Table VII. Dimension of Binuclear Mercapto-Bridged Iron Complexes

	Fe–Fe, Å	Fe–S, Å	Fe–S–Fe, deg	S–Fe–S, deg
$[Fe_2(\mu\text{-}SCH_3)_3(CO)_6]^+$	3.062 (4)	2.305 (2)	83.2 (1)	80.7 (2)
$[C_2H_5SFe(CO)_3]_2{}^a$	2.54 (1)	2.259 (7)	68.3 (3)	81.0 (3)
$[Fe(h^5\text{-}C_5H_5)(CO)(SC_6H_5)]_2{}^b$	3.39	2.262 (6)	98	81
$[Fe(h^5\text{-}C_5H_5)(CO)(SCH_3)]_2{}^+{}^c$	2.925 (4)	2.234 (4)	81.8 (1)	95.4 (1)
$[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2{}^d$	2.618 (2)	2.218 (2)	72.35 (7)	107.65 (7)

^{a} L. F. Dahl and C. H. Wei, *Inorg. Chem.*, 2, 328 (1963). ^{b} G. Ferguson, C. Hannaway, and K. M. S. Islam, *Chem. Commun.*, 1165 (1968). ^{c} N. G. Connelly and L. F. Dahl, *J. Amer. Chem. Soc.*, 92, 7472 (1970). ^{d} D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *Inorg. Chem.*, 9, 2775 (1970).

mation of a metal–metal bond. Finally, at the urging of a merciless referee, we measured the conductivity of the complex.[41] The value of $\Lambda = 50.3$ cm^2 ohm^{-1} M^{-1} which we obtained is in excellent agreement with values reported for known 1:1 electrolytes such as $[AsPh_4][Au(S_2C_2(CF_3)_2)_2]$ and $[(n\text{-}C_4H_9)N][Ni(S_2C_2(CF_3)_2)_2]$ in CH$_2$Cl$_2$ solution.[42] The cation–anion formulation of $[Fe_2(\mu\text{-}SCH_3)_3(CO)_6]^+ \cdot [Fe_2(\mu\text{-}SCH_3)_3(CO)_6]^+$- thus established. The referee, though merciless, was correct in his urging.

(41) The conductivity was measured using a Radiometer CDM2e conductivity meter with a Type CDC104 cell calibrated with 0.10 M KCl solution. The solvent used was CH$_2$Cl$_2$ and the concentration was approximately 2 × 10^{-4} M.

(42) A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, 6, 458 (1967).

In closing, it is worthwhile once again pointing out the utility of X-ray structure determination in the characterization of new and complex systems—even if it sometimes takes over 2 years for such studies.

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Crystal and Molecular Structure of 1,6,7,8-*Tetrahapto*heptafulveneiron Tricarbonyl, a Heptafulvene Complex of Iron(0) Containing a Trimethylenemethane–Iron Linkage

MELVYN ROWEN CHURCHILL* and BARRY G. DeBOER

1,6,7,8-*Tetrahapto*heptafulveneiron tricarbonyl, $(C_7H_6CH_2)Fe(CO)_3$, crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ ($C_{2h}{}^5$; No. 14) with $a = 6.119$ (2), $b = 6.979$ (2), $c = 24.954$ (7) Å; $\beta = 90.46$ (2)°; $\rho_{\text{obsd}} = 1.514 \pm 0.010$ and $\rho_{\text{calcd}} = 1.521$ g cm^{-3} for $M = 244.03$ and $Z = 4$. X-Ray diffraction data complete to $2\theta = 50°$ (Mo Kα radiation) were collected with a Picker FACS-1 diffractometer and the structure was solved using conventional Patterson, Fourier, and least-squares refinement techniques. All atoms, including hydrogens, were located, the final discrepancy indices being $R_F = 3.41\%$ and $R_{wF} = 4.29\%$ for 1886 independent reflections. The heptafulvene and Fe(CO)$_3$ moieties interact *via* a trimethylenemethane–metal linkage in which Fe–C(central) = 1.946 (2) and Fe–C(peripheral) = 2.120 (3), 2.175 (3), and 2.192 (3) Å.
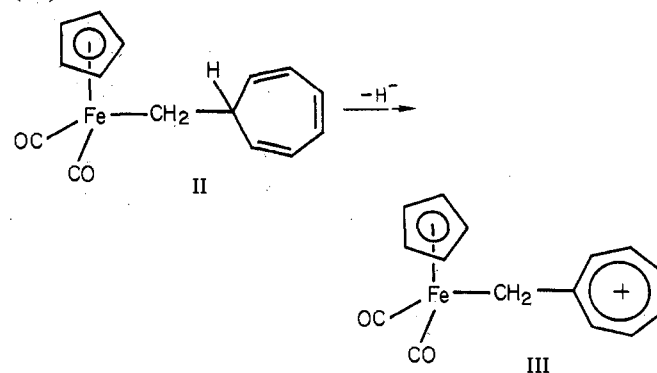
Introduction

Heptafulvene (I) is a conjugated nonbenzenoid hydrocar-

I
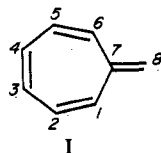
bon which is stable only in dilute solution at −170°. Attempts to concentrate a solution in propane by evaporation at −60° *in vacuo* resulted only in polymeric products.[1]

Kerber and coworkers[2] showed that a cationic heptafulvene derivative of iron(II) could be obtained by β-hydride abstraction from $\pi\text{-}C_5H_5Fe(CO)_2(\sigma\text{-}CH_2C_7H_7)$ (II) using

(1) W. von E. Doering and D. W. Wiley, *Tetrahedron*, 11, 183 (1960).

(2) D. J. Ehntholt, G. F. Emerson, and R. C. Kerber, *J. Amer. Chem. Soc.*, 91, 7547 (1969).

$[(C_6H_5)_3C^+][SbF_6^-]$; a subsequent crystallographic study[3] revealed that the product, $[\pi\text{-}C_5H_5Fe(CO)_2(C_8H_8)^+][SbF_6^-]$, contained a *monohapto* (or σ-bonded) heptafulvene fragment (III).

(3) M. R. Churchill and J. P. Fennessey, *Chem. Commun.*, 1056 (1970).

More recently, some π-bonded heptafulvene derivatives have been prepared; Ehntholt and Kerber[4] and Hunt, *et al.*,[5] have synthesized isomers of heptafulveneiron tricarbonyl which, apparently, are the 1,6,7,8-*tetrahapto*[4] and 1,2,3,4-*tetrahapto*[5] species IV and V.

IV   V
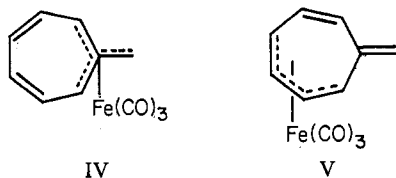
Since few structural studies of complexes with trimethylenemethane-to-metal linkages have been reported (see ref 6-9), and because of theoretical interest in the heptafulvene skeleton, we decided to investigate the molecular structure of 1,6,7,8-*tetrahapto*heptafulveneiron tricarbonyl *via* a single-crystal X-ray diffraction study. Our results are summarized below.

