total of 1695 reflections were collected with $2\theta \leqslant 40°$. The data were reduced to F^2 and $\sigma(F^2)$ by procedures similar to those previously described[3,4].* The polarization correction used was $P = 0.5(\cos^2 2\theta_m + \cos^2 2\theta)$ where θ_m is the Bragg angle of the monochromator crystal and θ is the Bragg angle of the observed reflection. Standard deviations were assigned to the corrected intensities by the formula:

$$\sigma(F^2) = [CT + 0.25(t_c/t_b)^2 \cdot (B_1 + B_2) + (p \cdot F^2)^2]^{\frac{1}{2}}$$

where CT is the total integrated peak count obtained in time t_c and B_1 and B_2 are the background counts each obtained in time t_b; F^2 is the corrected intensity and p was taken as 0.04.

The absorption coefficient for the compound for Mo-$K\alpha$ radiation is 12.81 cm^{-1}. The faces of the crystal were identified as {100}, {010}, and {001} and the crystal

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* The program used for data reduction was Raymond's UCFACS, itself a modification of Doedens and Ibers' PIKOUT. Other computer programs used included Zalkin's FORDAP Fourier summation program, Ibers' NUCLS group least-squares refinement program based on Busing and Levy's ORFLS, Busing and Levy's ORFFE, Johnson's ORTEP plotting program, and Corfield's RANGER weighting analysis programs. All computations were performed on a CDC 6400 computer.

carefully measured. Sample calculations showed that the absorption correction ranged from 1.13 to 1.20 and therefore no absorption correction was made.

SOLUTION AND REFINEMENT

The positions of the Fe atoms in the cell were readily determined from a three-dimensional Patterson function. Refinement was based on F_o, with $\Sigma w \cdot (|F_o|-|F_c|)^2$ being minimized. Weights of $4\,F_o^2/\sigma^2(F_o^2)$ were used. Scattering factors for Fe, C, N, and B were from the usual tabulation[5]. The effects of anomalous dispersion for Fe[6] were included in F_c using the values of $\Delta f'$ and $\Delta f''$ calculated by Cromer[7].

Refinement of the scale factor and the Fe atom coordinates gave $R_1 = \Sigma ||F_o|-|F_c||/\Sigma|F_o| = 0.413$ and $R_2 = [\Sigma w \cdot (|F_o|-|F_c|)^2/\Sigma w \cdot F_o^2]^{\frac{1}{2}} = 0.479$. A difference electron density map revealed all of the remaining non-hydrogen atoms. Four cycles of least-squares refinement assigning Fe anisotropic thermal parameters, the other atoms isotropic thermal parameters, and treating the cyclopentadienyl ring as a rigid group gave $R_1 = 0.161$ and $R_2 = 0.200$. A difference map revealed large residual electron density in the C_5H_5 ring (2.19 e/Å^3). An electron density profile of the ring was then obtained by calculating an electron density difference map (Fig. 1) through the plane of the ring using calculated structure factors from which the ring atoms had been omitted. The atoms were distinct but spread out such that the minimum electron density between atoms was ≈ 2 e/Å^3. Three additional cycles of refinement with all atoms assigned individual positional parameters and anisotropic thermal parameters resulted in convergence with $R_1 = 0.102$ and $R_2 = 0.132$ for the 987 data having $F_o^2 \geqslant 3\sigma(F_o^2)$.

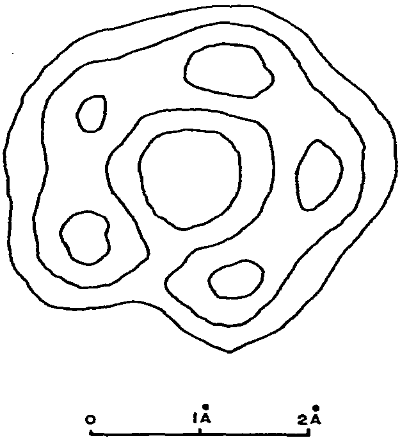

Fig. 1. Electron density map through the plane of the C_5H_5 ring. Contours start at 1e/Å^3 and are in intervals of 1e/Å^3.

The non-methyl hydrogens were then included in their idealized positions as fixed contributions to F_c assuming isotropic thermal parameters ($B = 5.0$ Å^2). Two additional cycles of refinement using the 1238 data with $F_o^2 \geqslant \sigma(F_o^2)$ gave $R_1 = 0.113$ and $R_2 = 0.127$. A final difference map had maximum peak heights of 1.17 e/Å^3 near the Fe atom and the C_5H_5 ring. The relatively large R factors and residual electron density may be due to the crystal decomposition before and during data collection and to the large thermal motion of the cyclopentadienyl ring.

An analysis of the weighting scheme showed that $w \cdot |\Delta F|^2$ was not a function of the indices, $|F_o|$, or $\sin \theta/\lambda$. The standard deviation of an observation of unit weight is 3.63 electrons.

