mole, the failure of anyone to anticipate structures II and III should not be considered too surprising. This entire situation is but another indication that present-day understanding of complex metal–olefin interactions is still in a primitive state.

Acknowledgments. We are grateful to Dr. Alfredo Musco for supplying the sample and to him and Professor Alan Davison for stimulating discussions. We also thank Dr. M. J. Bennett for his generous counsel and assistance.

The Structure of (1,3,5-Trimethyl-7-methylene-1,3,5-cyclooctatriene)diiron Pentacarbonyl, an Anomalous Reaction Product of 1,3,5,7-Tetramethylcyclooctatetraene with Polynuclear Iron Carbonyls[1]

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Abstract: The structure of a compound with the formula $C_{12}H_{16}Fe_2(CO)_5$, which is obtained by reaction of 1,3,5,7-tetramethylcyclooctatetraene with the polynuclear iron carbonyls and is isomeric with a compound already identified (Cotton and LaPrade, preceding paper) as a true $Fe_2(CO)_5$ derivative of tetramethylcyclooctatetraene, has been determined. The present compound contains an isomer of tetramethylcyclooctatetraene, namely 1,3,5-trimethyl-7-methylene-1,3,5-cyclooctatriene, to which one $Fe(CO)_2$ and one $Fe(CO)_3$ are attached. There is also an Fe–Fe bond. The olefinic macrocycle is bound to the $Fe_2(CO)_5$ group by two π-allyl–metal bonds and an olefin–metal bond. The principal crystallographic data are: space group $A\bar{1}$ (no. 2); unit cell dimensions, $a = 7.394$ Å, $b = 16.87$ Å, $c = 14.19$ Å, $\alpha = 103° 58'$, $\beta = 91° 58'$, $\gamma = 96° 47'$; density 1.60 g/cm³ (measured), 1.61 g/cm³ (calculated for $Z = 4$). The structure was solved from Patterson and electron density maps and refined by least squares to a residual of 0.040. All hydrogen atoms were unambiguously located.

As described in an earlier paper,[2] a study has been made in this laboratory of the reactions of 1,3,5,-7-tetramethylcyclooctatetraene, TMCOT, with the iron carbonyls. A number of distinct products have been isolated and in some cases their identity was postulated with reasonable certainty on the basis of the more routine types of physical data, *e.g.*, nmr and infrared spectra. In some cases, however, an acceptable level of certainty as to structure was not attainable by such means and, thus, for several of the products, the techniques of single-crystal X-ray crystallography were brought to bear.

This paper reports one such study. The compound in question has the empirical formula $C_{17}H_{16}Fe_2O_5$, which was presumed to correspond to (TMCOT)-$Fe_2(CO)_5$. The infrared spectrum of the compound contains five resolved CO stretching bands, and its nmr spectrum is extremely complex. It was not clear from these and similar data whether it was homologous to any known cyclooctatetraene (COT) derivative in the iron[3] or ruthenium[4] systems, though such homology appeared doubtful. As will be seen below, it is not homologous to any COT compound. Instead, it has a novel structure which would not be possible in a COT derivative.

Procedure

The compound $C_{12}H_{16}Fe_2(CO)_5$ was prepared as described elsewhere.[2] Suitable single crystals were grown by slow crystallization from pentane under nitrogen. Although the predominant crystal habit is platelike, a few crystals which were parallelepipeds with appreciable thickness were also found. One of these latter crystals was chosen for X-ray work and sealed in a thin-walled Lindemann glass capillary.

The systematic absences $k + l \neq 2n + 1$, as obtained from precession ($h0l$, $h1l$, $h2l$, $hk0$, $kk1$, and $hk2$ levels) and Weissenberg ($0kl$ and $1kl$ levels) photography, indicated the probable space groups A1 (no. 1) or A1 (no. 2) having the following equipoints, respectively: x, y, z; $x, \frac{1}{2} + y, \frac{1}{2} + z$; and x, y, z; x, y, z; $x, \frac{1}{2} + y, \frac{1}{2} + z$; $\bar{x}, \frac{1}{2} - y, \frac{1}{2} - z$. The following unit cell dimensions were obtained, at 22°, from the zero level precession photographs and by a method described elsewhere[5] from readings of 2θ made on the General Electric XRD-5 manually operated single-crystal diffractometer with Cu Kα radiation [λ(Kα_1) 1.5405 Å, λ(Kα_2) 1.5443 Å]: $a = 7.394 \pm 0.005$ Å, $b = 16.872 \pm 0.008$ Å, $c = 14.185 \pm 0.008$ Å, $\alpha = 103° 58' \pm 3'$, $\beta = 91° 58' \pm 3'$, $\gamma = 96° 47' \pm 3'$. The films were calibrated with a NaCl crystal whose cell dimensions are accurately known.[6] The main source

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[1] This work was supported, in part, by a grant from the Petroleum Research Fund, administered by the American Chemical Society.