Collection and Treatment of the X-Ray Diffraction Data

Dark red crystals of the complex were supplied by Professor R. C. Kerber. An approximately equidimensional portion was cut from a larger crystal and gently wedged into a thin-walled Lindemann glass capillary. The capillary was flushed with nitrogen, flame-sealed, and fixed into a brass pin on a eucentric goniometer with melted paraffin wax. [This method of mounting was chosen after the crystals had been found to decompose in air and dissolve in several adhesives.] The crystal was bounded by {001}, (0$\bar{1}$0), and (01$\bar{1}$) and terminated on one end by ($\bar{2}$05). The other, somewhat irregular, cut end approximated to a plane which made an angle of 74.6° with a^* at a distance of 0.327 mm from an origin defined by the intersection of the (00$\bar{1}$), (01$\bar{1}$), and ($\bar{2}$05) faces. The (001) and (0$\bar{1}$0) faces were, respectively, 0.335 and 0.325 mm from that origin; the greatest length of the prism was 0.545 mm.

Preliminary precession photographs gave approximate cell dimensions, revealed C_{2h} (2/m) Laue symmetry for the crystal, and exhibited systematic absences in $h0l$ for $l = 2n + 1$ and in $0k0$ for $k = 2n + 1$, consistent only with space group $P2_1/c$ (C_{2h}^5; No. 14).[10]

The crystal was then transferred to a Picker FACS-1 computer-controlled diffractometer. Since this paper describes the first structural study in which we have used this equipment, experimental techniques will be described in detail, the intention being to refer back to this description in future reports.

The FACS-1 diffractometer was equipped with a Dunlee DZ-1B standard-focus molybdenum X-ray tube operated at 44 kV and 16 mA (constant potential), 1.5-mm collimators, a series of copper-foil attenuators, a niobium filter between the crystal and scintillation counter (47% transmission of Mo Kα), and a pulse-height discriminator adjusted to pass approximately 95% of the Mo Kα peak. The crystal under investigation was used as a probe for both source and counter; each was found to have a satisfactory profile. The positioning of the X-ray source was checked and the true zeros of the diffractometer angles (2θ, ω, χ) were determined and set to read 0.00. The crystal was oriented to place a^* coincident with the ϕ axis and optically centered with respect to the ϕ and χ motions. Employing "high resolution" conditions, *i.e.*, the smallest takeoff angle to the X-ray tube anode and the smallest size of symmetrically variable detector aperture commensurate with retaining ~65% of the peak intensity (1.5° and ~1 mm × 1 mm, respectively), the instrument adjustment and crystal orientation and centering were verified by

the agreement of settings found by the automatic centering[11] of an $h00$ (and corresponding $\bar{h}00$) reflection at all combinations of ±2θ, $\chi = 90, 270°$, and $\phi = 0, 90, 180, 270°$. An approximate unit-cell/orientation matrix was obtained following the location of the $0k0$ and $00l$ sets of reflections. Again employing "high resolution" conditions, the 2θ, ω, and χ settings of the resolved Mo Kα_1 peaks of twelve high-angle (2θ = 33–51°) reflections, which were well dispersed in reciprocal space, were determined.[11] These values were used in a least-squares refinement of the cell parameters and orientation parameters,[11] using λ(Mo Kα_1) 0.70926 Å, which resulted in maximum and root-mean-square angular disagreements of 0.065 and 0.026°, respectively. The resulting cell dimensions (at 25°) and their estimated standard deviations are: $a = 6.1190$ (17) Å, $b = 6.9791$ (20) Å, $c = 24.9541$ (66) Å, and $\cos \beta = -0.0080$ (3), which corresponds to $\beta = 90.46$ (2)°. The unit cell volume is $V = 1065.6$ Å^3. The density observed ($\rho_{obsd} = 1.514 \pm 0.010$ g cm^{-3}) for a neutral-buoyancy aqueous solution of barium iodide is in excellent agreement with that calculated for $M = 244.03$ and $Z = 4$ ($\rho_{calcd} = 1.521$ g cm^{-3}). No symmetry is imposed upon the molecule by the crystal symmetry.

Intensity data were measured by executing a coupled θ–2θ (crystal-counter) scan from 0.8° in 2θ below the Kα_1 peak to 0.8° in 2θ above the Kα_2 peak at a rate of 2.0°/min, accumulating P counts in t_P seconds. Stationary-background counts, of 20-sec duration, were recorded at the low- and high-2θ limits of the scan, giving B_1 and B_2 counts, respectively, for a total background-counting time of $t_B = 40$ sec. Copper-foil attenuators, whose Mo Kα transmission factors had previously been experimentally determined, were inserted as required to keep the maximum counting rate below ~8500 counts/sec, thereby avoiding coincidence losses.

A 3.0° takeoff angle to the X-ray tube anode was employed and the detector aperture was approximately 3 mm × 4 mm (parallel and perpendicular to the plane of diffraction) and 33 cm from the crystal.

Before collecting intensity data, a strong axial reflection was measured (by a θ–2θ scan) at $\chi = 90°$ and from $\phi = 0°$ to $\phi = 360°$ at intervals of 10°. The variation of intensity with ϕ was later used as a check of the validity of the applied absorption correction. [The corrected intensity was no longer ϕ dependent.]

All reflections in the range $0 < 2\theta < 50°$ (*i.e.*, $0 < \lambda^{-1} \sin \theta < 0.596$) and with nonnegative values of h and k were measured. These included 1887 Laue-independent reflections, 178 $0kl$ ($l < 0$) reflections, and 177 systematically absent reflections (each of the latter was found to confirm the previously stated extinction rules). Three strong reflections, in approximately orthogonal directions in reciprocal space, were measured after each batch of 48 reflections in order to monitor any crystal decomposition or changes in orientation. No evidence for change in orientation was observed, but the intensities of the "check reflections" steadily declined by an intensity-weighted mean of 1.88% (range 1.3–2.5%).

Assuming a linear variation in background over the scan range (however, *vide infra*), the net integrated intensity, I, and its estimated standard deviation, $\sigma(I)$, were taken to be[12]

$$I = q[(P + 4.5) - \tau(B_1 + B_2 + 9.0)]$$

and

$$\sigma(I) = q[(P + 4.5) + \tau^2(B_1 + B_2 + 9.0) + 24.75 + q^{-2}p^2I^2]^{1/2}$$

Here $\tau = t_P/t_B$, the "ignorance factor" (p) was set equal to 0.04, q represents the combined corrections for crystal decomposition and attenuator used, and the numerical terms arise from the fact that the least significant digit of each count (P, B_1, B_2) is not recorded by the apparatus. Any I calculated to be negative was immediately reset to zero. The observed magnitudes of the unscaled structure factors, F_o, and their standard deviations were calculated as $F_o = (I/Lp)^{1/2}$ and $\sigma(F_o) = (\sigma(I)/Lp)^{1/2}$ for $\sigma(I) \geqslant I$ and $\sigma(F_o) = F_o - (F_o^2 - \sigma(I)/Lp)^{1/2}$ for $\sigma(I) < I$, where the Lorentz–polarization factor, Lp, is $(1 + \cos^2 2\theta)/(2 \sin 2\theta)$. The "expected" values of R_F and R_{wF}, obtained by substituting $\sigma(F_o)$ for $||F_o| - |F_c||$ in their definitions,[13]

(4) D. J. Ehntholt and R. C. Kerber, *Chem. Commun.*, 1451 (1970).

