on the thermal decomposition of C_3O_2. Use of their 2.5-eV value for the heat of formation of C_2O leads to the following: reaction 6 is 2.3 eV exothermic, the minimum excitation (E) in C_2O is 4.4 eV, and the minimum energy (E_0) required to decompose C_2O is 3.8 eV. If this 4.4 eV is present as vibrational energy in C_2O, the lifetime τ of this excited species would be 4×10^{-11} sec. While this is four times longer than the lifetime derived above, it is still 50 to 2500 times shorter than the time between collisions under the conditions of these experiments. Thus, this does not alter the tentative conclusion that vibrationally excited C_2O, if formed in this system, would not live long enough to experience collisions with other molecules. Again, the possibility of the formation of electronically excited C_2O (4.4 eV in this case) must be recognized, as well as the fact that this energy now greatly exceeds that expected[15] for the $^1\Delta$ and $^1\Sigma$ states.

We therefore conclude that the presently available results on the formation and collisional deactivation of excited ethylene formed in this system are best explained by the reactions of free carbon atoms or electronically excited C_2O and not by vibrationally excited C_2O.

The Crystal and Molecular Structure of (1,3,5-Cyclooctatriene)diiron Hexacarbonyl[1,2]

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Abstract: The crystal and molecular structures of the compound $(C_8H_{10})Fe_2(CO)_6$ obtained by reaction of cycloocta-1,3,5-triene with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ have been determined by three-dimensional X-ray crystallographic techniques. The intensities of 1898 independent reflections were collected on a counter-diffractometer, and the structure was solved by Patterson and Fourier methods. Full-matrix, least-squares refinement was carried out using 1206 statistically significant reflections and employing anisotropic thermal parameters to give a final unweighted discrepancy index of 0.067. The compound crystallizes in space group $P2_1/c$. Unit cell dimensions are $a = 13.39 \pm 0.01$ Å, $b = 7.684 \pm 0.004$ Å, $c = 14.31 \pm 0.01$ Å, $\beta = 92.83 \pm 0.04°$; density: ρ(obsd), 1.75 ± 0.01 g cm^{-1}; ρ(calcd), assuming $Z = 4$, 1.75 g cm^{-1}. The molecular structure is quite similar to that of $(C_8H_8)Ru_2(CO)_6$, which we recently reported, and permits us to give the compound the systematic name *cis*-(1,2,6-*trihapto*:3,4,5-*trihapto*cycloocta-1,3,5-triene)hexacarbonyldiiron. The molecule does not have a plane of symmetry and the metal atoms are not structurally equivalent, one $Fe(CO)_3$ group being bound to three carbon atoms (3, 4, 5) forming an allyl group while the other is bound to one carbon atom (6) by a two-center bond and to the olefinic group formed by two others (1, 2). The two $Fe(CO)_3$ groups lie on the same side of the ring and are united by an Fe–Fe bond.

It has been shown that from the reaction of 1,3,5-cyclooctatriene, C_8H_{10}, with either $Fe_3(CO)_{12}$[4] or $Fe_2(CO)_9$,[5] the red-orange, air-stable, crystalline compound $C_8H_{10}Fe_2(CO)_6$ can be isolated. King,[4] who first isolated the compound, proposed structure I for it. This structure, which has a mirror plane containing the iron atoms, is consistent with the infrared and proton nmr spectra which King also reported, and is, on the whole, a reasonable structure. It could not, however, be said to have been *proved* correct by the spectroscopic and chemical data cited by King.

A little later the same compound was prepared by Emerson, *et al.*,[5] who measured the Mössbauer spectrum. They concluded from the appearance of this spectrum that "the two iron atoms are chemically equivalent" in this complex. If this is true, then structure I is clearly not admissible. As an alternative, these workers proposed structure II, also having a mirror plane, now perpendicular to the Fe–Fe line. Structure II is also consistent with the nmr and infrared data and contains chemically equivalent iron atoms.