[2] F. A. Cotton and A. Musco, *J. Am. Chem. Soc.*, **90**, 1444 (1968).

[3] C. E. Keller, G. F. Emerson, and R. Pettit, *ibid.*, **87**, 1388 (1965).

[4] F. A. Cotton, A. Davison, and A. Musco, *ibid.*, **89**, 6796 (1967).

[5] M. J. Bennett, F. A. Cotton, and J. Takats, *ibid.*, **90**, 903 (1968).

of error in the cell edges is due to the angular term obtained from film data. A Delaunay reduction[7] did not reveal any higher symmetry. The observed density of 1.60 g cm^{-3} by flotation in aqueous zinc chloride solution agrees well with the calculated density of 1.61 g cm^{-3} for a formula weight of 411.6, $Z = 4$, and a unit cell volume of 1701 Å^3.

Intensity data were collected on the diffractometer from a crystal of dimensions 0.045 × 0.110 × 0.260 mm, oriented with a^* coincident with the φ axis of the instrument. The crystal was placed 5.73 in. from the source while the distance from the crystal to the detector with a circular aperture of 2° was 7.05 in. The integrated intensities of 2079 independent reflections (four nonequivalent sets with indices hkl, $h\bar{k}\bar{l}$, $\bar{h}\bar{k}\bar{l}$, $hk\bar{l}$) within the sphere $\theta \leq 22°$ were measured by using zirconium-filtered Mo Kα radiation. The intensities were measured with a scintillation counter, with a pulse height discriminator set to receive 95% of the Mo Kα radiation with the window centered on the Mo Kα peak. The data were collected using a $\theta/2\theta$ scan technique at a scan rate of 4°/min. The peak counts, P, were obtained from a 2θ scan of 2.66° from $2\theta_{\mathrm{calcd}} - 1.33°$ to $2\theta_{\mathrm{calcd}} + 1.33°$. Stationary background counts, B_1, B_2, of 20 sec were taken at each of the limits of the scan. The mosaic spread of the crystal and a take-off angle of 2° dictated the choice of 2.66° for the 2θ scan. From these readings the intensity, I, assuming a linear background between the two limits of the scan, is given by $I = P - B_1 - B_2$. Periodic checks of three standard reflections, with no 2θ dependence, showed a variation which was consistent with fluctuations in the electronic circuits rather than with crystal decomposition.

The experimental values of I were processed using a program, PMMO, written by Dr. M. J. Bennett of this laboratory. A number of reflections (774) were rejected as unreliable using the two criteria: (1) $I < 0$; (2) $3 > I/(P + B_1 + B_2)^{1/2}$. The remaining 1305 independent intensities were corrected for Lorentz and polarization effects and a set of $|F_o|^2$ and $|F_o|$ values (on a relative scale) thus obtained.

The irregular shape of the crystal was observed to cause appreciable variations in the intensities of the $h00$ reflections (a φ scan of several of these reflections indicated a variation of 15%). The crystal dimensions were therefore carefully measured and the equations of the crystal faces calculated. Absorption corrections ($\mu = 17.7$ cm^{-1}), based on these equations, were included in the final stages of refinement.

Solution and Refinement of the Structure. The positions of the two iron atoms were found from a three-dimensional Patterson map. A three-dimensional electron density synthesis phased by the two iron atoms ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.34$, where F_o and F_c are the observed and calculated structure factors, respectively) revealed all light atoms other than hydrogen atoms. A structure factor calculation at this point, with phases based on 2 iron, 17 carbon, and 5 oxygen atoms, had a discrepancy index $R_1 = 0.32$; the weighted residual, $R_2 = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$, using equal (unit) weights for all reflections was 0.34. The steps of the refinement[8] which was carried out using standard least-squares techniques, are listed in Table I.

Table I. Summary of the Steps in Least-Squares Refinement[a]

	Equal (unit) weights		Empirical weighting scheme[b]			
			A		B	
Parameters varied	R_1	R_2	R_1	R_2	R_1	R_2
1. All atoms isotropic; hydrogen atoms excluded	0.066	0.073				
2. All atoms isotropic;[c,d] H atoms fixed at Fourier coordinates with isotropic B's	0.060	0.065	0.055	0.065		
3. Fe, C, O anisotropic,[c,d] hydrogen atoms not refining but shifted according to carbon atoms			0.041	0.050	0.040	0.040