(5) G. T. Rodeheaver, G. C. Farrant, and D. F. Hunt, *J. Organometal. Chem.*, 30, C22 (1971).

(6) (a) M. R. Churchill and K. Gold, *Chem. Commun.*, 693 (1968); (b) M. R. Churchill and K. Gold, *Inorg. Chem.*, 8, 401 (1969).

(7) A. Almenningen, A. Haaland, and K. Wahl, *Chem. Commun.*, 1027 (1968); *Acta Chem. Scand.*, 23, 1145 (1969).

(8) A. N. Nesmeyanov, I. S. Astakhova, G. P. Zol'nikova, I. I. Kritskaya, and Yu. T. Struchkov, *Chem. Commun.*, 85 (1970).

(9) N. Yasuda, Y. Kai, N. Yasuoka, N. Kasai, and M. Kakudo, *J. Chem. Soc., Chem. Commun.*, 157 (1972).

(10) "International Tables for X-Ray Crystallography," Vol. 1, Kynoch Press, Birmingham, England, 1965, p 99.

(11) Diffractometer routines such as crystal orientation, centering of reflections, least-squares refinement of cell dimensions, and θ–2θ scan routines were performed by programs described by W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 22, 457 (1967), and adapted by Picker Corp. to the PDP-8/I which forms an integral part of the FACS-1 system.

(12) The following calculations were performed using REDUCE, a Fortran IV program by B. G. DeBoer.

(13) $R_F = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$ and $R_{wF} = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w |F_o|^2]^{1/2}$, where the weight $w = \sigma^{-2}(F_o)$.

were 3.8 and 2.9%, respectively. [This is actually a measure of the "strength" of the data set.]

Absorption corrections were calculated from measured crystal dimensions and an absorption coefficient of $\mu = 14.33$ cm^{-1} and applied to the data by the program DRAB.[14] This program also estimates the calculational error in transmission factors and includes it in the standard deviations assigned to the corrected F_o values in the form $\sigma^2(F_{o, cor}) = 0.25(\sigma(T)/T)^2 + (\sigma(F)/F)^2$. Secondary-extinction coefficients,[15] β, proportional to $(1 + \cos^4 2\theta)(1 + \cos^2 2\theta)^{-2}(-dT^{-1}/d\mu)$, where T is the transmission factor, were also calculated and recorded for possible future use. Transmission factors ranged from 0.689 to 0.595.

Finally, the equivalent $0kl$ and $0\bar{k}l$ pairs were averaged and their intensity replaced by their σ^{-2}-weighted average, with appropriately changed standard deviations.

It should be noted that *no reflections* were rejected from the data set on the basis of being "unobserved". While doing so has the esthetically pleasing effect of lowering the final discrepancy indices, this is hardly a valid criterion for ignoring information. Weak data may be deleted on the grounds of contributing only "noise" *if* they occur in a region of reciprocal space (typically, at high 2θ) where they represent insignificant constraints upon the structure, *i.e.*, in a region where almost any structure would result in very small F_c values. Weak reflections observed elsewhere (*e.g.*, small 2θ) place important constraints upon the allowed structure (destructive interference of atomic contributions) which are equally as useful as those imposed by strong reflections (constructive interference). There were no regions of the present data set in which a substantial fraction of the measured intensities was indistinguishable from zero.[16]

An Empirical Correction for Absorption by the β Filter

Just prior to the final cycles of least-squares refinement, it was discovered that the F_o values of low-angle reflections were systematically too large. This was explained and corrected for in the following manner. With nonmonochromatized molybdenum X-rays, the main contribution to the measured backgrounds arises from Bragg-scattered white radiation. At small values of 2θ, where the spectral dispersion is small, the constant 2θ offset at which B_1 is measured places the counter in a wavelength region which is heavily absorbed by the niobium β filter. This results in an anomalous reduction of B_1, a failure of the linear-background assumption, and erroneously large values for F_o.

An empirical correction was obtained by plotting $Y = \tau(B_1 + B_2 + 9.0)/I$ against $s = \lambda^{-1}\sin\theta$ for large I and small s. In the absence of the K-edge absorption, this function should be either constant or monotonically increasing with decreasing s. In the present case it is observed to increase to a maximum at $Y = Y_o = 0.288$ and $s = 0.1410$ and then decrease linearly through $Y = 0.100$ at $s = 0.0715$. The correction was applied by multiplying I, F_o^2, and $\sigma(F_o^2)$ by $[1 - Y_o + Y(s)]$ and F_o and $\sigma(F_o)$ by the square root of that quantity for the 23 reflections with $s < 0.1410$.

Because of the presence of an amorphously scattered nonspectral contribution to the background, a similar procedure based upon the difference $B_1 - B_2$ would be preferable. This is rendered impractical due to the wavelength dependence for transmission of X-rays through the copper attenuators (which are in use for intense low-angle reflections). However, this wavelength dependence is sufficiently close to linear that no correction for its effect was deemed necessary. It should be noted that any errors introduced into the above procedure (due to a nonspectral background component) will result in a conservative underestimation of the magnitude of the required correction.

Solution and Refinement of the Structure

Programs used in elucidating the structure include FORDAP (Fourier synthesis, by A. Zalkin), SFIX (a much-modified version of C. T. Prewitt's SFLS5, for full-matrix least-squares refinement), STAN1 (distances, angles, and their estimated standard deviations, by B. G. DeBoer), and ORTEP (thermal ellipsoid drawings, by C. K. Johnson).

(14) DRAB is a Fortran IV program by B. G. DeBoer for calculating absorption corrections and secondary-extinction coefficients.

(15) W. H. Zachariasen, *Acta Crystallogr.*, 16, 1139 (1963); 23, 558 (1967).

(16) We suspect that the same statement applies to many data sets from which "unobserved" data have been removed. We suggest that the *routine* removal of *all* weak data from accurate diffraction data sets (such as those collected carefully by a θ–2θ scan on a four-circle diffractometer) should be discontinued. One benefit should be a lowering of esd's on molecular parameters.