A little later, Keller, Emerson, and Pettit[6] prepared a cyclooctatetraene complex, $(C_8H_8)Fe_2(CO)_6$, which has a proton nmr spectrum extremely similar to that of $(C_8H_{10})Fe_2(CO)_6$ and also has a Mössbauer spectrum which these authors considered to indicate "both iron nuclei to be chemically equivalent." It was natural, then, for them to propose structure III for the $(C_8H_8)Fe_2(CO)_6$ molecule. Certainly III, like II, is a reasonable structure and does not, at face value, seem unlikely.

Nevertheless, we have been led to doubt that structures II and III are correct by our studies of ruthenium carbonyl derivatives of cyclooctatetraene.[7,8] The compound $(C_8H_8)Ru_2(CO)_6$, with an nmr spectrum virtually

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[1] Research supported by the National Science Foundation under Grant No. GP7034X.

[2] A systematic name (*cf.* F. A. Cotton, *J. Am. Chem. Soc.*, 90, 6230 (1968)) for this compound is *cis*-(1,2,6-*trihapto*:3,4,5-*trihapto*cycloocta-1,3,5-triene)hexacarbonyldiiron.

[3] National Institutes of Health Predoctoral Fellow, 1966–1968.

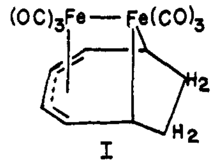
[4] R. B. King, *Inorg. Chem.*, 2, 807 (1963).

[5] G. E. Emerson, J. E. Mahler, R. Pettit, and R. Collins, *J. Am. Chem. Soc.*, **86**, 3590 (1964).

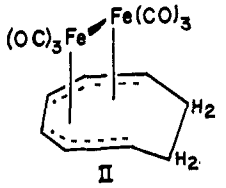
[6] C. E. Keller, G. F. Emerson, and R. Pettit, *ibid.*, **87**, 1388 (1965).

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

[8] F. A. Cotton and W. T. Edwards, *ibid.*, 90, 5412 (1968).



I



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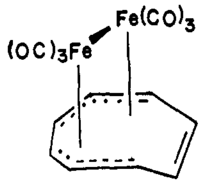
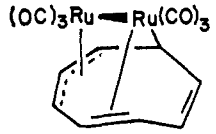


III



IV

identical with that of Keller, Emerson, and Pettit's $(C_8H_8)Fe_2(CO)_6$ compound mentioned above, was prepared[7] and the molecular structure in the crystal determined.[8] The structure is indicated schematically by IV, which is, clearly, very different from III, but grossly similar to I. This result suggested that structure III may not be the correct one for the iron compound, $(C_8H_8)Fe_2(CO)_6$. Since it is not impossible that $(C_8H_8)Fe_2(CO)_6$ and $(C_8H_8)Ru_2(CO)_6$ *could* have different structures, we have reversed final judgment; however, the great similarity of the nmr spectra does weigh strongly in favor of similarity of structure.

We now wish to report the structure of one of the diiron compounds, namely, $(C_8H_{10})Fe_2(CO)_6$. A sample of this compound from the original preparation was kindly provided by Professor R. B. King. Since this is the exact compound for which Mössbauer data were first adduced to support structure II, we feel that the results here should be crucial in determining whether structures of the type represented by II and III are actually important. Because of the similarity of nmr spectra of $(C_8H_8)Fe_2(CO)_6$ and $(C_8H_{10})Fe_2(CO)_6$, we did not anticipate finding structure II. With that in mind, we were then keenly interested in whether $(C_8H_{10})Fe_2(CO)_6$ would have structure I, with a plane of symmetry, or a structure analogous to IV which lacks a plane of symmetry.

Procedure

Experimental. The compound was obtained from Professor R. B. King. Crystals suitable for X-ray diffraction work were obtained from the sample. The red-orange plates were found to decompose if exposed to air during irradiation. The crystal selected for intensity measurements was therefore coated with shellac.