[a] The residuals listed are those obtained from convergence of each type of refinement listed (parameter changes less than esd's). [b] The empirical weighting schemes were chosen according to Cruickshank's criterion that $w\Delta^2$ should be constant: D. W. J. Cruickshank in "Computing Methods of Crystallography," J. S. Rollett, Ed., Pergamon Press, New York, N. Y., 1965, p 113. They are as follows: (A) For $|F_o| \leq 8.29$, $\sigma = (5.803 - 0.474|F_o|)^{1/2}$; for $8.29 < |F_o| \leq 27.64$, $\sigma = 1.367$; for $|F_o| > 27.64$, $\sigma = (0.226|F_o| - 4.385)^{1/2}$. (B) For $|F_o| \leq 12.95$, $\sigma = (2.810 - 0.175|F_o|)^{1/2}$; for $12.95 < |F_o| \leq 49.00$, $\sigma = 0.739$; for $|F_o| > 49.00$, $\sigma = 3.949$. [c] The isotropic model and the one without hydrogen atoms can be rejected at the 0.5% confidence level as indicated by Hamilton's R-factor test: W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965). [d] The isotropic B's assigned to the H atoms are as follows: 6.00 for methyl hydrogens, 4.00 for methylene hydrogens.

All 16 hydrogen atoms were found from a difference Fourier map following the cycle leading to $R_1 = 0.066$ and $R_2 = 0.073$. An attempt to refine the hydrogen atom positional parameters was unsuccessful; hence hydrogen atoms were not refined but were moved after each cycle by an amount equal to the shift of the carbon atom to which they are attached.

The final cycle of refinement showed no parameter shift greater than one-fifth of one esd. A difference Fourier map computed at this point did not have any feature greater than 0.4 e/Å^3. A structure factor calculation based on the rejected reflections gave no $|F_c|$ greater than twice the minimum observable. The final value of the function $[\Sigma w||F_o| - |F_c||^2/(m - n)]^{1/2}$, 1.038, where m is the number of reflections included in the refinement and n is the number of parameters varied, is satisfactorily close to the expected value of unity.

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(6) "International Tables for X-ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, p 122.

(7) L. V. Azaroff and M. J. Buerger in "The Powder Method in X-ray Crystallography," McGraw-Hill Book Co., Inc., New York, N. Y., 1958, pp 167–180.

(8) The scattering factors used during the analysis are those listed by J. A. Ibers in ref 6, p 202 (carbon and oxygen), p 211 (iron). For hydrogen we used the experimental values determined for H atoms in biphenyl by R. Mason and G. B. Robertson (*cf.* "Advances in Structure Research by Diffraction Methods," Vol. 2, R. Brill and R. Mason, Ed., Interscience Division of John Wiley and Sons, Inc., New York, N. Y., 1966, p 57). The atomic scattering factors for iron were corrected for the real ($\Delta f' = 0.4$ electron) and imaginary ($\Delta f'' = 1.0$ electron) part of anomalous dispersion. The function minimized in the least-squares refinements was $\Sigma w(|F_o| - |F_c|)^2$.

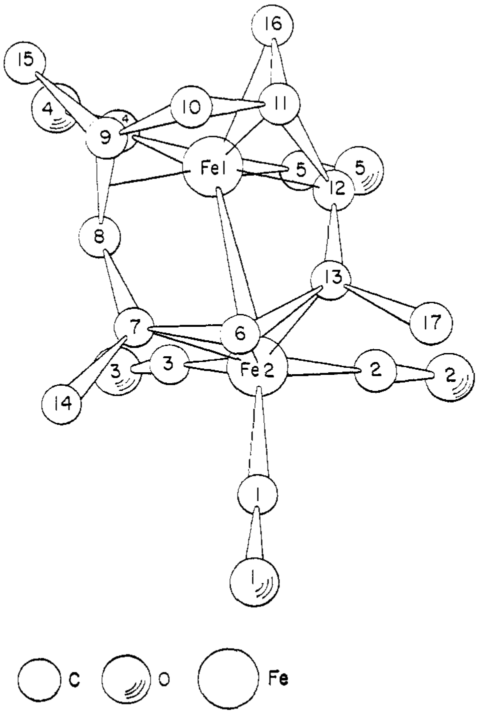

Figure 1. The molecular structure projected onto the plane defined by the *b* and *c** axes (the *YZ* plane of the orthogonal coordinate system). Hydrogen atoms are omitted for clarity.

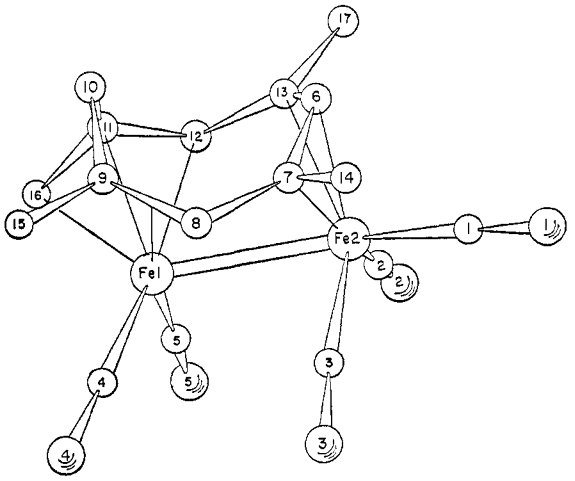

Figure 2. The molecular structure projected on a plane parallel to the mean plane of the atoms Fe_1, Fe_2, C_6, C_{10}. Hydrogen atoms are omitted for clarity.