Table I. Final Positional and Isotropic Thermal Parameters[a]

Atom	x	y	z	B, Å^2
Fe	0.34185 (5)	0.41424 (4)	0.144964 (12)	4.01[b]
CX1	0.1723 (4)	0.3714 (3)	0.08746 (10)	4.4
OX1	0.0641 (4)	0.3511 (3)	0.05101 (8)	6.8
CX2	0.5288 (4)	0.2180 (4)	0.13744 (13)	6.0
OX2	0.6494 (4)	0.0971 (3)	0.13340 (15)	9.9
CX3	0.1588 (5)	0.3178 (5)	0.19309 (11)	6.4
OX3	0.0435 (6)	0.2523 (4)	0.22350 (10)	10.5
C1	0.5710 (5)	0.6132 (4)	0.10872 (14)	5.7
C2	0.5314 (9)	0.6853 (6)	0.05686 (17)	8.4
C3	0.3718 (16)	0.7900 (8)	0.03831 (19)	10.5
C4	0.1842 (12)	0.8533 (5)	0.06510 (27)	10.2
C5	0.1246 (5)	0.8170 (4)	0.11651 (21)	7.4
C6	0.2472 (5)	0.7137 (4)	0.15755 (11)	5.4
C7	0.4702 (4)	0.6657 (3)	0.15725 (10)	5.0
C8	0.5378 (8)	0.5569 (5)	0.20292 (18)	8.2
H1	0.707 (6)	0.550 (4)	0.1122 (12)	7.3 (6)
H2	0.646 (8)	0.640 (6)	0.0248 (19)	11.7 (11)
H3	0.377 (7)	0.825 (7)	0.0048 (20)	11.5 (12)
H4	0.083 (9)	0.911 (6)	0.0475 (21)	11.4 (13)
H5	−0.005 (8)	0.857 (6)	0.1308 (17)	10.7 (11)
H6	0.179 (5)	0.713 (4)	0.1936 (12)	7.8 (7)
H8A	0.689 (8)	0.515 (7)	0.2028 (18)	11.1 (11)
H8B	0.426 (11)	0.584 (8)	0.2390 (26)	15.8 (20)

[a] Standard deviations are right adjusted to the last digit of the preceding number and are those derived from the inverse of the final least-squares matrix. [b] For nonhydrogen atoms, the "equivalent isotropic temperature factors" are listed. They correspond to a mean-square displacement which is the average of the mean-square displacements along the three principal axes of the anisotropic ellipsoid.

Scattering factors for iron, carbon, and oxygen were taken from the compilation of Cromer and Waber[17] and were modified for both the real and the imaginary component of anomalous dispersion.[18] Scattering factors for hydrogen are those of Mason and Robertson.[19] The function minimized in least-squares refinement processes was $\Sigma w(|F_o| - |F_c|)^2$.

The position of the iron atom was readily obtained from a three-dimensional Patterson function. An "observed" Fourier synthesis, phased only by the iron atom, revealed the positions of the remaining nonhydrogen atoms. Refinement of individual positional and isotropic thermal parameters led to $R_F = 11.9\%$ and $R_{wF} = 16.8\%$. Continued refinement, now using anisotropic thermal parameters for nonhydrogen atoms, led to convergence at $R_F = 5.1\%$, $R_{wF} = 7.1\%$. The eight hydrogen atoms were now introduced at calculated positions 0.95 Å from their respective carbon atoms; their positional and isotropic thermal parameters were included in subsequent cycles of full-matrix least-squares refinement, which converged at $R_F = 3.7\%$, $R_{wF} = 4.5\%$. Application of the β-filter correction described above, followed by two further cycles of full-matrix least-squares refinement of all above-specified parameters, led to the final values for the discrepancy indices, $R_F = 3.41\%$ and $R_{wF} = 4.29\%$.

The change in R_F and R_{wF} for the 23 corrected reflections (only) was from 7.3 and 7.9 to 2.3 and 4.1%, respectively. The magnitude of the correction probably was underestimated, since 22 of the 23 reflections still had $|F_o| > |F_c|$.

The 12$\bar{4}$ reflection was given zero weight for the final cycles. This reflection was measured as weak ($I = 0.37P$) and its calculated value is almost zero. We presume that the ~15σ disagreement is due to some mismeasurement, possibly to "streaking" from the strong 12$\bar{3}$ and/or 12$\bar{5}$ reflections.

In the final cycle of refinement no parameter shifted by more than 11% of its estimated standard deviation. The standard deviation of an observation of unit weight or "goodness of fit," $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 1.31, where the number of reflections (m) was 1886 and the number of refined parameters (n) was 168 ($m/n = 11.4$). This function was not dependent on θ or on $|F_o|$. Data were inspected for evidence of secondary extinction (F_o/F_c *vs.* $\beta I/T$), but none was found.

The correctness of the determined structure was confirmed by a

(17) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 18, 104 (1965).

(18) D. T. Cromer and D. Lieberman, *J. Chem. Phys.*, 53, 1891 (1970).

(19) R. Mason and G. B. Robertson, *Advan. Struct. Res. Diffr. Methods*, 2, 57 (1966).

Table II. Anisotropic Thermal Parameters[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U \rangle^b$
Fe	3.59 (2)	4.01 (2)	4.42 (2)	0.37 (1)	0.17 (1)	−0.06 (1)	(0.24, 0.23, 0.21)
CX1	4.7 (1)	3.7 (1)	4.9 (1)	−0.3 (1)	0.7 (1)	0.1 (1)	(0.26, 0.23, 0.21)
OX1	7.6 (1)	6.8 (1)	6.0 (1)	−0.8 (1)	−1.7 (1)	−0.4 (1)	(0.34, 0.30, 0.24)
CX2	4.4 (1)	4.5 (1)	9.3 (2)	0.3 (1)	−0.5 (1)	−0.5 (1)	(0.35, 0.24, 0.23)
OX2	6.2 (1)	5.2 (1)	18.3 (3)	2.0 (1)	−1.6 (1)	−1.7 (1)	(0.49, 0.30, 0.22)
CX3	5.8 (1)	8.0 (2)	5.3 (1)	0.8 (1)	0.5 (1)	1.7 (1)	(0.34, 0.27, 0.24)
OX3	8.9 (1)	14.4 (2)	8.2 (1)	0.0 (1)	2.7 (1)	5.0 (1)	(0.47, 0.35, 0.23)
C1	4.1 (1)	4.6 (1)	8.4 (1)	−0.9 (1)	1.7 (1)	−1.6 (1)	(0.35, 0.23, 0.21)
C2	11.1 (3)	7.2 (2)	7.1 (2)	−4.4 (2)	3.6 (2)	−1.4 (2)	(0.44, 0.27, 0.23)
C3	17.5 (6)	7.7 (3)	6.4 (2)	−6.4 (3)	−0.7 (3)	1.6 (2)	(0.51, 0.29, 0.23)
C4	14.0 (4)	4.3 (1)	12.0 (4)	−2.3 (2)	−7.5 (4)	2.5 (2)	(0.52, 0.26, 0.21)
C5	5.1 (1)	4.0 (1)	13.1 (3)	0.9 (1)	−1.9 (2)	−1.4 (2)	(0.42, 0.25, 0.21)
C6	5.4 (1)	4.7 (1)	6.2 (1)	0.7 (1)	0.9 (1)	−1.4 (1)	(0.30, 0.27, 0.20)
C7	4.8 (1)	4.1 (1)	6.2 (1)	−0.1 (1)	−1.1 (1)	−1.6 (1)	(0.31, 0.24, 0.20)
C8	8.8 (2)	7.3 (2)	8.3 (2)	0.3 (2)	−4.0 (2)	−1.2 (1)	(0.40, 0.30, 0.24)

[a] In units of $Å^2$ and for the form $\exp(-0.25\Sigma_i\Sigma_j h_i h_j a_i a_j B_{ij})$; $i, j = 1, 2, 3$, where h_i and a_i are the ith reflection index and reciprocal cell edge, respectively. Standard deviations were derived from the inverse of the final least-squares matrix. [b] These are the root-mean-square amplitudes of vibration (in Å) along the three principal axes of the anisotropic ellipsoid, in order of magnitude. For orientations, see figures.

