Crystal and Molecular Structure of Dicarbonyl*pentahapto*cyclopentadienyl(1-*monohapto*-3,3,4,4-tetracyano-1-methylcyclopentyl)iron(II), the Product of a [3 + 2] Cycloaddition of Tetracyanoethylene and a Transition Metal σ-Allyl

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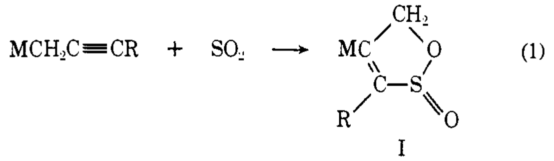
Abstract: Dicarbonyl*pentahapto*cyclopentadienyl(1-*monohapto*-3,3,4,4-tetracyano-1-methylcyclopentyl)iron(II), $(\pi\text{-}C_5H_5)Fe(CO)_2(C_4H_7C_2(CN)_4)$, prepared by the reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2CH_2C(CH_3){=}CH_2$ and tetracyanoethylene, has been investigated by means of a single-crystal X-ray diffraction study. The compound crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ [C_i^1; No. 2] with a = 13.1986 (28) Å, b = 10.1648 (16) Å, c = 13.8088 (43) Å, α = 115.55 (2)°, β = 103.46 (2)°, and γ = 87.06 (1)°. The observed density (1.45 (2) g cm^{-3}) is consistent with the value of 1.474 g cm^{-3} calculated for M = 360.16 and Z = 4. The crystal contains two crystallographically independent molecules. X-Ray diffraction data complete to 2θ = 45° (Mo Kα radiation) were collected with a Picker FACS-1 diffractometer, and the structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. All atoms, including hydrogens, were located and their positional and thermal parameters refined. The final discrepancy indices are R_F = 3.91% and R_{wF} = 3.57% for the 4553 independent reflections. Molecular parameters for the two independent molecules are essentially identical save for a change in conformation caused by rotation of the $-\overline{C(CH_3)CH_2C(CN)_2C(CN)_2CH_2}$ ligand about the iron–carbon σ bond. The crystal structure confirms that $C_2(CN)_4$ may undergo 1,3 addition to a σ-allyl derivative, accompanied by a 1,2 transfer of the σ-bonded metal atom. The $C(CN)_2$–$C(CN)_2$ bond lengths are 1.598 (3)–1.605 (3) Å and CH_2–$C(CN)_2$ bonds are 1.571 (3)–1.585 (2) Å in length, as compared to the normal C(sp^3)–C(sp^3) (nonsubstituted) distance of ∼1.54 Å. The two independent Fe–C (tertiary alkyl) bonds are 2.096 (2) and 2.099 (2) Å in length, suggesting an effective covalent radius of ∼1.33 Å for iron in $(\pi\text{-}C_5H_5)Fe(CO)_2X$ species.

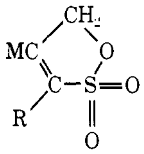
We have recently been interested in the various modes whereby sulfur dioxide can interact with metal–carbon[1-3] or metal–metal[4,5] bonds. One of the more interesting of these reactions is that of sulfur dioxide with a metal–(2-alkynyl) species[2,6] (see eq 1),



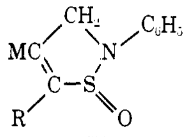
(1)

I

which involves a net [3 + 2] cycloaddition of sulfur dioxide to a σ-(2-alkynyl) system, with concomitant 1,2 transfer of the metal atom, yielding a sultine (I). This type of reaction is not confined to sulfur dioxide, and there are examples (*inter alia*) of sulfur trioxide addition to a 2-alkynyl derivative (yielding a sultone, II)[7,8] and *N*-thionylaniline (C_6H_5NSO) addition to a 2-alkynyl derivative (yielding III).[9]



II



III

Our attention has recently been drawn to reports that tetracyanoethylene can participate in [3 + 2] cycloaddition to transition metal σ-allyl derivatives.[10,11] The present structural analysis was undertaken to determine unequivocally the nature of the product formed from $(\pi\text{-}C_5H_5)Fe(CO)_2CH_2C(CH_3){=}CH_2$ and $C_2(CN)_4$ and to obtain an *accurate* value for an iron–carbon σ-bond distance. It should be noted that the present complex is the first species containing a (transition metal)–(tertiary alkyl) bond to be examined crystallographically. This complex also, apparently, is only the second such species to be synthesized,[11] the first being the *tert*-butyl derivative $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C(CH_3)_3)$.[12]

Collection and Treatment of the X-Ray Diffraction Data

Yellow crystals of $(\pi\text{-}C_5H_5)Fe(CO)_2(C_4H_7C_2(CN)_4)$ were kindly supplied to us by Professor A. Wojcicki of The Ohio State University.

The crystal selected for the X-ray diffraction study was multifaceted but approximated in shape to a prolate spheroid ∼0.4 mm in maximum length (along b) and having an equatorial radius of ∼0.1 mm. The (100) and ($\bar{1}$00) faces were the most obvious fea-

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(11) W. P. Giering and M. Rosenblum, *J. Amer. Chem. Soc.*, **93**, 5299 (1971).

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tures and there were smaller but distinct, (001), ($00\bar{1}$), (110), ($1\bar{1}0$), ($\bar{1}10$), ($\bar{1}\bar{1}0$), ($10\bar{1}$), ($\bar{1}01$), ($11\bar{1}$), ($\bar{1}\bar{1}1$), ($22\bar{3}$), and ($\bar{2}\bar{2}3$), faces.

Preliminary precession photographs for the levels (0–2)*kl* and *hk*(0–2) and Weissenberg photographs for the levels *h*(0–1)*l*, all taken with Mo Kα radiation, yielded approximate cell dimensions and revealed no systematic absences nor any diffraction symmetry other than the $C_i(\bar{1})$ axis imposed by the Friedel condition. The cell parameters derived above were shown to be true values (rather than submultiples) by means of cone-axis photographs taken about the *a* and *c* axes and an oscillation photograph taken about the *b* axis. The crystal was assumed to be truly triclinic.

The crystal was transferred to a Picker FACS-1 diffractometer and was accurately centered and aligned along its b^* axis. An approximate unit cell/orientation matrix was obtained following the location of the *h*00 and 00*l* diffraction rows. The 2θ, ω, and χ settings of the resolved Mo Kα_1 (λ 0.70926 Å) component of 12 high-angle (2θ = 34–50°) reflections, which were well dispersed in reciprocal space, were used in a least-squares refinement of the unit cell and orientation parameters. The resulting cell parameters (at 25°) and their estimated standard deviations are a = 13.1986 (28) Å, b = 10.1648 (16) Å, c = 13.8088 (43) Å, cos α = −0.43124 (30), cos β = −0.23282 (30), and cos γ = 0.05128 (20). (Corresponding angles are α = 115.55 (2), β = 103.46 (2), and γ = 87.06 (1)°.)

The unit cell volume is V = 1623.0 Å^3. The observed density (ρ_{obsd} = 1.454 g cm^{-3}, by flotation in aqueous barium iodide) is in reasonable agreement with that calculated for M = 360.16 and Z = 4 (ρ_{calcd} = 1.474 g cm^{-3}). The structural analysis thus required the location of *two* independent molecules in the centrosymmetric triclinic space group $P\bar{1}$ [No. 2; C_i^1] or (a thought rather unpleasant to contemplate) *four* independent molecules in the noncentrosymmetric triclinic space group $P1$ [No. 1; C_1^1]. Happily, the successful completion of the study showed the former to be the true case.

Intensity data were collected[13] using Mo Kα radiation (*i.e.*, Mo radiation filtered through Nb foil, placed between sample and counter, of such thickness that it transmitted ~47% of the incident Mo Kα radiation) in conjunction with a coupled θ (crystal)–2θ (counter) scan of reflections in the horizontal plane. The scan was from 0.5° in 2θ below the Mo Kα_1 peak to 0.5° in 2θ above the Mo Kα_2 peak. A total of P counts was thereby accumulated in t_P seconds, the scan rate being 1.0°/min. Stationary-crystal, stationary-counter background counts, of 20 sec duration each, were recorded at the high and low 2θ limits of the scan, yielding $B2$ and $B1$ counts, respectively. The total background-counting time was t_B = 40 sec.