Results

The molecular structure is shown in Figures 1 and 2. The numbering system shown in these figures is followed in Tables II–VIII. A table of the final calculated and observed structure factors multiplied by 10 has been deposited with the ADI.[9] Final atomic coordinates are to be found in Table II. Intramolecular distances and bond angles are given in Tables III and IV, while Table V shows some selected intermolecular contacts. The anisotropic thermal parameters and the root-mean-square amplitudes of vibrations are collected in Tables VI and VII, respectively.

The following comments can be made about the thermal parameters. The values of the isotropic *B*'s are reasonable, the order being as expected: $O > C_{\text{methyl}} > C_{\text{ring}} \simeq Fe$. We may also note that C_{10}, the only nonbonded carbon atom in the ring, has the largest *B* among the ring carbon atoms. For the oxygen atoms the medium and major axis of vibration is considerably greater than the minor one, indicating vibration in the directions approximately perpendicular to the C–O bond axis. The relative magnitudes of these amplitudes are physically reasonable indicating that the thermal parameters have physical significance.

Discussion

The molecular geometry can be seen in Figures 1 and 2. The complex consists of an $Fe(CO)_3$ and an $Fe(CO)_2$ group bonded to 1,3,5-trimethyl-7-methylene-1,3,5-cyclooctatriene (an isomer of 1,3,5,7-tetramethylcyclooctatetraene obtained by a hydrogen shift). Both iron atoms are on the same side of the ring, and there is an iron–iron bond. As a result of the hydrogen shift, the cyclic olefin can form two allylic systems, $C_{13}C_6C_7$ and $C_{12}C_{11}C_{16}$, the latter being an *exo*-ring allyl group, and one separate double bond (C_8–C_9). The $Fe(CO)_2$ group (containing Fe1) is associated with both the *exo*-allylic group and the double bond. The coordination and the strain in the molecule cause the lengthening of this bond to 1.386 Å. The $Fe(CO)_3$ group (containing Fe_2) is bonded only to three of the ring carbon atoms ($C_{13}C_6C_7$) forming the second π-allyl to metal bond. The observed Fe–Fe distance, 2.766 Å, is indicative of metal–metal bonding. Donation of two electrons from the double bond and from each carbonyl group, three from each π-allyl group, and one from the metal–metal bond gives each iron atom the formal noble gas configuration. The coordination of each iron atom can be crudely described as octahedral, if each allyl group is considered to occupy two coordination positions, although the octahedral coordination is distorted, especially for the $Fe(CO)_2$ group. The iron–iron distance (2.766 Å) in this molecule is quite long; in fact, in organometallic molecules the only longer one, 2.782 Å, was observed[10] in $C_{10}H_8Fe_2(CO)_5$ ($C_{10}H_8$ = azulene). The observed length may be due to the following factors: (1) absence of a carbonyl bridge in the compound, which usually shortens the metal–metal bond;[10] (2) the rather strained nature of the organic part of the complex; (3) van der Waals repulsion between terminal carbonyls (the best planes through $O_5C_5Fe_1C_4O_4$ and $O_2C_2Fe_2C_3O_3$ are nearly parallel (dihedral angle, ~15°) and the distances between eclipsed pairs of carbon and oxygen atoms are 3.192, 2.980 Å and 3.606, 3.218 Å).

The dimensions of the carbonyl groups, with average Fe–C and C–O bond lengths of 1.760 ± 0.008 and 1.158 ± 0.011 Å, respectively, are comparable to the corresponding distances in other similar organoiron compounds (*cf.* Table IX). The nonlinearity of the Fe–C–O groups is small, except for Fe_2–C_3–O_3 with an angle of

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[9] This table has been deposited as Document No. 9875 with the ADI Auxiliary Publications Project Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by an advance remittance ($1.25 for photoprints or $1.25 for 35-mm microfilm) payable to: Chief, Photoduplication Service, Library of Congress.

[10] M. R. Churchill, *Inorg. Chem.*, 6, 190 (1967).