Table III. Intramolecular Distances[a] (Å) with Estimated Standard Deviations

Atoms	Dist	Atoms	Dist
(a) Distances from Iron Atom			
Fe-C7	1.946 (2)	Fe-CX1	1.789 (3)
Fe-C1	2.175 (3)	Fe-CX2	1.795 (3)
Fe-C6	2.192 (3)	Fe-CX3	1.781 (3)
Fe-C8	2.120 (3)		
(b) Distances within Heptafulvene Fragment			
C7-C1	1.412 (4)	C1-C2	1.408 (6)
C7-C6	1.405 (4)	C2-C3	1.302 (8)
C7-C8	1.428 (5)	C3-C4	1.404 (8)
C1···C8	2.393 (6)	C4-C5	1.360 (8)
C8···C6	2.369 (5)	C5-C6	1.456 (5)
C6···C1	2.438 (4)		
(c) Distances Involving Carbonyl Groups			
CX1-OX1	1.130 (3)	CX1···CX2	2.724 (4)
CX2-OX2	1.126 (3)	CX2···CX3	2.755 (4)
CX3-OX3	1.136 (3)	CX3···CX1	2.664 (4)
(d) Carbon-Hydrogen Distances			
C1-H1	0.95 (3)	C5-H5	0.91 (5)
C2-H2	1.11 (5)	C6-H6	0.99 (3)
C3-H3	0.87 (5)	C8-H8A	0.97 (5)
C4-H4	0.86 (6)	C8-H8B	1.15 (7)

[a] Not corrected for thermal motion. Standard deviations (right adjusted, in parentheses) were calculated from the esd's of the atomic coordinates and cell dimensions and include the effect of all positional correlation coefficients of magnitude ≥0.10.

final difference Fourier synthesis, on which the principal features were two maxima (0.35 and 0.30 e $Å^{-3}$) and a minimum (−0.30 e $Å^{-3}$), all within 0.9 Å of the iron position. No other feature was outside the range ±0.2 e $Å^{-3}$.

A table of observed and calculated structure factor amplitudes is available.[20] Final positional parameters are collected in Table I; anisotropic thermal parameters are listed in Table II.

The Molecular Structure

Intramolecular distances and their estimated standard deviations (esd's) are shown in Table III; interatomic angles and their esd's are given in Table IV. The overall stereochemistry of the molecule is illustrated in Figure 1.

The molecule is, as predicted,[4] a 1,6,7,8-*tetrahapto*heptafulvene derivative and, as such, contains a (substituted) trimethylenemethane-to-metal π linkage. This diamagnetic

Table IV. Interatomic Angles (deg) with Estimated Standard Deviations[a]

Atoms	Angle	Atoms	Angle
(a) Angles around Iron Atom			
CX1-Fe-CX2	98.9 (1)	C8-Fe-C1	67.7 (2)
CX1-Fe-CX3	96.5 (1)	C8-Fe-C6	66.6 (1)
CX2-Fe-CX3	100.8 (1)	C1-Fe-C6	67.9 (1)
(b) Angles between Trimethylenemethane Fragment and CO Groups			
C7-Fe-CX1	120.5 (1)	C8-Fe-CX2	94.2 (2)
C7-Fe-CX2	116.6 (1)	C8-Fe-CX3	94.2 (2)
C7-Fe-CX3	119.3 (1)	C1-Fe-CX1	98.3 (1)
C8-Fe-CX1	161.2 (1)	C6-Fe-CX1	97.0 (1)
C1-Fe-CX3	158.9 (1)	C1-Fe-CX2	91.7 (1)
C6-Fe-CX2	155.7 (1)	C6-Fe-CX3	95.5 (1)
(c) Angles in Carbonyl Groups			
Fe-CX1-OX1	177.6 (2)	Fe-CX3-OX3	178.5 (4)
Fe-CX2-OX2	178.4 (3)		
(d) Angles Showing Pyramidal Nature of Trimethylenemethane Fragment			
Fe-C7-C1	79.0 (1)	Fe-C7-C8	76.1 (2)
Fe-C7-C6	79.9 (2)		
(e) Angles within Heptafulvene System			
C7-C1-C2	128.5 (3)	C5-C6-C7	127.5 (3)
C1-C2-C3	130.6 (4)	C6-C7-C1	119.9 (2)
C2-C3-C4	128.4 (4)	C8-C7-C1	114.9 (3)
C3-C4-C5	128.1 (4)	C8-C7-C6	113.4 (3)
C4-C5-C6	127.9 (4)		
(f) Angles Involving Hydrogen Atoms			
H1-C1-C7	116 (2)	H5-C5-C4	124 (3)
H1-C1-C2	113 (2)	H5-C5-C6	109 (3)
H2-C2-C1	117 (3)	H6-C6-C5	115 (2)
H2-C2-C3	112 (3)	H6-C6-C7	115 (2)
H3-C3-C2	118 (3)	H8A-C8-C7	115 (3)
H3-C3-C4	114 (3)	H8B-C8-C7	111 (3)
H4-C4-C3	120 (4)	H8A-C8-H8B	129 (4)
H4-C4-C5	112 (4)		

[a] See footnote a to Table III.

compound may be considered as a d^8 iron(0) derivative in which the central iron atom achieves the appropriate noble gas configuration (*i.e.*, that of krypton) by the donation of two electrons from each of the three carbonyl groups and four electrons from the π-trimethylenemethane residue. The iron atom is located directly beneath the central carbon atom, C7, of the trimethylenemethane system and is π bonded to all four carbon atoms of this fragment, individual distances being Fe-C7 = 1.946 (2), Fe-C8 = 2.120 (3), Fe-C1 = 2.175 (3), and Fe-C6 = 2.192 (3) Å. [Analogous distances in other species containing a trimethylenemethane-
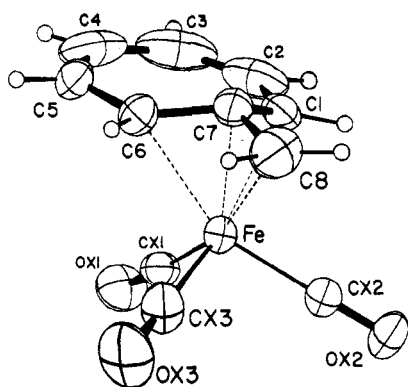
Figure 1. A general view of the $(C_7H_6CH_2)Fe(CO)_3$ molecule [ORTEP diagram, showing 30% probability ellipsoids for all atoms other than hydrogens, which are artificially reduced].