A takeoff angle of 3.0° was found to be appropriate. The detector aperture was 6 × 6 mm and 330 mm from the crystal. Copper foil attenuators, whose transmission coefficients for Mo Kα radiation had previously been accurately experimentally determined (and which reduced the incident beam by successive factors of ~3.3) were inserted as required to keep the maximum counting rate below ~8500 counts/sec. Coincidence losses are therefore negligible.

All reflections in the range $0 < 2\theta < 45°$ and having positive k indices were measured. Three strong "check reflections" (520, 150, $0\bar{4}4$) were collected after each batch of 48 reflections in order to monitor any possible crystal deterioration or misorientation and any electronic instability. The root-mean-square deviations of 1.20, 1.84, and 2.12% from the mean values were changed to 1.33, 1.28, and 1.52% (respectively) upon application of a linear decay correction[14] to the entire data set. Clearly the crystal was not appreciably disrupted by X-rays.

The integrated intensity, I, and its estimated standard deviation, $\sigma(I)$, were calculated *via* the expressions

$$I = q[(P + 4.5) - (t_P/t_B)(B1 + B2 + 9.0)]$$

and

$$\sigma(I) = q[(P + 4.5) + (t_P/t_B)^2(B1 + B2 + 9.0) + 24.75 + q^{-2}p^2I^2]^{1/2}$$

The "ignorance factor" (p) was set equal to 0.04, q represents the combined correction for crystal decomposition and attenuator used, and all numerical terms arise from the fact that the last digit of all counts (P, $B1$, $B2$) was truncated in the output process.

Any I calculated to be negative was reset to zero. Unscaled structure factor amplitudes, F, and their estimated standard deviations, $\sigma(F)$, were calculated as

$$F = (I/\text{Lp})^{1/2}$$

$$\sigma(F) = (\sigma(I)/\text{Lp})^{1/2} \text{ for } I < \sigma(I)$$

$$\sigma(F) = [F - (F^2 - \sigma(I)/\text{Lp})^{1/2}] \text{ for } I > \sigma(I)$$

Here, the multiplicative Lorentz–polarization correction, (1/Lp), is given by $(2 \sin 2\theta)/(1 + \cos^2 2\theta)$.

A total of 4553 reflections, representing a unique set of data to 2θ = 45°, were collected. *No data were rejected on the basis of being "not significantly above background;" all were retained.*

At the termination of data collection a test was made to determine whether an absorption correction was necessary. A strong axial reflection (020) was measured (by a θ–2θ scan) at χ = 90° and at 10° intervals from ϕ = 0° to ϕ = 360°. (This is conveniently accomplished on the FACS-1 diffractometer by decoupling the ϕ drive and setting the ϕ angle manually before taking the reflection.) The maximum variation in intensity was ~3.8% from the mean value; this can be translated into a maximum possible systematic error of ~1.9% in F. No absorption correction was deemed necessary (μ-Mo Kα = 9.59 cm^{-1}).

Solution and Refinement of the Structure

Scattering factors for neutral iron, oxygen, nitrogen, and carbon were taken from the compilation of Cromer and Waber;[15] both the real and the imaginary components of anomalous dispersion[16] for these atoms were included in the calculation. Scattering factors used for hydrogen were those of Mason and Robertson.[17] The function minimized in least-squares refinement processes was $\Sigma w(|F_o| - |F_c|)^2$.

Discrepancy indices used below are defined as

$$R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

and

$$R_{wF} = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$$

Computer programs used during the structural analysis include FORDAP (Fourier synthesis, by A. Zalkin], SFIX (a much-modified version of SFLS5, by C. T. Prewitt, for full-matrix least-squares refinement), STAN1 (calculation of distances, angles, and their estimated standard deviations, by B. G. DeBoer), and ORTEP (thermal ellipsoid drawings, by C. K. Johnson).

The positions of the two independent iron atoms were determined from a three-dimensional Patterson synthesis. An "observed" Fourier synthesis, phased only by these two atoms (R_F = 50.5%, R_{wF} = 54.3%) led to the location of all nonhydrogen atoms. Least-squares refinement of individual atomic positional and isotropic thermal parameters converged at R_F = 9.9% and R_{wF} = 11.1%. Further refinement, now using anisotropic thermal parameters for the iron atoms, led to R_F = 8.7% and R_{wF} = 10.0%. At this stage anisotropic thermal parameters were applied to all nonhydrogen atoms. The large number of parameters (nine parameters for each of the 48 nonhydrogen atoms, plus a scale factor; 433 variables in all) necessitated the use of two steps for each "cycle of refinement." Firstly, all parameters of molecule A, the parameters for Fe(B), and the scale factor were refined; secondly all parameters for molecule B and Fe(A) and the scale factor were refined. Two such complete cycles led to convergence with R_F = 6.2% and R_{wF} = 7.2%. A difference-Fourier synthesis at this point revealed the positions of all hydrogen atoms in the structure. Peak heights ranged from 0.81 e Å^{-3} down to 0.34 e Å^{-3}, but the peaks attributed to hydrogen atoms were the 24 highest features on the difference-Fourier map.

With hydrogen atoms included in their observed positions, each being assigned a thermal parameter of 5.5 Å^2, *and before any further refinement of parameters*, the discrepancy indices were R_F = 4.8%

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(13) An extensive description of the apparatus and the experimental technique have appeared previously: M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **12**, 525 (1973).

(14) All data reduction routines and data analysis were performed using the FORTRAN IV program DRAB, by B. G. DeBoer.