Table II. Final Atomic Positional Coordinates[a]

	x	*y*	*z*
Fe_1	0.0976 (1)	−0.0818 (1)	0.2330 (1)
Fe_2	0.1654 (1)	0.0882 (1)	0.2732 (1)
C_1	0.2022 (11)	0.1918 (6)	0.2695 (6)
C_2	0.0554 (11)	0.1108 (5)	0.3846 (6)
C_3	−0.0304 (11)	0.0589 (5)	0.1905 (6)
C_4	−0.0685 (11)	−0.1374 (5)	0.1419 (6)
C_5	−0.0720 (11)	−0.0692 (5)	0.3172 (6)
C_6	0.4399 (9)	0.0750 (4)	0.2580 (5)
C_7	0.3449 (10)	0.0444 (4)	0.1651 (5)
C_8	0.2643 (9)	−0.0416 (5)	0.1222 (5)
C_9	0.3260 (10)	−0.1139 (5)	0.1319 (6)
C_{10}	0.4625 (10)	−0.1145 (4)	0.2126 (6)
C_{11}	0.3384 (10)	−0.1052 (5)	0.2972 (6)
C_{12}	0.3040 (9)	−0.0270 (5)	0.3498 (5)
C_{13}	0.3970 (9)	0.0537 (5)	0.3455 (5)
C_{14}	0.3909 (11)	0.0920 (5)	0.0884 (6)
C_{15}	0.2782 (12)	−0.1927 (5)	0.0547 (6)
C_{16}	0.2023 (11)	−0.1727 (5)	0.2964 (6)
C_{17}	0.4907 (10)	0.1068 (5)	0.4406 (6)
O_1	0.2217 (9)	0.2598 (4)	0.2648 (6)
O_2	−0.0150 (8)	0.1272 (4)	0.4571 (5)
O_3	−0.1549 (9)	0.0467 (4)	0.1348 (5)
O_4	−0.1801 (8)	−0.1745 (4)	0.0836 (4)
O_5	−0.1858 (8)	−0.0624 (4)	0.3719 (5)
H_6	0.5566	0.1178	0.2624
H_8	0.1429	−0.0574	0.0766
H_{101}	0.5107	−0.1746	0.1957
H_{102}	0.5393	−0.0566	0.2277
H_{12}	0.1987	−0.0292	0.3966
H_{141}	0.4990	0.0654	0.0434
H_{142}	0.4329	0.1568	0.1271
H_{143}	0.2740	0.0891	0.0353
H_{151}	0.1706	−0.1789	0.0165
H_{152}	0.3942	−0.2045	0.0087
H_{153}	0.2424	−0.2445	0.0874
H_{161}	0.2620	−0.2290	0.2657
H_{162}	0.1050	−0.1745	0.3449
H_{171}	0.5816	0.2708	0.4716
H_{172}	0.3920	0.1255	0.4958
H_{173}	0.5686	0.1620	0.4256

[a] Numbers in parentheses are the estimated standard deviations occurring in the last digit listed.

Table III. Intramolecular Distances[a]

Atoms	Distance, Å	Atoms	Distance, Å
Fe_1–Fe_2	2.766 (1)		
Fe_1–C_4	1.758 (8)	Fe_2–C_1	1.750 (10)
Fe_1–C_5	1.757 (8)	Fe_2–C_2	1.782 (8)
		Fe_2–C_3	1.775 (8)
Fe_1–C_6	3.381 (7)	Fe_2–C_6	2.080 (6)
Fe_1–C_7	2.999 (7)	Fe_2–C_7	2.117 (7)
Fe_1–C_8	2.214 (7)	Fe_2–C_8	2.853 (7)
Fe_1–C_9	2.283 (8)	Fe_2–C_9	3.856 (8)
Fe_1–C_{10}	2.828 (8)	Fe_2–C_{10}	4.212 (7)
Fe_1–C_{11}	2.094 (8)	Fe_2–C_{11}	3.727 (8)
Fe_1–C_{12}	2.163 (7)	Fe_2–C_{12}	2.724 (7)
Fe_1–C_{13}	3.078 (7)	Fe_2–C_{13}	2.173 (7)
Fe_1–C_{16}	2.159 (8)		
C_4–O_4	1.157 (10)	C_1–O_1	1.158 (12)
C_5–O_5	1.161 (10)	C_2–O_2	1.158 (11)
		C_3–O_3	1.158 (11)
C_3–C_4	3.192 (10)	O_3–O_4	3.606 (10)
C_2–C_5	2.980 (10)	O_2–O_5	3.218 (10)
C_6–C_7	1.420 (10)	C_{12}–C_{13}	1.468 (10)
C_7–C_8	1.474 (10)	C_{13}–C_6	1.409 (10)
C_8–C_9	1.386 (11)	C_7–C_{14}	1.525 (11)
C_9–C_{10}	1.502 (11)	C_9–C_{15}	1.501 (11)
C_{10}–C_{11}	1.525 (11)	C_{11}–C_{16}	1.424 (11)
C_{11}–C_{12}	1.407 (11)	C_{13}–C_{17}	1.519 (10)

[a] See footnote *a*, Table II.