iron linkage are Fe–C(central) = 1.932 (10), Fe–C(peripheral) = 2.098 (11), 2.118 (10), and 2.161 (9) Å in phenyltrimethylenemethaneiron tricarbonyl;[6] Fe–C(central) = 1.938 (5), Fe–C(peripheral) = 2.123 (5) Å from an electron diffraction study of trimethylenemethaneiron tricarbonyl;[7] Fe–C(central) = 1.95, Fe–C(peripheral) = 2.10, 2.11, and 2.11 Å (all ± 0.04 Å) in $(C_{10}H_7CH_2)_2Fe(CO)_3$;[8] Fe–C(central) = 1.94 (1), Fe–C(peripheral) = 2.12 (1), 2.12 (1), and 2.17 (1) Å in an isomer of $(C_9H_{12})Fe_2(CO)_6$.[9]]

As may clearly be seen in Figure 2, the 1,6,7,8-h^4-heptafulveneiron tricarbonyl molecule has approximate, *but not exact*, C_s symmetry in the solid state, with the trimethylenemethane and $Fe(CO)_3$ groups adopting a mutually staggered conformation.

The carbon atom skeleton of the trimethylenemethane moiety adopts a pyramidal configuration in which the central carbon atom, C7, lies 0.285 Å above the plane defined by C1···C6···C8 [plane I of Table V] and the iron atom lies 1.660 Å below this plane (*cf.* values of 0.315 Å above and 1.616 Å below in phenyltrimethylenemethaneiron tricarbonyl[6]).

The dihedral angle between the peripheral carbon atoms of the trimethylenemethane fragment (*i.e.*, C1···C6···C8) and the three carbonyl carbons (CX1, CX2, CX3) is 4.50°. This slight, but significant, deviation from a truly parallel situation is not in keeping with the approximate C_s molecular symmetry, since C7–Fe–CX1 = 120.5 (1)° while C7–Fe–CX2 and C7–Fe–CX3 are 116.6 (1) and 119.3 (1)°, respectively. We presume that these deviations result from intermolecular packing forces.

The trans angles C1–Fe–CX3, C6–Fe–CX2, and C8–Fe–CX1 are, again, nonequivalent, with values of 158.9 (1), 155.7 (1), and 161.2 (1)°, respectively. The analogous cis angles at the metal, between peripheral trimethylenemethane carbon atoms and carbonyl carbon, similarly have a wide range—from 91.7 (1) to 98.3 (1)°.

It should be noted that the pyramidal nature of the trimethylenemethane fragment is emphasized by the angles Fe–C7–C1, Fe–C7–C6, and Fe–C7–C8, which are 79.0 (1), 79.9 (2), and 79.9 (2)°, respectively. [*Cf.* values of 76.1 (6), 77.0 (6), and 78.3 (5)° in phenyltrimethylenemethaneiron tricarbonyl[6] and 76.4 (2)° in trimethylenemethaneiron tricarbonyl.[7]]

The nonbonding distances, C1···C8, C8···C6, and C6···C1 are 2.393 (6), 2.369 (5), and 2.438 (4) Å, indicating deviations of the carbon atoms defining the present (substituted) trimethylenemethane framework from positions of idealized C_{3v} symmetry.
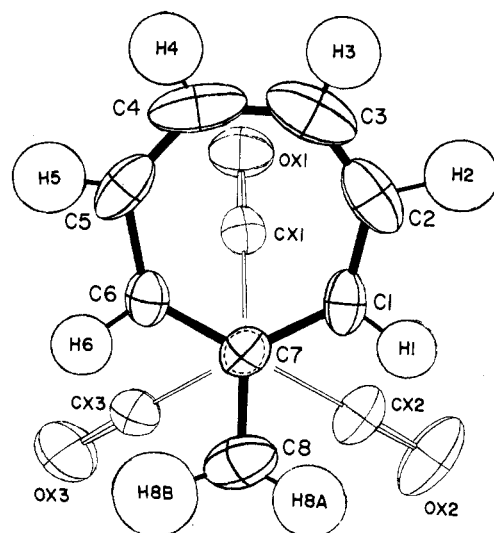

Figure 2. The $(C_7H_6CH_2)Fe(CO)_3$ molecule, showing its *approximate* C_s symmetry [ORTEP diagram, 30% probability envelopes for all atoms].

Table V. Important Planes[a-c] within the $(C_7H_6CH_2)Fe(CO)_3$ Molecule

Atoms	Dev, Å	Atoms	Dev, Å
Plane I:	$0.4268X + 0.8846Y + 0.1880Z = 5.777$		
C1*	0.000	C2	+0.103
C6*	0.000	C5	+0.129
C8*	0.000	H1	−0.020
C7	+0.285	H6	−0.016
Fe	−1.660	H8A	+0.136
		H8B	+0.043
Plane II:	$0.4689X + 0.8393Y + 0.2752Z = 5.949$		
C1*	+0.018	H1	+0.061
C2*	−0.025	H2	−0.177
C3*	+0.005	H3	+0.001
C4*	+0.019	H4	−0.052
C5*	−0.016	H5	−0.058
C6*	+0.008	H6	+0.053
C7	+0.365	H8A	+0.420
C8	+0.231	H8B	+0.315
Fe	−1.559		
Plane III:	$0.2341X + 0.9574Y - 0.1689Z = 4.452$		
C1*	0.000	C7*	0.000
C6*	0.000		
Plane IV:	$0.3694X + 0.9179Y + 0.1450Z = 3.079$		
CX1*	0.000	CX3*	0.000
CX2*	0.000		

[a] Planes are defined as $C_1X + C_2Y + C_3Z = d$, where X, Y, Z are cartesian coordinates which are related to the monoclinic cell coordination (x, y, z) by the transformation $[X, Y, Z] = [xa + zc \cos \beta, yb, zc \sin \beta]$. Dihedral angles between two planes are then given by $\cos^{-1} [C_1C_1' + C_2C_2' + C_3C_3']$ and the deviation of an atom at X', Y', Z' from a plane is given by $[C_1X' + C_2Y' + C_3Z' - d]$ Å. [b] Least-squares planes were calculated using unit weights for all atoms marked with an asterisk and zero weights for all other atoms. [c] Dihedral angles: I/III = 4.50°; II/IV = 29.88°.

The bonding between a trimethylenemethane fragment and a transition metal ion has been discussed previously[6b] and will not further be dealt with in the present article.

Geometry of the Heptafulvene Ligand

The heptafulvene ring does not adopt its possible planar geometry, due, principally, to the trimethylenemethane-to-iron bonding (*vide supra*). Atoms C1-C2-C3-C4-C5-C6 are approximately coplanar (root-mean-square deviation 0.018 Å; see plane II of Table V), but C7 and C8 lie 0.365 and 0.231 Å above the plane.