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

Atom	*x*	*y*	*z*	B,[b] A^2	Atom	*x*	*y*	*z*	B,[b] Å^2
		(a) Molecule A					(b) Molecule B		
Fe(A)	1.040098 (24)	0.709708 (33)	0.368842 (25)	2.825	Fe(B)	0.450370 (24)	1.201441 (33)	0.347092 (25)	2.806
O(1)	0.87189 (14)	0.82339 (20)	0.22514 (17)	5.60	O(1)	0.62758 (14)	1.34590 (20)	0.33426 (16)	5.12
O(2)	0.91838 (15)	0.62951 (22)	0.48725 (14)	5.48	O(2)	0.56495 (16)	1.13934 (23)	0.52720 (15)	6.16
N(1)	0.76011 (20)	0.14393 (28)	0.18233 (25)	7.22	N(1)	0.44499 (20)	0.55715 (25)	0.24945 (20)	5.83
N(2)	0.83845 (17)	0.20147 (26)	−0.07650 (17)	5.09	N(2)	0.38836 (18)	0.60741 (26)	−0.04489 (17)	5.49
N(3)	1.10408 (17)	0.11054 (25)	0.01414 (17)	4.95	N(3)	0.66667 (20)	0.70783 (29)	0.01763 (20)	6.48
N(4)	1.02525 (19)	0.07008 (25)	0.27719 (19)	5.41	N(4)	0.70804 (19)	0.69333 (31)	0.33082 (21)	6.51
C(1)	1.00560 (16)	0.50465 (23)	0.23318 (16)	2.71	C(1)	0.48354 (16)	1.00094 (22)	0.22782 (16)	2.68
C(2)	0.89247 (19)	0.44612 (24)	0.20327 (20)	3.28	C(2)	0.42075 (18)	0.87773 (24)	0.22498 (19)	2.91
C(3)	0.89252 (17)	0.27446 (24)	0.13537 (17)	3.07	C(3)	0.47462 (17)	0.73305 (24)	0.16526 (17)	2.99
C(4)	1.01007 (16)	0.23702 (23)	0.17502 (17)	2.76	C(4)	0.59420 (17)	0.78619 (24)	0.19347 (17)	3.07
C(5)	1.06521 (18)	0.38907 (23)	0.26162 (18)	2.92	C(5)	0.59568 (19)	0.95801 (25)	0.25689 (21)	3.40
C(6)	1.03204 (24)	0.50997 (31)	0.13270 (21)	4.05	C(6)	0.46260 (24)	1.00453 (31)	0.11539 (21)	4.07
C(7)	0.81710 (19)	0.19918 (27)	0.16004 (21)	4.16	C(7)	0.45963 (19)	0.62868 (25)	0.20958 (19)	3.69
C(8)	0.86266 (17)	0.23217 (25)	0.01523 (19)	3.52	C(8)	0.42815 (19)	0.66226 (25)	0.04614 (19)	3.61
C(9)	1.06214 (17)	0.16672 (24)	0.08304 (18)	3.21	C(9)	0.63575 (19)	0.73982 (27)	0.09414 (20)	4.03
C(10)	1.01594 (19)	0.13829 (25)	0.22890 (19)	3.57	C(10)	0.65948 (19)	0.73009 (28)	0.26797 (21)	4.10
C(11)	1.19983 (19)	0.69216 (28)	0.36432 (22)	4.11	C(11)	0.29198 (19)	1.16032 (29)	0.26077 (24)	4.42
C(12)	1.18760 (20)	0.70423 (30)	0.46511 (22)	4.48	C(12)	0.33353 (19)	1.28716 (27)	0.26222 (22)	3.87
C(13)	1.14509 (22)	0.84093 (30)	0.51729 (21)	4.58	C(13)	0.36504 (19)	1.38915 (27)	0.37469 (21)	3.95
C(14)	1.12966 (20)	0.90911 (28)	0.44732 (22)	4.26	C(14)	0.34443 (21)	1.32581 (29)	0.44013 (24)	4.54
C(15)	1.16270 (19)	0.81597 (28)	0.35045 (22)	4.06	C(15)	0.30005 (21)	1.18169 (31)	0.36900 (26)	4.68
C(21)	0.93741 (18)	0.77681 (24)	0.29947 (20)	3.57	C(21)	0.55811 (18)	1.28549 (25)	0.33721 (19)	3.49
C(22)	0.96497 (19)	0.66115 (25)	0.43880 (18)	3.58	C(22)	0.51973 (19)	1.16223 (26)	0.45436 (19)	3.81
H(2A)	0.8657 (17)	0.4636 (24)	0.2723 (18)	4.6 (6)	H(2A)	0.3486 (18)	0.8739 (24)	0.1895 (18)	4.4 (6)
H(2B)	0.8410 (19)	0.4861 (26)	0.1603 (20)	5.3 (8)	H(2B)	0.4272 (16)	0.8922 (24)	0.3016 (18)	4.4 (6)
H(5A)	1.0625 (16)	0.3972 (24)	0.3330 (18)	4.3 (6)	H(5A)	0.6161 (16)	0.9787 (24)	0.3337 (19)	4.5 (6)
H(5B)	1.1392 (18)	0.3847 (25)	0.2579 (18)	4.7 (7)	H(5B)	0.6416 (17)	0.9994 (26)	0.2341 (18)	4.9 (8)
H(6A)	1.1118 (23)	0.5374 (32)	0.1447 (23)	7.3 (8)	H(6A)	0.5015 (22)	1.0781 (34)	0.1195 (23)	7.4 (9)
H(6B)	1.0240 (19)	0.4128 (31)	0.0672 (21)	6.0 (7)	H(6B)	0.4830 (17)	0.9141 (26)	0.0603 (18)	4.6 (6)
H(6C)	0.9962 (19)	0.5795 (28)	0.1178 (20)	5.4 (10)	H(6C)	0.3903 (21)	1.0157 (28)	0.0854 (21)	5.9 (7)
H(11)	1.2237 (16)	0.6210 (24)	0.3147 (18)	4.3 (8)	H(11)	0.2692 (19)	1.0764 (30)	0.2020 (22)	6.1 (8)
H(12)	1.2041 (17)	0.6317 (26)	0.4899 (18)	4.8 (7)	H(12)	0.3424 (17)	1.3005 (25)	0.2048 (19)	4.5 (8)
H(13)	1.1278 (18)	0.8738 (27)	0.5809 (21)	5.4 (9)	H(13)	0.3962 (19)	1.4859 (29)	0.4029 (20)	5.8 (7)
H(14)	1.0968 (19)	0.9975 (30)	0.4563 (21)	6.1 (8)	H(14)	0.3625 (20)	1.3683 (31)	0.5186 (23)	6.6 (7)
H(15)	1.1629 (20)	0.8365 (29)	0.2892 (21)	6.5 (8)	H(15)	0.2801 (19)	1.1205 (29)	0.3952 (20)	5.8 (8)

[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. These correspond to a mean-square displacement which is the average of the mean-square displacements along the principal axes of the anisotropic atomic vibration ellipsoid.

and R_{wF} = 4.8%. Clearly, the incorporation of hydrogen atoms into the structure provided a truly significant improvement.

A further two cycles of refinement, with the hydrogen atoms' positional and isotropic thermal parameters now also allowed to vary, led to final convergence at R_F = 3.91% and R_{wF} = 3.57%.

In the last cycle of refinement no parameter shifted by more than 10% of its estimated standard deviation. The final "goodness-of-fit," given by $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 1.169, where the number of observations (m) was 4553 and the number of variables (n) was 529 (m/n = 8.6). The function $\Sigma w(|F_o| - |F_c|)^2$ was not markedly dependent either on $(\sin \theta/\lambda)$ or on $|F_o|$ thus indicating a correctly chosen weighting scheme. Data were inspected for evidence of secondary extinction or of absorption by the β filter;[18] none was found.

The correctness and completeness of the refined structure was confirmed by a final difference Fourier synthesis, on which the maximum feature was a "peak" of height 0.25 eÅ^{-3}.

A table of observed and calculated structure factor amplitudes is available for inspection.[19] Positional parameters are listed in Table I; thermal parameters are collected in Table II.

The Molecular Structure

Interatomic distances and their estimated standard deviations (esd's) are shown in Table III; bond angles and their esd's are collected in Table IV. The overall stereochemistry of the two crystallographically independent molecules that constitute the asymmetric unit is shown in Figures 1 and 2. These two molecules have bond distances which agree within the limits of experimental error, and their molecular geometries differ only in the rotational orientation of their $-C_4H_7C_2(CN)_4$ groups about the Fe–C(1) σ bonds.

In each molecule, the central iron atom is in a formal oxidation state of +II, has a d^6 electronic configuration, and attains the appropriate noble gas configuration by the donation of six electrons from a π-cyclopentadienyl anion, two electrons from each of the carbonyl ligands, and two electrons from the (substituted) tertiary alkyl fragment $-C_4H_7C_2(CN)_4$. The arrangement of ligands about the metal ion may be described as pseudooctahedral (with the π-C_5H_5 ligand being considered formally tridentate) or as "resembling a three-legged piano stool," in common with other $(\pi\text{-}C_5H_5)ML_3$ (M = metal, L = monodentate ligand) species.

The angles between the monodentate ligands (C(1)–Fe–C(21) = 88.19 (10), C(1)–Fe–C(22) = 91.13 (9), and C(21)–Fe–C(22) = 96.02 (11)° for molecule A; C(1)–Fe–C(21) = 89.64 (10), C(1)–Fe–C(22) = 91.76 (10), and C(21)–Fe–C(22) = 94.88 (11)° for molecule B) are consistent with this view. We may note that there is some precedent for observing the (OC)–Fe–(CO) angle to be greater than the remaining (OC)–Fe–C angles; *e.g.*, in $(\pi\text{-}C_5H_5)Fe(CO)_2C_4H_5SO_2$[2] (IV) the (CO)–Fe–(CO) angle is 96.1 (5)° whereas the other (CO)–Fe–C angles are 93.0 (4) and 88.9 (4)°.

The distribution of monodentate ligands relative to

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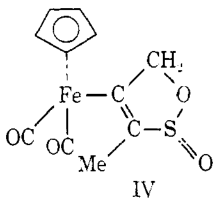
(18) This phenomenon is discussed in ref 13.