Table IV. Bond Angles[a]

Atoms	Angle, deg	Atoms	Angle, deg
Fe_1–C_4–O_4	178.4 (0.7)	Fe_2–C_1–O_1	177.7 (0.8)
Fe_1–C_5–O_5	178.6 (0.7)	Fe_2–C_2–O_2	178.6 (0.8)
		Fe_2–C_3–O_3	173.9 (0.7)
C_4–Fe_1–C_5	89.6 (0.4)	C_1–Fe_2–C_2	92.9 (0.4)
		C_2–Fe_2–C_3	99.2 (0.4)
		C_3–Fe_2–C_1	97.7 (0.4)
C_6–C_7–C_8	126.1 (0.6)	C_6–C_7–C_{14}	116.8 (0.6)
C_7–C_8–C_9	129.0 (0.6)	C_8–C_7–C_{14}	112.7 (0.6)
C_8–C_9–C_{10}	121.6 (0.7)	C_8–C_9–C_{15}	121.0 (0.7)
C_9–C_{10}–C_{11}	99.5 (0.6)	C_{10}–C_9–C_{15}	116.9 (0.7)
C_{10}–C_{11}–C_{12}	121.1 (0.7)	C_{10}–C_{11}–C_{16}	117.4 (0.7)
C_{11}–C_{12}–C_{13}	127.8 (0.6)	C_{12}–C_{11}–C_{16}	116.6 (0.7)
C_{12}–C_{13}–C_6	123.6 (0.6)	C_{12}–C_{13}–C_{17}	115.8 (0.6)
C_{13}–C_6–C_7	127.6 (0.6)	C_6–C_{13}–C_{17}	118.8 (0.6)

[a] See footnote *a*, Table II.

Table V. Selected Intermolecular Contacts

Atom I	Atom J	Vector from molecule containing I to molecule containing J	Distance, Å
C_{15}	C_2	$(x, {}^1/_2 + y, {}^1/_2 + z)$	3.755
C_{16}	C_4	$(-x, -{}^1/_2 - y, {}^1/_2 - z)$	3.561
C_{15}	C_{14}	$(1 - x, -y, -z)$	3.744
C_{17}	C_{15}	$(x, {}^1/_2 + y, {}^1/_2 + z)$	3.913
C_{16}	C_{16}	$(-x, -{}^1/_2 - y, {}^1/_2 - z)$	3.705
C_1	O_1	$(-x, {}^1/_2 - y, {}^1/_2 - z)$	3.379
C_{15}	O_2	$(-x\ -{}^1/_2 + y, {}^1/_2 - z)$	3.473
C_{14}	O_4	$(-x, -y, -z)$	3.494
C_{16}	O_4	$(-x, -{}^1/_2 - y, {}^1/_2 - z)$	3.408

174°. Slight nonlinearity is both common in other metal carbonyls and to be expected on theoretical grounds when linearity is not demanded by molecular symmetry.[11] From an estimate of the Fe single bond radius of 1.35 Å in $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_5H_5)$,[12] it has been calculated that a single bond from low-valent iron to sp-hybridized carbon should be 2.05 Å. The observed value of 1.760 Å thus shows considerable π character in the Fe–C bond, being comparable to formally zerovalent iron complexes such as $Fe(CO)_5$ in which the average Fe–C bond length[13] is 1.81 Å.

The 1,3,5-trimethyl-7-methylene-1,3,5-cyclooctatriene has an irregular structure. Within the molecular framework of the coordinated olefin, we can define four planar sections formed by $C_{13}C_6C_7$, $C_7C_8C_{12}C_{13}$, $C_8C_9C_{11}C_{12}$, and $C_9C_{10}C_{11}$, the dihedral angles between the respective planes being, in the order listed, 151, 138, and 118°. Both carbon atoms C_6 and C_{10} are bent away from the iron atoms; the angle between the two planes containing these carbon atoms is 47°. The C–C bond lengths in the ring show quite a range, reflecting the bonding between differently hybridized carbon atoms. The average distance between ring and methyl carbon atoms, 1.515 ± 0.011 Å, agrees well with the standard single bond between sp^2- and sp^3-hybridized atoms of 1.51 Å. It is also gratifying to see that the distances between C_{10}, which has become an sp^3-hybridized atom due to the hydrogen transfer, and its

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[11] S. F. A. Kettle, *J. Chem. Soc.*, 1661 (1965).

[12] M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Am. Chem. Soc.*, **88**, 4371 (1966).