Table VI. Intermolecular Distances in the
$(C_7H_6CH_2)Fe(CO)_3$ Crystal

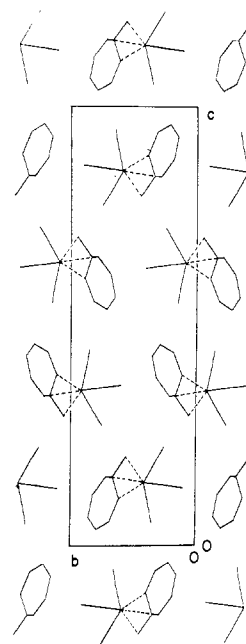| Atoms	Dist, Å	Approx (x, y, z) of 2nd atom
	I. Nonhydrogen Contacts, to 3.6 Å	
OX1···OX1	3.374 (4)	(−0.06, 0.65, −0.05)
···C4	3.559 (5)	(−0.18, 0.15, −0.07)
···C4	3.568 (5)	(0.18, −0.15, 0.07)
···C3	3.600 (7)	(−0.37, 0.21, −0.04)
OX2···C7	3.261 (4)	(0.47, −0.33, 0.16)
···OX3	3.458 (4)	(1.04, 0.25, 0.22)
···C1	3.466 (3)	(0.57, −0.39, 0.11)
···C2	3.523 (4)	(0.53, −0.31, 0.06)
···C5	3.532 (4)	(1.12, −0.18, 0.12)
OX3···C8	3.423 (5)	(0.46, 0.06, 0.30)
···OX2	3.458 (4)	(−0.35, 0.10, 0.13)
···C6	3.483 (4)	(−0.25, 0.21, 0.34)
	II. Contacts Involving Hydrogen, to 3.1 Å[a]	
CX1···H2	3.02 (5)	(0.35, 0.36, −0.02)
OX1···H2	2.60 (5)	(0.35, 0.36, −0.02)
···H1	3.01 (3)	(−0.29, 0.55, 0.11)
···H4	3.07 (4)	(0.08, −0.09, 0.05)
OX2···H5	2.70 (5)	(1.00, −0.14, 0.13)
OX3···H6	2.50 (3)	(−0.18, 0.21, 0.31)
···H8A	2.88 (5)	(−0.31, 0.52, 0.20)
···H8A	2.96 (5)	(0.31, 0.02, 0.30)
H1···H5	2.81 (6)	(1.00, 0.86, 0.13)
H4···H4	2.86 (11)	(−0.08, 1.09, −0.05)
H3···H3	2.87 (10)	(0.62, 1.17, −0.00)
H2···H2	2.92 (9)	(0.35, 0.36, −0.02)

[a] The present structural study yields an average C–H bond length of 0.98 Å, as opposed to the true internuclear separation of 1.08 Å. [This effect is characteristic of X-ray diffraction studies and results from the electron density around hydrogen having a centroid which is not coincident with the nucleus but which is displaced along the C–H bond toward carbon.] The *true* intermolecular vectors in-volving hydrogen are therefore expected to be as much as 0.1 Å (for C···H or O···H) or 0.2 Å (for H···H) *shorter* than the values listed here.

Within the seven-membered carbocyclic ring, the dihedral angle between the planes defined by C1 through C6 and by C6-C7-C1 is 29.88°.

Carbon–carbon distances within the trimethylenemethane portion of the heptafulvene ligand are C7-C1 = 1.412 (4), C7-C6 = 1.405 (4), and C7-C8 = 1.428 (5) Å, with the un-substituted C-CH$_2$ bond being the longest. [In trimethyl-lenemethaneiron tricarbonyl,[7] the C–C distances are 1.437 (3) Å; in phenyltrimethylenemethaneiron tricarbonyl,[6] the C(central)–C(peripheral) distances are 1.405 (13), 1.406 (13), and 1.436 (12) Å, with the substituted C-CH(C$_6$H$_5$) bond being the longest.]

Angles within the trimethylenemethane fragment are C6-C7-C1 = 119.9 (2), C8-C7-C1 = 114.9 (3), and C8-C7-C6 = 113.4 (3)°. Here, as expected, the largest angle is the internal angle of the seven-membered ring. [Note that the average internal angle of a *planar* heptagon must be 128.57°.] Corresponding angles for other species are 114.4 (8), 115.0 (8), and 116.2 (9)° in phenyltrimethylenemethaneiron tri-carbonyl[6] and 114.6 (2)° in trimethylenemethaneiron tri-carbonyl.[7]

Carbon–carbon distances within the noncoordinated 1,3-diene system, defined by C(2)-C(3)-C(4)-C(5), are C2-C3 = 1.302 (8), C3-C4 = 1.404 (8), and C4-C5 = 1.360 (8) Å; the bonds bridging the 1,3-diene and trimethylenemethane frag-ments are C1-C2 = 1.408 (6) and C5-C6 = 1.456 (5) Å. Clearly, these values are not in complete agreement with the bond lengths determined for *trans*-buta-1,3-diene [1.337 (5), 1.483 (10), 1.337 (5) Å],[21] the accepted C(sp^2)-C(sp^2) bond

(21) A. Almenningen, O. Bastiansen, and M. Traettenberg, *Acta Chem. Scand.*, 12, 1221 (1958).

Figure 3. Packing diagram, viewed down a^*.

lengths of 1.465 (5) Å,[22] or the approximate C_s symmetry of the present molecule.

Unfortunately, while the *precision* of the present structural analysis is high, the *accuracy* does not meet the same standards. The basic problem is that the molecule (or, at least, the heptafulvene moiety) appears to be undergoing a rigid-body libration about an axis perpendicular to the seven-membered ring and intersecting this plane at a point lying about one-third of the way along from C7 to the midpoint of C3-C4. The carbon atoms exhibiting the greatest amount of thermal motion are C3 and C4 (with $B_{av} = 10.5$ and 10.2 Å^2, respectively—see Table I). Interatomic distances between these oscillating atoms are thus subject to systematic error. Happily, significant errors (as judged by internal consistency and comparison with known distances, *etc*.) appear to be confined to atoms C2-C3-C4-C5. It is also of interest to note that certain off-diagonal elements of the correlation matrix between positional parameters of these atoms had values as high as 0.7!

Carbon–hydrogen distances range from 0.86 (6) to 1.15 (7) Å, all hydrogen atoms are in chemically sensible positions, and hydrogen atom thermal parameters run essentially paral-lel to those of their attached carbon atoms (*cf.* Table I).

The Fe(CO)$_3$ Group

Individual OC-Fe-CO angles are 96.5 (1), 98.9 (1), and 100.8 (1)°—again indicative of slight distortions of the mole-cule from C_s symmetry.

The iron–carbonyl linkages are close to linear with Fe-CX1-OX1 = 177.6 (2), Fe-CX2-OX2 = 178.4 (3), and Fe-CX3-OX3 = 178.5 (4)°. Average Fe-CO and C-O bond lengths are 1.788 and 1.131 Å, respectively, in good agree-ment with values from related species [*viz.*, 1.782 and 1.126 Å in phenyltrimethylenemethaneiron tricarbonyl;[6] 1.810 (3) and 1.153 (2) Å in trimethylenemethaneiron tricarbonyl[7]].