Weissenberg and precession photography showed the crystals to be monoclinic. The systematic absences, $0k0$ for $k = 2n + 1$ observed on the $hk0$ net, and $h0l$ for $l = 2n + 1$ observed on the $h0l$ and $h1l$ nets, uniquely determine the space group as $P2_1/c$ (no. 14). The unit cell dimensions are $a = 13.39 \pm 0.01$, $b = 7.684 \pm 0.004$, and $c = 14.31 \pm 0.01$ Å with $\beta = 92.70 \pm 0.04°$ at 23°. The method used to determine a, b, and c employing cobalt radiation ($\lambda K\alpha_1 = 1.7889$, $\lambda K\alpha_2 = 1.7928$) has been described elsewhere.[9] The crystal used for intensity measurements was mounted along its b axis which allowed β to be measured on the φ circle of the diffractometer.

The observed density of 1.75 ± 0.01 g cm^{-3}, measured by flotation in aqueous zinc bromide solution, agrees well with the calculated density of 1.749 g cm^{-3} for a molecular weight of 385.93 and a unit cell volume of 1465 Å^3 with $Z = 4$.

Intensity data were collected on a G. E. XRD-5 manual diffractometer using a crystal of dimensions 0.30 mm × 0.15 mm × 0.073 mm. The intensities of 1898 independent reflections (including space group forbidden reflections in the two nonequivalent sets hkl, $\bar{h}kl$) within a sphere bounded by $\theta = 69°$ were measured using Co $K\alpha$ radiation filtered through iron oxide film. The integrated intensities were measured using a scintillation counter with the pulse height discriminator set to accept 95% of the Co $K\alpha$ radiation and the counter window centered on the Co $K\alpha$ peak. Peak counts (P) were taken using a $\theta/2\theta$ scan of 2.66° at a scan rate of 4°/min with stationary background counts (B_1 and B_2) of 20 sec each at $2\theta_{\text{calcd}} \pm 1.33°$. Intensities ($I$) were taken as $I = P - B_1 - B_2$. Periodic checks of five standard reflections showed a maximum variation of ~3% which was random with time showing no evidence of crystal decomposition. A variation of ~15% was observed in a φ scan of the 040 reflection. Appropriate absorption corrections were therefore made ($\mu = 39.6$ cm^{-1}); transmission factors were in the range 0.56–0.75.

The data were tested for statistical reliability and 692 were rejected as unreliable using the two criteria $I \leq 0$ and $I < 3(P + B_1 + B_2)^{1/2}$. The remaining 1206 reflections were corrected for Lorentz and polarization effects, and a set of $|F_o|$ was calculated.

Solution and Refinement of the Structure. The positions of the two iron atoms were found by solution of a three-dimensional Patterson map. Using the signs supplied by these two atoms ($R_1 = \Sigma(|F_o| - |F_c|)/\Sigma F_o = 0.44$), a three-dimensional electron density map was calculated in which all other atoms (except hydrogen atoms) could be identified.

Refinement[10,11] of all nonhydrogen atoms in the asymmetric unit was then carried to convergence. The various stages are summarized in Table I. In the final cycle of refinement there was no parameter shift greater than 0.2 of one esd, and a final difference Fourier map showed no peak greater than 0.6 e/Å^3. A table of the final F_c's and the $|F_o|$'s has been deposited with the ASIS National Auxiliary Publications Service.[12]

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(9) M. J. Bennett, F. A. Cotton, and J. Takats, *J. Am. Chem. Soc.*, 90, 903 (1968).

(10) "International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham, England, 1965: (a) atomic scattering factors for Fe^0, C^0, O^0 from J. A. Ibers, Vol. 3, Table 3.31, p 202; (b) anomalous dispersion corrections ($\Delta f' = -1.1$ e, $\Delta f'' = +3.3$) for Fe from C. H. Dauben and D. Templeton, Vol. 3, Table 3.32, p 213.