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Table VI. Anisotropic Temperature Factors ($\times 10^4$)[a]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Equivalent[b] isotropic *B*
Fe_1	119 (3)	28 (1)	39 (1)	2 (1)	10 (1)	11 (1)	2.799
Fe_2	124 (3)	28 (1)	39 (1)	11 (1)	9 (1)	7 (1)	2.837
C_1	185 (20)	39 (5)	67 (6)	19 (7)	17 (8)	9 (4)	4.395
C_2	145 (18)	44 (4)	48 (6)	6 (7)	2 (8)	3 (4)	3.905
C_3	161 (19)	35 (4)	48 (6)	17 (7)	7 (8)	10 (4)	3.561
C_4	153 (18)	37 (4)	49 (5)	8 (7)	11 (8)	21 (4)	3.481
C_5	144 (18)	39 (4)	34 (5)	−7 (6)	−2 (8)	8 (3)	3.325
C_6	93 (15)	23 (3)	54 (6)	3 (5)	25 (7)	9 (3)	2.847
C_7	133 (16)	25 (4)	35 (5)	7 (6)	14 (7)	7 (3)	2.700
C_8	124 (16)	37 (4)	31 (4)	4 (6)	14 (6)	7 (3)	2.980
C_9	162 (18)	28 (4)	53 (6)	13 (7)	39 (8)	11 (4)	3.438
C_{10}	168 (18)	28 (4)	64 (6)	21 (6)	12 (8)	10 (4)	3.758
C_{11}	153 (18)	42 (5)	56 (6)	18 (7)	1 (8)	28 (4)	3.706
C_{12}	106 (15)	31 (4)	40 (5)	20 (6)	−4 (7)	8 (3)	2.832
C_{13}	115 (16)	30 (4)	35 (5)	11 (6)	1 (7)	1 (3)	2.860
C_{14}	278 (22)	33 (4)	52 (5)	−3 (7)	32 (9)	21 (4)	4.347
C_{15}	245 (22)	35 (4)	61 (6)	8 (7)	35 (9)	1 (4)	4.671
C_{16}	193 (20)	42 (4)	69 (6)	24 (7)	17 (8)	34 (4)	4.220
C_{17}	150 (17)	46 (4)	46 (5)	−6 (7)	−13 (7)	1 (4)	4.114
O_1	318 (19)	31 (3)	150 (7)	12 (6)	28 (9)	21 (4)	7.136
O_2	252 (16)	75 (4)	62 (4)	15 (6)	46 (7)	0 (3)	6.262
O_3	237 (16)	55 (3)	77 (5)	21 (6)	−53 (7)	7 (3)	5.736
O_4	224 (14)	50 (3)	61 (4)	−17 (5)	−36 (6)	15 (3)	5.032
O_5	189 (14)	89 (4)	61 (4)	5 (6)	47 (7)	26 (3)	5.897

[a] Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^3 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Numbers in parentheses are esd's occurring in the last digit listed. [b] The equivalent isotropic *B*'s were calculated by the program VIBELL.

Table VII. Root-Mean-Square Amplitudes of Vibrations (Å)

Atom	Minor axis	Medium axis	Major axis
Fe_1	0.169	0.194	0.201
Fe_2	0.177	0.194	0.196
C_1	0.210	0.235	0.260
C_2	0.197	0.209	0.257
C_3	0.200	0.215	0.221
C_4	0.178	0.206	0.241
C_5	0.176	0.191	0.243
C_6	0.142	0.179	0.236
C_7	0.171	0.182	0.201
C_8	0.159	0.190	0.227
C_9	0.171	0.193	0.253
C_{10}	0.179	0.221	0.249
C_{11}	0.167	0.210	0.262
C_{12}	0.151	0.196	0.215
C_{13}	0.172	0.174	0.221
C_{14}	0.160	0.239	0.287
C_{15}	0.198	0.232	0.290
C_{16}	0.168	0.225	0.285
C_{17}	0.175	0.229	0.271
O_1	0.200	0.292	0.381
O_2	0.202	0.278	0.346
O_3	0.195	0.266	0.330
O_4	0.195	0.248	0.303
O_5	0.172	0.271	0.347

Table VIII. Best Weighted Least-Squares Planes[a]

Atoms	Plane	*L*	*M*	*N*	*D*
$C_{13}C_6C_7$	1	−0.5864	0.7819	0.2115	5.9640
$C_7C_8C_{12}C_{13}$	2	−0.9008	0.4157	0.1253	2.1003
$C_8C_9C_{11}C_{12}$	3	0.9590	0.2806	0.0402	3.1981
$C_9C_{10}C_{11}$	4	0.1967	0.9624	0.1873	5.8981