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

Table II. Anisotropic Thermal Parameters[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U\rangle^{b}$
				(a) Molecule A			
FeA	3.31 (1)	2.22 (1)	2.54 (1)	0.02 (1)	0.25 (1)	0.87 (1)	(0.17, 0.18, 0.22)
O(1)	4.5 (2)	5.1 (3)	7.6 (3)	0.2 (2)	−0.4 (2)	4.1 (2)	(0.20, 0.24, 0.34)
O(2)	6.3 (3)	6.6 (3)	4.1 (2)	−0.4 (2)	1.7 (2)	2.5 (2)	(0.21, 0.27, 0.30)
N(1)	6.8 (2)	5.1 (2)	10.8 (4)	−0.0 (3)	5.1 (3)	2.9 (2)	(0.21, 0.26, 0.40)
N(2)	4.9 (2)	5.6 (2)	3.3 (3)	−0.4 (2)	−0.2 (2)	1.1 (2)	(0.19, 0.27, 0.28)
N(3)	4.8 (2)	5.0 (2)	4.2 (2)	0.2 (2)	1.7 (2)	0.9 (2)	(0.21, 0.25, 0.29)
N(4)	7.4 (2)	4.2 (2)	5.3 (2)	0.0 (2)	1.2 (2)	2.8 (2)	(0.20, 0.26, 0.31)
C(1)	3.2 (1)	2.4 (1)	2.2 (1)	−0.1 (1)	0.4 (1)	0.8 (1)	(0.17, 0.18, 0.21)
C(2)	3.6 (1)	2.3 (1)	3.2 (1)	0.2 (1)	0.6 (1)	0.7 (1)	(0.17, 0.21, 0.23)
C(3)	3.4 (2)	2.5 (2)	2.8 (2)	−0.6 (2)	0.6 (2)	0.6 (2)	(0.16, 0.20, 0.23)
C(4)	3.1 (2)	2.4 (2)	2.7 (2)	0.3 (2)	0.7 (2)	1.1 (2)	(0.17, 0.19, 0.20)
C(5)	3.4 (1)	2.3 (1)	2.5 (1)	0.1 (1)	0.4 (1)	0.7 (1)	(0.17, 0.19, 0.22)
C(6)	5.9 (2)	3.5 (2)	3.0 (1)	−0.3 (1)	1.2 (1)	1.5 (1)	(0.18, 0.21, 0.28)
C(7)	4.1 (2)	4.1 (2)	4.4 (2)	−1.0 (2)	−1.0 (2)	1.8 (3)	(0.20, 0.22, 0.27)
C(8)	5.1 (2)	4.2 (2)	2.8 (2)	−1.0 (2)	−0.3 (2)	0.5 (2)	(0.18, 0.21, 0.24)
C(9)	4.5 (2)	2.8 (2)	4.4 (2)	−0.6 (2)	−0.1 (2)	1.0 (2)	(0.18, 0.21, 0.22)
C(10)	3.7 (2)	3.7 (2)	4.4 (2)	−0.9 (2)	0.3 (2)	1.6 (2)	(0.18, 0.22, 0.24)
C(11)	3.2 (1)	3.4 (2)	4.6 (2)	−0.2 (1)	0.3 (1)	0.9 (1)	(0.19, 0.22, 0.28)
C(12)	4.1 (1)	4.0 (2)	4.4 (2)	−0.6 (1)	−1.0 (1)	1.8 (1)	(0.18, 0.22, 0.30)
C(13)	5.1 (1)	4.2 (2)	2.8 (1)	−1.0 (1)	−0.3 (1)	0.5 (1)	(0.17, 0.26, 0.28)
C(14)	4.5 (1)	2.8 (1)	4.4 (1)	−0.6 (1)	−0.1 (1)	1.0 (1)	(0.18, p.23, 0.28)
C(15)	3.7 (1)	3.7 (1)	4.4 (2)	−0.9 (1)	0.3 (1)	1.6 (1)	(0.19, 0.24, 0.25)
C(21)	3.9 (3)	2.6 (2)	4.0 (3)	−0.3 (2)	0.5 (2)	1.5 (2)	(0.17, 0.22, 0.24)
C(22)	4.5 (3)	2.9 (2)	2.5 (2)	0.3 (2)	0.3 (2)	0.7 (2)	(0.17, 0.21, 0.25)
				(b) Molecule B			
FeB	3.36 (1)	2.31 (1)	2.54 (1)	−0.15 (1)	0.60 (1)	0.87 (1)	(0.17, 0.19, 0.21)
O(1)	4.6 (2)	4.3 (2)	6.4 (2)	−0.7 (2)	1.6 (2)	2.0 (2)	(0.20, 0.26, 0.29)
O(2)	7.7 (2)	7.0 (3)	3.7 (2)	−0.6 (2)	−0.3 (2)	3.0 (2)	(0.19, 0.29, 0.34)
N(1)	8.0 (2)	4.4 (2)	6.4 (2)	0.0 (2)	2.6 (2)	3.2 (2)	(0.20, 0.28, 0.32)
N(2)	6.4 (2)	4.9 (2)	3.5 (2)	−0.6 (2)	0.1 (2)	0.7 (2)	(0.20, 0.28, 0.30)
N(3)	7.4 (2)	6.4 (1)	5.0 (1)	−0.8 (1)	3.3 (1)	1.0 (1)	(0.21, 0.27, 0.36)
N(4)	5.5 (1)	8.5 (1)	6.6 (1)	1.1 (1)	0.6 (1)	4.7 (1)	(0.22, 0.29, 0.33)
C(1)	3.2 (1)	2.3 (1)	2.3 (1)	−0.3 (1)	0.5 (1)	0.9 (1)	(0.17, 0.18, 0.21)
C(2)	3.3 (1)	2.6 (1)	2.6 (1)	−0.1 (1)	0.6 (1)	0.8 (1)	(0.17, 0.19, 0.21)
C(3)	3.6 (1)	2.5 (1)	2.9 (1)	0.1 (1)	0.8 (1)	1.2 (1)	(0.18, 0.19, 0.21)
C(4)	3.3 (1)	2.9 (1)	2.9 (1)	0.3 (1)	0.8 (1)	1.2 (1)	(0.19, 0.19, 0.21)
C(5)	3.6 (1)	2.9 (1)	3.4 (1)	−0.2 (1)	0.9 (1)	1.0 (1)	(0.19, 0.21, 0.23)
C(6)	6.2 (2)	3.4 (1)	2.7 (1)	0.1 (1)	1.0 (1)	1.3 (1)	(0.18, 0.21, 0.28)
C(7)	4.6 (1)	2.7 (1)	3.6 (1)	−0.2 (1)	1.0 (1)	1.0 (1)	(0.18, 0.22, 0.25)
C(8)	4.4 (1)	2.5 (1)	3.2 (1)	−0.3 (1)	0.7 (1)	0.7 (1)	(0.17, 0.22, 0.24)
C(9)	4.2 (1)	3.6 (1)	4.1 (1)	−0.3 (1)	1.4 (1)	1.2 (1)	(0.20, 0.21, 0.26)
C(10)	3.7 (1)	4.4 (1)	4.4 (1)	0.4 (1)	1.0 (1)	2.1 (1)	(0.22, 0.23, 0.24)
C(11)	3.0 (1)	3.3 (1)	5.7 (2)	0.4 (1)	0.5 (1)	1.1 (1)	(0.19, 0.21, 0.30)
C(12)	3.7 (1)	3.5 (1)	4.5 (2)	0.9 (1)	1.0 (1)	2.0 (1)	(0.19, 0.23, 0.24)
C(13)	4.2 (1)	2.8 (1)	4.7 (1)	0.4 (1)	1.5 (1)	1.2 (1)	(0.19, 0.22, 0.26)
C(14)	5.0 (1)	3.8 (1)	5.0 (2)	0.8 (1)	2.5 (1)	1.5 (1)	(0.20, 0.23, 0.28)
C(15)	4.4 (1)	4.0 (1)	6.5 (2)	0.4 (1)	2.4 (1)	2.6 (1)	(0.20, 0.22, 0.29)
C(21)	3.9 (2)	2.6 (2)	3.4 (2)	0.1 (2)	0.7 (2)	0.8 (2)	(0.18, 0.22, 0.23)
C(22)	4.7 (3)	3.4 (2)	2.8 (2)	−0.5 (2)	0.7 (2)	1.0 (2)	(0.19, 0.21, 0.25)

[a] These anisotropic thermal parameters are analogous to the usual form of the isotropic thermal parameters and have units of Å². They enter the expression for the structure factor in the form: $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}\cdot klb^*c^*)]$. [b] These values correspond to the root-mean-square amplitudes of vibration (in Å) of the atom along the three principal axes (minor, median, major, respectively) of its vibration ellipsoid. For relative orientations, see the figures.