(11) The following computer programs were used in this investigation: MIXG2A, by D. P. Shoemaker (1962), generates diffractometer settings; PMMO, by M. J. Bennett, a general data reduction routine; GONO9A, by W. C. Hamilton, an absorption and extinction correction program; SFLS5, by C. T. Prewitt (improved by M. J. Bennett, B. M. Foxman, and L. N. Becka), a full-matrix crystallographic least-squares program with rigid body option; FORDAP II, a modified (B. M. Foxman) version of A. Zalkin's general Fourier program; MGEOM, by J. S. Wood, a molecular geometry program; DISTAN, by D. P. Shoemaker, an intermolecular distance and dihedral angle program; and PUBTAB, by R. C. Elder, a routine for preparing publishable structure factor tables.

(12) For this table, order NAPS Document No. NAPS-00223 from ASIS, National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001, remitting \$1.00 for microfiche or \$3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

Results

A view of the molecule which also shows the numbering scheme is given in Figure 1. As the entire molecule constitutes the asymmetric unit, no crystallographic symmetry is imposed upon it. Final atomic positional parameters are presented in Table II. Molecular dimensions are listed in Tables III and IV, and the anisotropic thermal parameters (β's) together with the equivalent values of the isotropic thermal parameters (B's) are collected in Table V. Shortest intermolecular distances are reported in Table VI.

Discussion

The structure of the $(C_8H_{10})Fe_2(CO)_6$ molecule is essentially the same as that of the $(C_8H_8)Ru_2(CO)_6$ molecule in the solid state.[8] Again, the $M_2(CO)_6$ moiety has a "sawhorse" structure, an approximately linear OCFeFeCO sequence constituting the beam and four

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

	Conditions	R_1	R_2[b]
1.	Fe atoms only; positional and isotropic temperature factors varied	0.443	0.560
2.	Positional and isotropic temperature factors varied for all atoms (except H); four cycles	0.098	0.130
3.	Positional and anisotropic thermal parameters varied for all atoms; two cycles	0.072	0.106
4.	Final cycle; reflections apparently suffering from extinction removed[c]	0.067	0.086

[a] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. Hydrogen atoms were neglected throughout. [b] $R_2 = (\Sigma w||F_o| - |F_c||)/\Sigma w|F_o|$. σ, the standard deviation of corrected intensities (*cf.* R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967)), is defined as $\sigma(I) = (\Delta I^2 + PI^2)^{1/2}$, where P, the uncertainty factor, was assigned a value of 0.002. The weighting scheme used was $w = 1/\sigma^2$, $\sigma = \sigma(F^2)/2F_o$, where $\sigma(F^2)$ is the Lorentz and polarization corrected $\sigma(I)$. [c] Those removed, with the value of $(|F_o| - |F_c|)/\sigma$ at convergence in stage 3 given in parentheses, were: 002 (−20.7), 102 (−18.5), 202 (−20.9).

Table II. Final Atomic Positional Parameters[a]

Atom	x	y	z
Fe(1)	0.2988 (1)	0.1208 (2)	0.3048 (1)
Fe(2)	0.1734 (1)	−0.0896 (3)	0.4035 (1)
C(1)	0.2007 (7)	−0.2447 (16)	0.3140 (9)
C(2)	0.0557 (10)	−0.0059 (16)	0.3575 (9)
C(3)	0.1153 (8)	−0.2499 (18)	0.4747 (8)
C(4)	0.3498 (8)	−0.0302 (15)	0.2220 (7)
C(5)	0.1858 (8)	0.1474 (14)	0.2347 (7)
C(6)	0.3626 (8)	0.3058 (16)	0.2605 (7)
C(7)	0.4251 (7)	0.1322 (14)	0.4067 (7)
C(8)	0.3821 (7)	−0.0347 (14)	0.4136 (6)
C(9)	0.3118 (8)	−0.0911 (14)	0.4824 (7)
C(10)	0.2402 (8)	0.0151 (15)	0.5235 (7)
C(11)	0.1906 (7)	0.1582 (14)	0.4755 (6)
C(12)	0.2359 (7)	0.2725 (13)	0.4075 (6)
C(13)	0.3202 (8)	0.3843 (13)	0.4548 (7)
C(14)	0.4113 (7)	0.2738 (14)	0.4818 (7)
O(1)	0.2169 (7)	−0.3468 (11)	0.2598 (6)
O(2)	−0.0214 (6)	0.0437 (14)	0.3334 (8)
O(3)	0.0806 (7)	−0.3536 (13)	0.5167 (7)
O(4)	0.3808 (7)	−0.1165 (12)	0.1677 (6)
O(5)	0.1178 (7)	0.1780 (13)	0.1864 (6)
O(6)	0.4016 (7)	0.4177 (11)	0.2263 (6)