[a] The equations are of the form $LX + MY + NZ = D$; they are expressed in orthogonal coordinates. The matrix to transform triclinic to orthogonal coordinates is

$$\begin{bmatrix} 7.3423 & -0.8729 & 0.0 \\ 0.0 & 16.8720 & 0.0 \\ -0.8982 & -3.4245 & 13.7361 \end{bmatrix}$$

neighbors, which are sp^2 hybridized, are 1.502 and 1.525 Å (average 1.514 ± 0.011 Å), in agreement with the accepted value. An interesting feature of this part of the molecule is the small angle formed by $C_9C_{10}C_{11}$, *viz.*, 99.5°. Though unusual, this is not the first case where such a contraction of an sp^3-hybridized carbon angle from its tetrahedral value has been observed. For instance, in π-cyclopentadienyl-1-phenylcyclopentadienecobalt, Churchill and Mason[14] observed a value of 93.9° for the angle subtended at the free carbon atom. A similar observation was made by Gerloch and Mason[15] for an sp^2-hybridized carbon atom in tetrakis(trifluoromethyl)cyclopentadienone-π-cyclopentadienylcobalt where the angle was 100.1°. In both of these cases the same carbon atom is tipped away from the metal. Although the circumstances here are not identical, it is felt that the comparison is a valid one and that the observed small angle is not unreasonable.

The distances within the two bonded π-allylic fragments are as expected in comparison with other π-allyl complexes. The carbon–carbon distances (1.420, 1.409 ± 0.010 Å; and 1.424, 1.407 ± 0.011 Å) and the values of 127.6 and 116.6° for the apical angles are similar to these found in other organoiron complexes (see Table IX) and are within the expected range from studies on other π-allyl-metal systems.[16,17] The two sets of iron–carbon distances are 2.159, 2.094, 2.163 Å and 2.117, 2.080, 2.173 Å with the central carbon atom being closest to the iron atom. Similar variations in Fe–C bond lengths have been observed before by Churchill,[10] Fleischer, *et al.*,[18] and also by King[19] in

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(16) A. E. Smith, *Acta Cryst.*, **18**, 331 (1965): [π-$C_3H_5PdCl]_2$.

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Table IX. Some Distances and Angles in Comparable Iron Compounds

Atoms	Compound	Distance, A	Angle, deg	Ref
Fe–Fe	(1) $C_8H_8Fe_2(CO)_5$	2.742		18
	(2) $TMCOTFe_2(CO)_5$	2.724		*a*
	(3) $C_{10}H_8Fe_2(CO)_5$	2.782		10
Fe–C(allyl)	(1)	2.136, 2.113, 2.123		18
	(2)	2.115, 2.116, 2.109		*a*
		2.107, 2.065, 2.130		
	(3)	2.200, 2.050, 2.142		10
C–C(allyl)	(1)	1.398, 1.410		18
	(2)	1.399, 1.356		*a*
		1.372, 1.345		
	(3)	1.432, 1.391		10
Angle C–C–C(allyl)	(2)		126.2, 127.7	*a*
	(3)		122.8	10

[a] F. A. Cotton and M. D. LaPrade, *J. Am. Chem. Soc.*, **90**, 2026 (1968).

$Fe_2(CO)_6(C_6H_5C_2H)_3$. Although the differences, keeping in mind that the mean esd for an Fe–C distance is 0.007 Å, appear to be significant, it should be remembered that in $[\pi\text{-}C_3H_5PdCl]_2$ similar variations seemed to occur[20] but were not substantiated by a low-temperature crystallographic study.[16]

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Structure and Photodecomposition Studies of the Complex Acid, Hydrogen Aqueoethylenediaminetetraacetatoferrate(III), and Several of Its Metal(I) Salts

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Abstract: The alkali metal, ammonium, and tetramethylammonium salts of the aquoethylenediaminetetraacetatoferrate(III) anion, $Fe(OH_2)Y^-$, were prepared and characterized by elemental analyses, thermogravimetric analyses, and infrared spectroscopy. All were found to be less photosensitive to ultraviolet radiation in the 250 to 400 mμ region than the parent complex acid, $HFe(OH_2)Y$. Photosensitivity was measured as the rate of evolution of carbon dioxide and was found to increase generally with decrease in surface charge density (increase in ionic radius) of the companion cation. The influence of the companion cation is upon the Fe–O bonds between the iron and the ligand, and probably is due to its interaction with the oxygen atoms of the coordinated carboxylate groups.

Hoard, *et al.*,[2] have found from X-ray diffraction studies that the aquoethylenediaminetetraacetatoferrate(III) anion in both $LiFe(OH_2)Y \cdot 2H_2O$ and $RbFe(OH_2)Y \cdot H_2O$ is sexadentate and seven-coordinate, with an irregular pentagonal bipyramidal structure. Lambert, Godsey, and Seitz[3] found the diprotic complex acid, $HFe(OH_2)Y$, to be six-coordinate. A free carboxylic acid group of the ligand and the coordinated water molecule are the proton-donating groups. X-Ray studies by Hoard, Kennard, and Smith[4] substanti-

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