IV

the Cp[20]–Fe vector is far more regular; thus, angles within molecule A are Cp–Fe–C(1) = 123.73 (11), Cp–Fe–C(21) = 124.39 (12), and Cp–Fe–C(22) = 123.67 (12)° and within molecule B are Cp–Fe–C(1) = 123.23 (11), Cp–Fe–C(21) = 123.90 (12), and Cp–Fe–C(22) = 124.05 (13)°.

As shown clearly in Figure 3, in each molecule the three monodentate ligands adopt a symmetrical conformation relative to the π-cyclopentadienyl ligand with the Fe–(tertiary alkyl) bond passing immediately below atom C(11) of the π-cyclopentadienyl group. The Fe(II) ion is thus in a local environment which approximates to C_s symmetry.

Iron–carbon distances within the π-cyclopentadienyl rings of the two molecules range from 2.099 (3) to 2.120 (3) Å, the mean value being 2.107 Å, while the Fe···Cp[20] distances are 1.737 (3) Å for molecule A and 1.732 (3) Å for molecule B.

Each of the π-cyclopentadienyl ligands is planar within the limits of experimental error (see Table V, planes A and B). Carbon–carbon distances range from 1.388 (4) to 1.419 (4) Å (av 1.403 Å) in molecule A and from 1.393 (4) to 1.426 (4) Å (av 1.410 Å) in

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(20) Cp is the centroid of the π-cyclopentadienyl ligand.

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

Atoms	Molecule A	Molecule B
	(a) Iron–Carbon Distances	
Fe–C(1)	2.0961 (21)	2.0993 (21)
Fe–C(11)	2.120 (3)	2.113 (3)
Fe–C(12)	2.100 (3)	2.101 (3)
Fe–C(13)	2.100 (3)	2.099 (3)
Fe–C(14)	2.106 (3)	2.112 (3)
Fe–C(15)	2.111 (3)	2.107 (3)
Fe···Cp[b]	1.737 (3)	1.732 (3)
Fe–C(21)	1.756 (2)	1.757 (3)
Fe–C(22)	1.751 (2)	1.741 (3)
	(b) "Normal" C(sp^3)–C(sp^3) Distances	
C(1)–C(2)	1.532 (3)	1.519 (3)
C(1)–C(5)	1.521 (3)	1.533 (3)
C(1)–C(6)	1.530 (3)	1.528 (3)
	(c) C(sp^3)–C(CN)$_2$– Distances	
C(2)–C(3)	1.585 (3)	1.571 (3)
C(4)–C(5)	1.570 (3)	1.579 (3)
	(d) –C(CN)$_2$–C(CN)$_2$– Distances	
C(3)–C(4)	1.605 (3)	1.598 (3)
	(e) Distances Involving Cyano Groups	
C(3)–C(7)	1.467 (3)	1.476 (3)
C(3)–C(8)	1.480 (3)	1.468 (3)
C(4)–C(9)	1.473 (3)	1.473 (3)
C(4)–C(10)	1.475 (3)	1.473 (3)
C(7)–N(1)	1.130 (4)	1.131 (3)
C(8)–N(2)	1.133 (3)	1.134 (3)
C(9)–N(3)	1.132 (3)	1.131 (3)
C(10)–N(4)	1.137 (3)	1.140 (3)
	(f) Distances within the π-Cyclopentadienyl Systems	
C(11)–C(12)	1.391 (4)	1.417 (4)
C(12)–C(13)	1.418 (4)	1.419 (4)
C(13)–C(14)	1.388 (4)	1.393 (4)
C(14)–C(15)	1.419 (4)	1.426 (4)
C(15)–C(11)	1.401 (4)	1.393 (4)
	(g) Distances in Carbonyl Groups	
C(21)–O(1)	1.144 (3)	1.147 (3)
C(22)–O(2)	1.152 (3)	1.153 (3)
	(h) C–H (methylene) Distances	
C(2)–H(2A)	1.03 (2)	0.96 (2)
C(2)–H(2B)	0.99 (2)	0.99 (2)
C(5)–H(5A)	0.96 (2)	0.96 (2)
C(5)–H(5B)	0.99 (2)	0.93 (2)
	(i) C–H (methyl) Distances	
C(6)–H(6A)	1.06 (3)	0.90 (3)
C(6)–H(6B)	1.00 (3)	0.98 (2)
C(6)–H(6C)	0.90 (3)	0.97 (3)
	(j) C–H (π-cyclopentadienyl) Distances	
C(11)–H(11)	0.86 (2)	0.89 (3)
C(12)–H(12)	0.94 (2)	0.89 (2)
C(13)–H(13)	0.88 (2)	0.96 (3)
C(14)–H(14)	0.95 (3)	0.95 (3)
C(15)–H(15)	0.95 (3)	0.92 (3)

[a] Esd's are calculated by considering those elements of the correlation matrix whose magnitudes are greater than 0.1. This calculation was performed using the FORTRAN IV program STAN1 by B. G. DeBoer. Contributions from errors in the unit cell dimensions are included. No distances have been corrected for possible librational effects. [b] Cp is the centroid of the π-cyclopentadienyl system.

molecule B. A contraction from the true C–C (π-cyclopentadienyl) distance of ~1.43 Å is generally observed in X-ray crystallographic studies on species containing unsubstituted π-cyclopentadienyl ligands and is the result of a systematic error in the model, caused by neglect of the libration of the π-cyclopentadienyl system about its M···Cp axis (*cf.* ref 5).

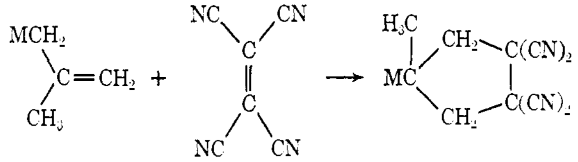
Carbon–hydrogen distances within the π-cyclopentadienyl ligands range from 0.86 (2) to 0.95 (3) Å (av = 0.92 Å) for molecule A and from 0.89 (3) to 0.96 (3) Å (av = 0.92 Å) for molecule B. These values are consistent with other X-ray determined C–H distances;[21] the contraction from the true internuclear value of ~1.08 Å is caused by the centroid of electron density about the hydrogen atom not being coincident with its nuclear position but being displaced along the H(nucleus)–C(nucleus) vector toward carbon.

Angles within the π-cyclopentadienyl ligands are fairly regular, with individual C–C–C angles ranging from 106.75 (24) to 109.19 (24)° (av = 107.995°) and individual C–C–H angles ranging from 122.4 (16) to 129.9 (16)° (av = 125.95°). The idealized values for a system of precise D_{5h} symmetry are, of course, 108.00 and 126.00°, respectively.

The Carbonyl Ligands. The four independent Fe–CO bond distances range from 1.741 (3) to 1.757 (3) Å (av = 1.751 Å), while C–O distances range from 1.144 (3) to 1.153 (3) Å, averaging 1.149 Å. For comparison we may note that average Fe–CO and C–O distances in other molecules include 1.763 and 1.140 Å in $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$[5], 1.768 and 1.140 Å in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(SO_2)$,[4] 1.766 and 1.145 Å in $[(\pi\text{-}C_5(CH_3)_5]Fe(CO)_2SO_2CH_2CH{=}CHC_6H_5$,[3] and 1.776 and 1.129 Å in $(\pi\text{-}C_5H_5)Fe(CO)_2C_4H_5SO_2$.[2]

The Fe–C–O angles range from 177.05 (21) to 178.43 (22) Å. As has been pointed out by Kettle,[22] M–C–O systems are expected to be precisely linear only in situations of high molecular symmetry.