[a] Figures in parentheses are standard deviations occurring in the last significant figure given.

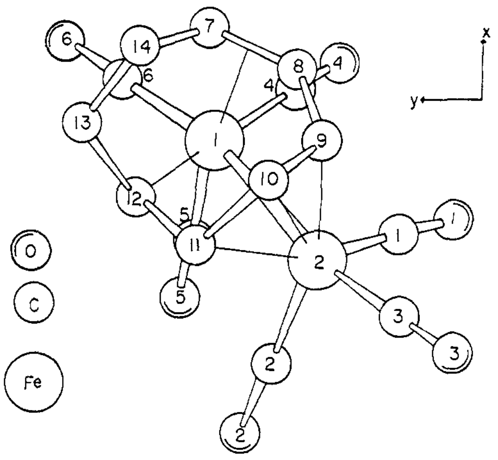


Figure 1. The $C_8H_{10}Fe_2(CO)_6$ molecule viewed down the crystallographic c^* axis.

Table III. Intramolecular Distances, Ångströms[a]

Atoms	Distance	Atoms	Distance
Fe(1)–Fe(2)	2.764 (3)	C(1)–O(1)	1.14 (2)
Fe(2)–C(1)	1.80 (1.6)	C(2)–O(2)	1.13 (2)
Fe(2)–C(2)	1.83 (1.6)	C(3)–O(3)	1.11 (2)
Fe(2)–C(3)	1.79 (1.6)	C(4)–O(4)	1.11 (1.8)
Fe(1)–C(4)	1.83 (1.4)	C(5)–O(5)	1.14 (1.8)
Fe(1)–C(5)	1.82 (1.4)	C(6)–O(6)	1.14 (1.8)
Fe(1)–C(6)	1.78 (1.5)	C(7)–C(8)	1.40 (1.8)
Fe(1)–C(7)	2.18 (1.3)	C(8)–C(9)	1.45 (1.7)
Fe(1)–C(8)	2.22 (1.2)	C(9)–C(10)	1.41 (1.9)
Fe(1)–C(9)	3.01 (1.3)	C(10)–C(11)	1.42 (1.9)
Fe(1)–C(10)	3.36 (1.3)	C(11)–C(12)	1.47 (1.7)
Fe(1)–C(11)	2.91 (1.2)	C(12)–C(13)	1.54 (1.8)
Fe(1)–C(12)	2.08 (1.2)	C(13)–C(14)	1.52 (1.9)
Fe(1)–C(13)	2.97 (1.3)	C(14)–C(7)	1.55 (1.8)
Fe(1)–C(14)	3.12 (1.3)		
Fe(2)–C(7)	3.76 (1.3)		
Fe(2)–C(8)	2.82 (1.3)		
Fe(2)–C(9)	2.12 (1.3)		
Fe(2)–C(10)	2.06 (1.3)		
Fe(2)–C(11)	2.17 (1.3)		
Fe(2)–C(12)	2.91 (1.3)		
Fe(2)–C(13)	4.20 (1.3)		
Fe(2)–C(14)	4.34 (1.4)		

[a] Figures in parentheses are standard deviations occurring in the last significant figure given.