Final structure parameters appear in Table 1. A list of $10\,|F_o|$ and $10\,|F_c|$ is available[*].

DESCRIPTION AND DISCUSSION

A stereo view of the molecule with thermal ellipsoids is shown in Fig. 2. The numbering scheme and a view showing the configuration of the heterocyclic ring is shown in Fig. 3. Final atomic parameters are shown in Table 1 with distances and angles calculated from these parameters shown in Table 2. The estimated standard deviations for the distances and angles were derived from the inverse least-squares matrix of the final refinement.

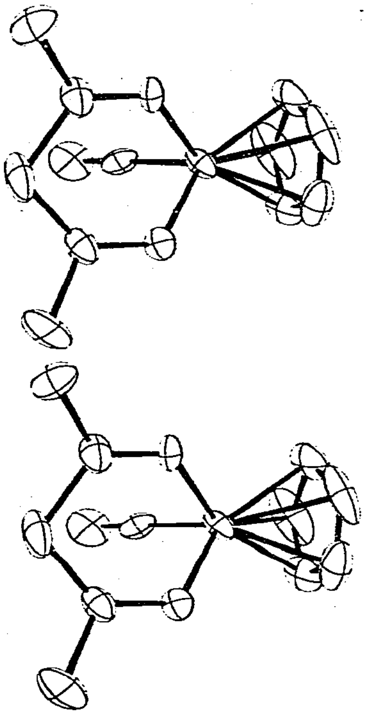

Fig. 2. Stereo view of the π-$C_5H_5Fe(CO)[(CHNCH_3)_2BH_2]$ molecule.

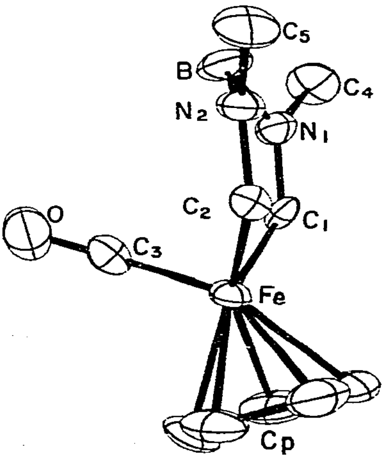

Fig. 3. Numbering scheme and configuration of the π-$C_5H_5Fe(CO)[(CHNCH_3)_2BH_2]$ molecule.

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[*] The Table of structure factors has been deposited as NAPS Document No. 01915, with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 Third Avenue, New York, New York 10022. A copy may be secured by citing the document number and by remitting \$2.00 for a microfiche or \$5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

TABLE 1

FINAL ATOMIC PARAMETERS[a]

Atom	*x*	*y*	*z*	$10^3\beta_{11}$	$10^3\beta_{22}$	$10^3\beta_{33}$	$10^3\beta_{12}$	$10^3\beta_{13}$	$10^3\beta_{23}$
Fe	0.0559(1)	0.1011(4)	−0.1825(1)	5.2(2)	41.2(8)	2.2(1)	0.7(3)	0.1(1)	0.2(3)
O	−0.105(1)	−0.216(2)	−0.158(1)	13(1)	62(6)	7(1)	−1(2)	4(1)	2(2)
N_1	0.026(1)	−0.142(2)	−0.338(1)	7(1)	45(5)	4(1)	−4(2)	2(1)	−4(1)
N_2	−0.114(1)	0.162(2)	−0.339(1)	6(1)	43(5)	3(1)	0(2)	0(1)	−1(1)
C_1	0.090(1)	−0.071(2)	−0.267(1)	6(1)	24(5)	5(1)	−6(2)	1(1)	−1(2)
C_2	−0.053(1)	0.253(2)	−0.268(1)	7(1)	30(5)	3(1)	−1(2)	1(1)	−1(2)
C_3	−0.040(1)	−0.091(2)	−0.170(1)	11(2)	19(4)	4(1)	3(2)	2(1)	2(2)
C_4	0.066(1)	−0.289(3)	−0.396(1)	13(2)	48(7)	6(1)	1(3)	4(1)	−9(2)
C_5	−0.207(1)	0.301(3)	−0.394(1)	9(1)	57(8)	4(1)	5(3)	−2(1)	6(2)
B	−0.101(2)	−0.068(4)	−0.370(1)	8(2)	71(10)	4(1)	−7(4)	0(1)	−9(3)
RC_1[b]	0.132(2)	0.393(3)	−0.137(1)	17(3)	39(7)	5(1)	−10(4)	−3(1)	2(3)
RC_2	0.082(2)	0.314(4)	−0.080(1)	9(2)	61(10)	4(1)	3(3)	−2(1)	−4(2)
RC_3	0.131(2)	0.136(7)	−0.052(1)	12(2)	144(21)	2(1)	−12(6)	−1(1)	1(4)
RC_4	0.215(2)	0.082(4)	−0.095(2)	8(2)	69(10)	6(1)	3(3)	−3(1)	−5(3)
RC_5	0.212(2)	0.261(7)	−0.149(1)	8(2)	119(17)	4(1)	−18(4)	1(1)	−6(4)