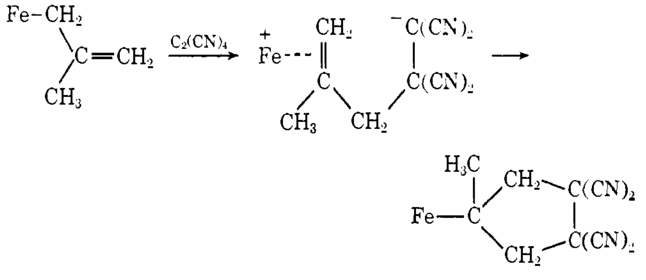
The $C_4H_7C_2(CN)_4$ Ligand. As expected,[10,11] the addition of tetracyanoethylene to the σ-(2-methylallyl) fragment gives rise to a 1-*monohapto*-3,3,4,4-tetracyano-1-methylcyclopentyl group, the product being formed by a net [3 + 2] cycloaddition reaction with a concomitant 1,2 migration of the metal atom (eq 2).



(2)

We emphasize that eq 2 represents only the net reaction, *i.e.*, identity of reactants and final product, and should not be interpreted in terms of a concerted cycloaddition reaction. Indeed, Giering and Rosenblum[11] state that reactions of this nature are "best interpreted in terms of the formation of dipolar intermediates." (Scheme I below shows Giering and Rosenblum's suggestion for the mechanism; it has been modified so as to be specific to the present system.)

Scheme I



(21) M. R. Churchill, *Inorg. Chem.*, 12, 1213 (1973).

(22) S. F. A. Kettle, *Inorg. Chem.*, 4, 1661 (1965).

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

Atom	Molecule A	Molecule B
(a) Angles about Iron Atoms		
Cp-Fe-C(1)[b]	123.73 (11)	123.23 (11)
Cp-Fe-C(21)[b]	124.39 (12)	123.90 (12)
Cp-Fe-C(22)[b]	123.67 (12)	124.05 (13)
C(1)-Fe-C(21)	88.19 (10)	89.64 (10)
C(1)-Fe-C(22)	91.13 (09)	91.76 (10)
C(21)-Fe-C(22)	96.02 (11)	94.88 (11)
C(11)-Fe-C(12)	38.48 (10)	39.31 (11)
C(12)-Fe-C(13)	39.46 (11)	39.51 (10)
C(13)-Fe-C(14)	39.54 (11)	38.63 (11)
C(14)-Fe-C(15)	39.32 (10)	39.51 (11)
C(15)-Fe-C(11)	38.66 (10)	38.54 (12)
(b) Angles about C(1)		
Fe-C(1)-C(2)	114.28 (14)	109.70 (14)
Fe-C(1)-C(5)	109.93 (14)	113.46 (14)
Fe-C(1)-C(6)	109.88 (16)	110.15 (16)
C(2)-C(1)-C(5)	101.60 (18)	101.69 (18)
C(2)-C(1)-C(6)	109.70 (19)	112.27 (19)
C(5)-C(1)-C(6)	111.22 (19)	109.37 (20)
(c) Other Angles within the $(C_4H_7C_2(CN)_4$ Ligand		
C(1)-C(2)-C(3)	106.29 (18)	106.53 (18)
C(2)-C(3)-C(4)	103.86 (17)	103.47 (17)
C(3)-C(4)-C(5)	104.04 (17)	104.60 (17)
C(4)-C(5)-C(1)	106.96 (18)	106.57 (18)
C(2)-C(3)-C(7)	111.00 (19)	109.21 (18)
C(2)-C(3)-C(8)	110.79 (19)	111.74 (18)
C(4)-C(3)-C(7)	111.62 (19)	112.69 (18)
C(4)-C(3)-C(8)	112.37 (18)	112.78 (18)
C(7)-C(3)-C(8)	107.26 (19)	106.98 (19)
C(3)-C(4)-C(9)	112.49 (17)	112.65 (18)
C(3)-C(4)-C(10)	112.56 (18)	110.66 (18)
C(5)-C(4)-C(9)	111.74 (18)	111.68 (19)
C(5)-C(4)-C(10)	109.22 (18)	108.59 (19)
C(9)-C(4)-C(10)	106.84 (18)	108.57 (19)
C(3)-C(7)-N(1)	177.92 (31)	174.70 (26)
C(3)-C(8)-N(2)	178.79 (28)	177.14 (27)
C(4)-C(9)-N(3)	177.82 (27)	178.00 (30)
C(4)-C(10)-N(4)	174.84 (25)	175.82 (29)
(d) Angles within the π-Cyclopentadienyl System		
C(15)-C(11)-C(12)	109.19 (24)	109.00 (24)
C(11)-C(12)-C(13)	107.29 (24)	106.75 (24)
C(12)-C(13)-C(14)	108.31 (23)	108.67 (24)
C(13)-C(14)-C(15)	108.13 (23)	108.01 (26)
C(14)-C(15)-C(11)	107.05 (24)	107.55 (26)
(e) Angles within the Carbonyl Groups		
Fe-C(21)-O(1)	178.43 (22)	177.05 (21)
Fe-C(22)-O(2)	177.85 (23)	178.35 (23)
(f) $C(sp^3)$-$C(sp^3)$-H Angles		
C(1)-C(2)-H(2A)	112.2 (12)	112.3 (14)
C(1)-C(2)-H(2B)	115.7 (14)	108.4 (13)
C(3)-C(2)-H(2A)	106.3 (13)	112.3 (13)
C(3)-C(2)-H(2B)	109.6 (14)	107.5 (13)
C(1)-C(5)-H(5A)	113.2 (13)	110.5 (13)
C(1)-C(5)-H(5B)	115.3 (14)	111.5 (14)
C(4)-C(5)-H(5A)	106.3 (13)	104.9 (14)
C(4)-C(5)-H(5B)	106.9 (13)	109.0 (14)
C(1)-C(6)-H(6A)	113.6 (16)	110.2 (18)
C(1)-C(6)-H(6B)	113.7 (15)	110.8 (14)
C(1)-C(6)-H(6C)	109.6 (16)	113.8 (15)
(g) $C(sp^2)$-$C(sp^2)$-H Angles		
C(15)-C(11)-H(11)	122.4 (16)	123.7 (17)
C(12)-C(11)-H(11)	128.4 (16)	127.1 (18)
C(11)-C(12)-H(12)	123.9 (14)	127.8 (15)
C(13)-C(12)-H(12)	128.8 (14)	125.4 (15)
C(12)-C(13)-H(13)	125.6 (17)	126.9 (15)
C(14)-C(13)-H(13)	126.0 (17)	124.4 (15)
C(13)-C(14)-H(14)	128.1 (17)	125.7 (17)
C(15)-C(14)-H(14)	123.5 (16)	126.0 (18)
C(14)-C(15)-H(15)	126.3 (16)	122.5 (16)
C(11)-C(15)-H(15)	126.6 (16)	129.9 (16)
(h) H-$C(sp^3)$-H Angles		
H(2A)-C(2)-H(2B)	106.4 (18)	109.7 (18)
H(5A)-C(5)-H(5B)	107.6 (18)	113.9 (20)
H(6A)-C(6)-H(6B)	100.1 (21)	106.4 (23)
H(6A)-C(6)-H(6C)	105.9 (22)	108.4 (24)
H(6B)-C(6)-H(6C)	113.4 (20)	107.0 (20)

[a] See footnote *a* to Table III. [b] Cp is the centroid of the π-cyclopentadienyl ring.

As shown clearly in Figure 2, within both molecule A and molecule B the (substituted) cyclopentyl rings are markedly nonplanar. Presumably the observed conformation minimizes repulsive interactions between substituents on adjacent carbon atoms.

Within each molecule the system C(2)–C(3)–C(4)–C(5) is approximately planar (rms deviations are 0.003 Å for molecule A and 0.028 Å for molecule B—see Table V). The dihedral angle between this plane and the plane defined by C(5)–C(1)–C(2) is 140.44° in molecule A and 140.89° in molecule B.