Intermolecular Contacts

The packing of molecules within the unit cell, as viewed down a^*, is shown in Figure 3. Quantitative data on inter-

(22) *Chem. Soc., Spec. Publ.*, No. 18, S15s (1965).

molecular contacts are collected in Table VI. The individual molecules of $(C_7H_6CH_2)Fe(CO)_3$ are separated by normal van der Waals distances, closest approaches (of each type) being as follows: oxygen·· ·oxygen, 3.374 (4) Å; oxygen· ·· carbon, 3.261 (4) Å; oxygen· · ·hydrogen, 2.50 (3) Å; car-bon· · ·hydrogen, 3.02 (5) Å; hydrogen· · ·hydrogen, 2.81 (6) Å.

Contribution from the Departments of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680, and Harvard University, Cambridge, Massachusetts 02138

X-Ray Crystallographic Studies on Fluxional Pentacoordinate Transition Metal Complexes. III.[1,2] (Cycloocta-1,5-diene)[1,3-bis(diphenylphosphino)propane]methyliridium(I)

MELVYN ROWEN CHURCHILL* and SUSAN A. BEZMAN

The fluxional pentacoordinate complex (cycloocta-1,5-diene)[1,3-bis(diphenylphosphino)propane]methyliridium(I), $(C_8H_{12})[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]Ir(CH_3)$, crystallizes in the centrosymmetric monoclinic space group $C2/c$ (C_{2h}^6; No. 15) with $a = 23.92$ (3), $b = 18.44$ (2), $c = 15.77$ (1) Å, and $\beta = 119.80$ (8)°. Observed and calculated densities are 1.61 (2) and 1.601 g cm^{-3} (respectively) for $M = 727.8$ and $Z = 8$. X-Ray diffraction data were collected with a Supper–Pace auto-mated diffractometer and the structure was solved using a combination of Patterson, Fourier, and least-squares refinement techniques. The final discrepancy index is $R_F = 7.6\%$ for the 3573 independent nonzero reflections out to sin $\theta = 0.86$ (Cu Kα radiation). The iridium atom is in a slightly distorted trigonal-bipyramidal coordination environment, with the che-lating 1,3-bis(diphenylphosphino)propane ligand occupying two equatorial sites, the methyl ligand being in an axial site, and with the cycloocta-1,5-diene ligand spanning the remaining axial and equatorial positions. Important bond distances include: Ir–P = 2.309 (4) and 2.337 (4), Ir–CH$_3$ = 2.153 (18), Ir–olefin(equatorial) = 2.033 (12), and Ir–olefin(axial) = 2.127 (12) Å. The diequatorial angle P(1)–Ir–P(2) is 93.4 (1)°.

Introduction

We have previously reported crystallographic studies on the fluxional pentacoordinate iridium(I) species $(C_8H_{12})[(C_6H_5)(CH_3)_2P]_2Ir(CH_3)$[1] and $(C_8H_{12})[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]Ir(CH_3)$[2] which have been synthesized (and their variable-temperature ^{1}H nmr spectra investigated) by Shapley and Osborn.[3,4] In the present paper we report the results of a crystallographic study of $(C_8H_{12})[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]Ir(CH_3)$. Correlations between molecular geometry and fluxional behavior[3,4] are interpreted in terms of stereo-isomeric interconversions *via* the Berry ("pseudorotation") mechanism.[5]

Unit Cell and Space Group

Crystals of (cycloocta-1,5-diene)[1,3-bis(diphenylphosphino)-propane]methyliridium(I), hereafter referred to as $(C_8H_{12})(DPPP)Ir(CH_3)$, were supplied by Dr. J. R. Shapley and Professor J. A. Osborn of Harvard University. In the crystalline state the complex is air sta-ble for several months and does not decompose upon irradiation with X-rays. Examination of the crystal form and the reciprocal lattice symmetry of $2/m$ (C_{2h}) indicated that the crystals belonged to the monoclinic system.

Sets of $h'k'(0-1)$ and $h'(0-1)l'$ Weissenberg photographs, along with c'- and b'-axis oscillation photographs, were taken with Cu Kα radiation; $(0-1)k'l'$, $h'k'(0-1)$, and $h'0l'$ precession photographs along with a'-, b'-, and c'-cone-axis photographs were taken with Mo Kα ra-

diation. The systematic absences thus identified were $h'k'l'$ for $h' + k' + l' = 2n + 1$ and $h'0l'$ for $h' = 2n + 1$, consistent with space groups $I2/a$ or Ia.[6]

Unit cell parameters, obtained from calibrated (lead nitrate, $a_{24} = 7.8566$ Å) precession photographs taken with Mo Kα radiation ($\bar{\lambda}$ 0.7107 Å) at 24 ± 2° are $a' = 15.77$ (1), $b' = 18.44$ (2), $c' = 21.12$ (3) Å; and $\beta' = 100.60$ (8)°.

These (primed) parameters were those used during data collection. They were later transformed to conform to the standard setting for space group $C2/c$ (C_{2h}^6; No. 15) by the transformation

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix} \begin{pmatrix} a' \\ b' \\ c' \end{pmatrix}$$

The new cell thus defined has the parameters $a = 23.92$ (3), $b = 18.44$ (2), $c = 15.77$ (1) Å; and $\beta = 119.80$ (8)°.

The volume of the unit cell is 6037 Å^3; the observed density, $\rho_{obsd} = 1.61$ (2) g cm^{-3} (by neutral buoyancy in aqueous zinc iodide solution), indicates eight molecules per unit cell. The calculated den-sity is $\rho_{calcd} = 1.601$ g cm^{-3} for $M = 727.8$ and $Z = 8$.

The satisfactory solution of the crystal structure confirms the true space group to be the centrosymmetric $C2/c$ with one molecule in the asymmetric unit rather than the noncentrosymmetric possibility, Cc. No crystallographic symmetry is imposed upon the molecule.

Collection and Reduction of the X-Ray Diffraction Data

The complex crystallizes as colorless parallelepipeds. Two crys-tals were used during the analysis. Crystal I (0.23 × 0.23 × 0.30 mm, referred to as a', b', c') was aligned along the b' axis; crystal II (0.28 × 0.18 × 0.38 mm, with respect to a', b', c') was aligned along its c' axis.

Intensity data were collected with Cu Kα radiation ($\bar{\lambda}$ 1.5418 Å) on a 0.01°-incrementing Supper-Pace "Buerger Automated diffrac-tometer" using a stationary-background, ω-scan, stationary-back-ground counting sequence and equiinclination Weissenberg geometry.

(1) Part I: M. R. Churchill and S. A. Bezman, *Inorg. Chem.*, 11, 2243 (1972).

(2) Part II: M. R. Churchill and S. A. Bezman, *Inorg. Chem.*, 12, 260 (1973).

(3) J. R. Shapley and J. A. Osborn, *J. Amer. Chem. Soc.*, 92, 6976 (1970).

(4) J. R. Shapley, Ph.D. Thesis, Department of Chemistry, Harvard University, 1971.

(5) R. S. Berry, *J. Chem. Phys.*, 32, 933 (1960).

(6) Apart from an origin shift of $^1/_4$ in y, $I2/a$ is identical to $I2/c$ and Ia is identical to Ic.