[a] Standard deviation of least significant figure given in parentheses. Anisotropic thermal parameters have the form $\exp[-(\beta_{11}\cdot h^2+\beta_{22}\cdot k^2+\beta_{33}\cdot l^2+2\beta_{12}\cdot h\cdot k+2\beta_{13}\cdot h\cdot l+2\beta_{23}\cdot k\cdot l)]$. [b] RC_i is a C atom of the cyclopentadienyl group. RC_3 is under C_3 and RC_2 is on the same side of the molecule as C_2.

TABLE 2

DISTANCES AND ANGLES

Atoms	*Distance (Å)*	*Atoms*	*Angle (deg.)*
Fe–C_1	1.863(15)	C_1–Fe–C_2	89.7(7)
Fe–C_2	1.901(14)	C_1–Fe–C_3	89.4(6)
Fe–C_3	1.718(17)	C_2–Fe–C_3	92.5(7)
C_3–O	1.161(17)	Fe–C_1–N_1	130.4(11)
C_1–N_1	1.293(17)	Fe–C_2–N_2	124.1(10)
C_2–N_2	1.337(16)	C_1–N_1–B	120.9(13)
N_1–B	1.588(23)	C_2–N_2–B	126.1(12)
N_2–B	1.518(25)	C_1–N_1–C_4	123.2(13)
N_1–C_4	1.466(18)	C_2–N_2–C_5	116.7(13)
N_2–C_5	1.519(17)	B–N_1–C_4	115.9(12)
Fe–RC_1	2.065(19)	B–N_2–C_5	117.2(13)
Fe–RC_2	2.077(19)	N_1–B–N_2	110.0(12)
Fe–RC_3	2.095(18)	Fe–C_3–O	176.8(14)
Fe–RC_4	2.107(16)	RC_1–RC_2–RC_3	107.4(22)
Fe–RC_5	2.103(18)	RC_2–RC_3–RC_4	111.3(23)
RC_1–RC_2	1.321(28)	RC_3–RC_4–RC_5	102.6(21)
RC_2–RC_3	1.275(33)	RC_4–RC_5–RC_1	106.3(18)
RC_3–RC_4	1.422(29)	RC_5–RC_1–RC_2	112.2(22)
RC_4–RC_5	1.405(31)		
RC_1–RC_5	1.330(30)		

It is apparent that structure (Ia) is the correct one. The structure of this molecule as well as the structures of other ligands resulting from the formal addition of A–H (where A–H is hydrazine, alcohol, amine, thiol, or borohydride) across the C≡N bond of a coordinated isocyanide can be adequately explained by the polarity of the A–H bond. Protonic reagents such as alcohols, amines, and thiols react to give A–C bonds and N–H bonds as in structure (II). On the other hand, a hydridic reagent such as BH_4^- yields A–N bonds and C–H bonds. In the absence of kinetic data for the addition reactions, extensive speculation about probable mechanisms seems inappropriate.

Figure 3 shows the "boat" geometry of the six-membered heterocyclic ring. Atoms C_1, C_2, N_1, N_2 are planar within experimental error. The "boat" is formed by folding the ring along the Fe–B vector such that each half (Fe–C–N–B) is planar with the two planes forming a dihedral angle of 147(2)°. Each methyl group is within 0.08 Å (4σ) of its Fe–C–N–B plane, indicative of an sp^2 hybridized N atom. The average C–N distance of 1.31 Å is in the range for a C–N double bond[8] and is similar to distances found previously in complexes of this type[9,10]. The average B–N distance of 1.55 Å is comparable to the 1.57 Å single bonds found in cubic BN.

There are several factors which may cause the "boat" configuration of the heterocyclic ring. The C_1–Fe–C_2 angle of 89.7(7)° (ideally 90°), the N–B–N angle of 110(1)° (ideally 109.5°), and the Fe–C distance of 1.88 (av.) all suggest that a planar hexagonal ring would be a highly strained structure for this compound. A chair conformation is precluded by the geometrical requirements of the C–N double bonds in the ring. The average Fe–C(sp^2) distance of 1.88 Å in the heterocyclic ring is not significantly different from the Fe–C(methyl isocyanide) distances of (II). On the other hand, the Fe–C(sp^2) distances found in the heterocyclic ring of (II)[2] are 2.02 Å. The distances found in the cyclopentadienyl and carbonyl portion of the molecule are similar to those found in $[(\pi\text{-}C_5H_5Fe(CO)_2]_2C_4H_4$[11].

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