Within the pentaatomic carbocyclic rings, the C–C–C angles form three sets: at the metal-bonded atom C(1), the internal angle C(2)–C(1)–C(5) is 101.60 (18)° for molecule A and 101.69 (18)° for molecule B; angles at the methylene groups, *i.e.*, C(1)–C(2)–C(3) and C(4)–C(5)–C(1), range from 106.29 (18)° to 106.96 (18)°, while angles at the cyano substituted carbon atoms, *i.e.*, C(2)–C(3)–C(4) and C(3)–C(4)–C(5), vary from 103.47 (17)° to 104.60 (17)°.

Carbon–carbon distances within the carbocyclic rings fall into three distinct categories: (1) "normal" $C(sp^3)$–$C(sp^3)$ distances, represented by C(1)–C(2) and C(1)–C(5), for which individual values range from 1.519 (3) to 1.533 (3), averaging 1.526 Å; (2) CH_2–$C(CN)_2$ single bonds, represented by C(2)–C(3) and C(5)–C(4), which range from 1.570 (3) to 1.585 (3), averaging 1.576 Å in length; and (3) $C(CN)_2$–$C(CN)_2$ single bonds, given by C(3)–C(4), for which individual values are 1.605 (3) and 1.598 (3) Å (av = 1.602 Å).

Presumably the incremental increase in $C(sp^3)$—$C(sp^3)$ bond length observed upon replacing a $-CH_2-$ by a $-C(CN)_2-$ group is simply a result of the withdrawal of electron density from the carbon–carbon σ bond by the highly electron-attracting cyano substituents. The magnitude of the effect (*i.e.*, $C(CN)_2$–CH_2 > CH_2–CH_2 by ~0.050 Å, and $C(CN)_2$–$C(CN)_2$ > $C(CN)_2$–CH_2 by ~0.026 Å) is, however, surprisingly large.

The $C(sp^3)$–CH_3 bond, C(1)–C(6), is 1.530 (3) Å in molecule A and 1.528 (3) Å in molecule B; the average value of 1.529 Å is not significantly different from the intra-ring "normal" $C(sp^3)$–$C(sp^3)$ distance of 1.526 Å.

We may note here that the eight independent $C(sp^3)$–CN distances range from 1.467 (3) to 1.480 (3) Å. The average value of 1.473 Å is in reasonable agreement with the tabulated[23] C–CN distance of 1.464 ± 0.005 Å and with the accepted[23] $C(sp^3)$–C(sp) single bond distance of 1.459 ± 0.005 Å.

The cyano groups are approximately, but not precisely, linear, with C—C≡N angles ranging from

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

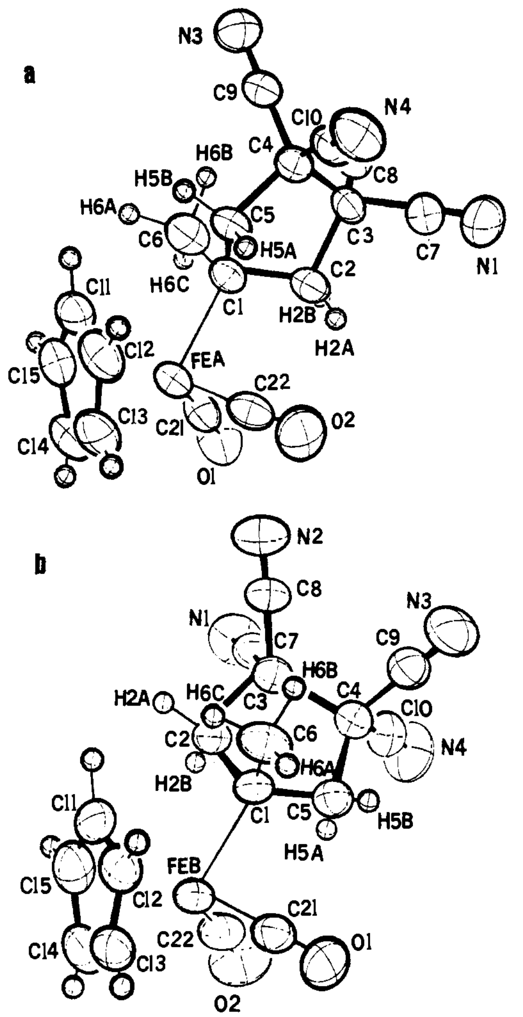

Figure 1. Views showing the different rotational conformations of the molecules about their Fe–C(1) bonds: (a) molecule A, (b) molecule B. Note that in (a) atom N(3) lies below atoms C(10) and N(4) and is hidden from view.

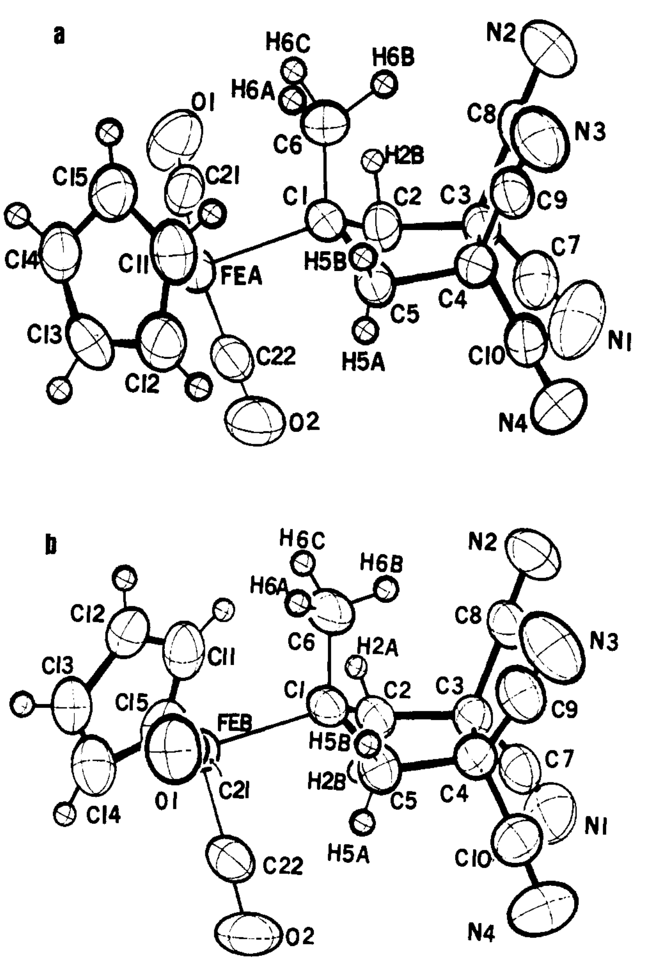

Figure 2. Equivalent views of the two molecules, showing the nonplanarity of the cyclopentane ring in each: (a) molecule A, (b) molecule B.

174.70 (26) to 178.79 (28)°. The eight $C\equiv N$ bond distances are self-consistent, ranging from 1.130 (4) to 1.140 (3) Å in length. The average value of 1.134 Å seems to be slightly shorter than the accepted distance of 1.157 ± 0.005 Å,[24] but is consistent with $C\equiv N$ distances reported in certain other recent structural studies—*viz.*, 1.142 (7) Å in $Ni[C_2(CN)_4][(CH_3)_3CNC]_2$,[25] 1.134 (6) Å in $C_2(CN)_4$,[26] 1.141 (12) Å in $IrBr(CO)[C_2(CN)_4][P(C_6H_5)_3]_2$,[27] 1.129 (1) Å (X-ray diffraction value) and 1.136 (2) Å (neutron diffraction value) for $C_2(CN)_4O$,[28] 1.144 (3) Å in *cis*-1,2,3-tricyanocyclopropane,[29] and 1.140 (1) Å in 7,7,8,8-tetracyanoquinodimethane.[30]

Carbon–hydrogen distances within the methyl groups range from 0.90 (3) to 1.06 (3) Å (av = 0.97 Å); within methylene groups the C–H distances vary from 0.93 (2) to 1.03 (2) Å, averaging 0.98 Å.

The Iron–Carbon σ Bond. The present structural analysis provides an excellent opportunity to determine *accurately* the length of an iron–alkyl bond in a $(\pi\text{-}C_5H_5)Fe(CO)_2R$ species. The two independent measurements are Fe–C(1) = 2.0961 (21) Å in molecule A and Fe–C(1) = 2.0993 (21) Å in molecule B. The mean value is thus 2.0977 (23) Å (using $\sigma_{\text{mean}} = (\sigma_1^2 + \sigma_2^2)^{1/2}$). This value is consistent with but is an order of magnitude more precise than the values reported previously for $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_5H_5)$ (Fe–CH< = 2.11 (2) Å)[31] and $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}CH_2CO_2H)$ ($Fe\text{-}CH_2CO_2H$ = 2.06 (2) Å).[32]

The covalent radius of iron in $(\pi\text{-}C_5H_5)Fe(CO)_2X$ species may thus be estimated as ~1.33 Å (by subtracting 0.77 Å, the C(sp^3) radius, from the iron–alkyl bond distance).

The present precise determination of an iron–carbon single bond length is of considerable value in providing a standard against which contractions in metal–carbon distances can be measured. (This general topic has

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[24] Reference 23, p S20s; see also D. Britton, *Perspect. Struct. Chem.*, 1, 109 (1967), especially Table 1, p 113.

[25] J. K. Stalick and J. A. Ibers, *J. Amer. Chem. Soc.*, 92, 5333 (1970).

[26] D. A. Bekoe and K. N. Trueblood, private communication—reported in footnote 20 of ref 25; see also D. A. Bekoe and K. N. Trueblood, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, 113, 1 (1960).

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[30] R. E. Long, R. A. Sparks, and K. N. Trueblood, *Acta Crystallogr.*, 18, 932 (1965).

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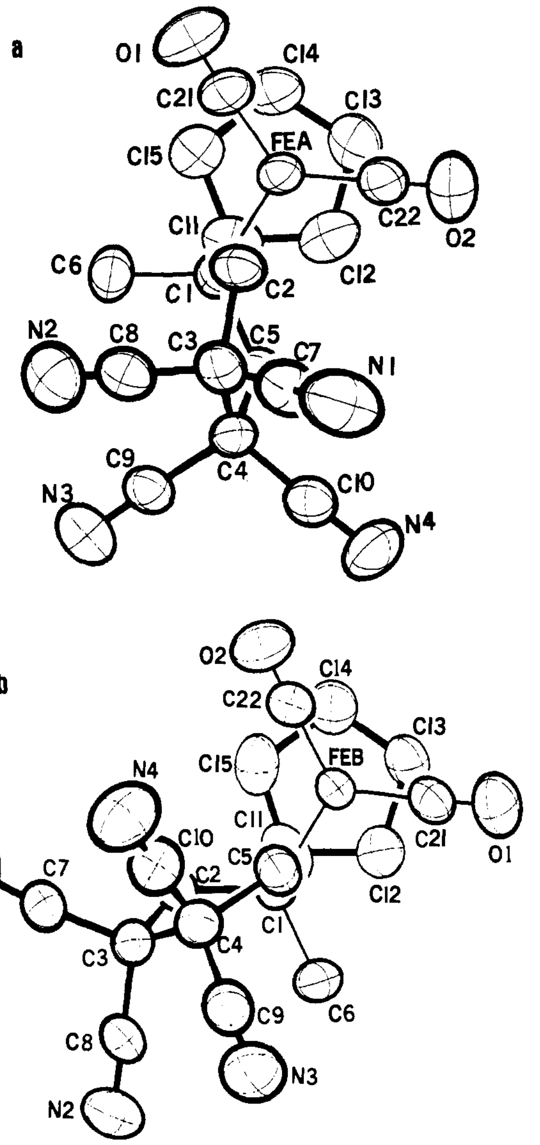

Figure 3. The two molecules projected onto the planes of their π-cyclopentadienyl rings (hydrogen atoms are omitted for the sake of clarity): (a) molecule A, (b) molecule B.

been the subject of a review article by one of us.[33]) In this light we may note that our present iron–alkyl distance of 2.0977 (23) Å indicates that iron–(σ-vinyl) distances are contracted by ~0.10–0.11 Å relative to an Fe–C(sp^3) single bond or by ~0.07–0.08 Å relative to an Fe–C(sp^2) bond of unit bond order. (Relevant data are: Fe–(CH=) = 1.987 (5) Å in (π-C_5H_5)Fe-$(CO)_2$(CH=CHCH=CH)$(OC)_2$Fe(π-C_5H_5),[34] Fe–(C$\lessgtr$) = 1.996 (8) Å in (π-C_5H_5)Fe$(CO)_2$(C=CMeSOO-CH_2)[2] (IV), and Fe–(C$\lessgtr$) = 1.99 (2) Å in $(C_6H_5C_2CO_2CH_3)_3$ $Fe(CO)_3$.[35])

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Table V. Least-Squares Planes, with Deviations[a,b]

Atom	Dev, Å	Atom	Dev Å
(A) π-Cyclopentadienyl Ligand (Molecule A) $0.8427X + 0.3275Y + 0.4274Z = 16.1671$			
C(11)*	0.011	Fe(A)	−1.737
C(12)*	−0.009	H(11)	0.007
C(13)*	0.004	H(12)	−0.045
C(14)*	0.002	H(13)	−0.032
C(15)*	−0.008	H(14)	−0.069
		H(15)	0.015
(B) π-Cyclopentadienyl Ligand (Molecule B) $0.9268X - 0.3734Y + 0.0417Z = -0.8937$			
C(11)*	−0.010	Fe(B)	1.732
C(12)*	0.006	H(11)	0.034
C(13)*	−0.001	H(12)	0.060
C(14)*	−0.005	H(13)	0.006
C(15)*	0.009	H(14)	0.052
		H(15)	0.004
(C) C(5)–C(1)–C(2) Plane (Molecule A) $-0.2815X + 0.1004Y + 0.9543Z = -0.4003$			
C(5)*	0.000	Fe(A)	1.682
C(1)*	0.000	C(6)	−1.275
C(2)*	0.000		
(D) C(2)–C(3)–C(4)–C(5) Plane (Molecule A) $-0.4429X - 0.5180Y + 0.7317Z = -5.1797$			
C(2)*	−0.002	C(4)*	−0.003
C(3)*	0.003	C(5)*	0.002
(E) C(5)–C(1)–C(2) Plane (Molecule B) $-0.2055X + 0.1056Y + 0.9729Z = 2.4776$			
C(5)*	0.000	Fe(B)	1.705
C(1)*	0.000	C(6)	−1.263
C(2)*	0.000		
(F) C(2)–C(3)–C(4)–C(5) Plane (Molecule B) $0.0053X - 0.5186Y + 0.8550Z = -1.7462$			
C(2)*	0.022	C(4)*	0.033
C(3)*	−0.033	C(5)*	−0.022
Dihedral Angles			
$C/D = 140.44°$			
$E/F = 140.89°$			

[a] Equations for planes are in Cartesian coordinates such that $X = xa \sin \gamma + [zc(\cos \beta - \cos \alpha \cos \gamma)/\sin \gamma]$, $Y = yb + xa \cos \gamma + zc \cos \alpha$, and $Z = zc[(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)/\sin^2 \gamma]^{1/2}$. This corresponds to defining the mutually orthogonal directions as bXc^*, b, and c^*. [b] Planes are derived using unit weights for atoms marked with an asterisk and zero weight for all other atoms.

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 Street, N.W. Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-5931.

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(33) M. R. Churchill, *Perspect. Struct. Chem.*, **3**, 91 (1970), see particularly pp 128–131 and pp 153–155.

(34) M. R. Churchill and J. Wormald, *Inorg. Chem.*, **8**, 1936 (1969).

(35) L. F. Dahl, R. J. Doedens, W. Hübel, and J. Nielsen, *J. Amer. Chem. Soc.*, **88**, 446 (1966).