Table IV. Bond Angles, Degrees[a]

Atoms	Angle	Atoms	Angle
Fe(1)–C(4)–O(4)	176.1 (1.3)	Fe(1)–Fe(2)–C(1)	83.2 (0.4)
Fe(1)–C(5)–O(5)	173.8 (1.3)	Fe(1)–Fe(2)–C(2)	98.3 (0.5)
Fe(1)–C(6)–O(6)	174.4 (1.3)	Fe(1)–Fe(2)–C(3)	167.9 (0.5)
Fe(2)–C(1)–O(1)	178.6 (1.4)	Fe(2)–Fe(1)–C(4)	102.5 (0.4)
Fe(2)–C(2)–O(2)	175.5 (1.5)	Fe(2)–Fe(1)–C(5)	80.5 (0.4)
Fe(2)–C(3)–O(3)	177.2 (1.5)	Fe(2)–Fe(1)–C(6)	162.7 (0.5)
C(4)–Fe(1)–C(5)	92.8 (0.6)	C(7)–Fe(1)–C(8)	37.1 (0.4)
C(4)–Fe(1)–C(6)	94.7 (0.6)	C(9)–Fe(2)–C(10)	27.3 (0.4)
C(5)–Fe(1)–C(6)	97.0 (0.6)	C(10)–Fe(2)–C(11)	24.7 (0.3)
C(1)–Fe(2)–C(2)	99.9 (0.7)	Fe(1)–C(12)–C(13)	109.1 (1.0)
C(1)–Fe(2)–C(3)	93.0 (0.7)	Fe(1)–C(12)–C(11)	108.8 (1.0)
C(2)–Fe(2)–C(3)	93.7 (0.7)		
C(7)–C(8)–C(9)	126.3 (1.1)		
C(8)–C(9)–C(10)	126.2 (1.2)		
C(9)–C(10)–C(11)	123.2 (1.2)		
C(10)–C(11)–C(12)	125.7 (1.1)		
C(11)–C(12)–C(13)	110.9 (1.1)		
C(12)–C(13)–C(14)	110.1 (1.1)		
C(13)–C(14)–C(7)	109.9 (1.0)		
C(14)–C(7)–C(8)	122.0 (1.1)		

[a] Figures in parentheses are standard deviations occurring in the last significant figure given.

Table V. Components of Anisotropic Thermal Tensor[a] (×10^4) and Equivalent B[b]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B
Fe(1)	59 (1)	166 (4)	43 (1)	12 (2)	8 (1)	34 (1)	3.88
Fe(2)	57 (1)	179 (4)	63 (1)	−7 (2)	6 (1)	2 (2)	4.49
C(1)	33 (7)	166 (26)	59 (8)	−7 (11)	−16 (6)	9 (12)	3.77
C(2)	48 (9)	175 (27)	71 (8)	−20 (13)	13 (7)	−17 (12)	4.45
C(3)	53 (8)	190 (30)	69 (8)	−45 (13)	14 (7)	14 (12)	4.63
C(4)	49 (7)	177 (25)	25 (5)	16 (11)	−3 (5)	−13 (10)	3.29
C(5)	50 (8)	160 (23)	32 (6)	3 (11)	0 (6)	−9 (10)	3.52
C(6)	53 (8)	174 (25)	39 (6)	20 (12)	9 (6)	14 (11)	3.69
C(7)	38 (6)	111 (22)	37 (5)	0 (10)	0 (5)	10 (9)	2.84
C (8)	39 (6)	145 (22)	18 (5)	3 (9)	−15 (4)	−5 (8)	2.63
C(9)	41 (7)	92 (20)	48 (6)	−17 (9)	1 (5)	5 (9)	3.03
C(10)	48 (7)	170 (25)	43 (6)	−27 (11)	16 (5)	−15 (10)	3.65
C(11)	41 (6)	135 (23)	33 (5)	−3 (10)	10 (4)	−20 (9)	2.95
C(12)	41 (6)	105 (20)	26 (5)	1 (9)	1 (5)	−13 (8)	2.54
C(13)	68 (8)	79 (20)	47 (6)	3 (10)	4 (6)	−16 (10)	3.56
C(14)	48 (7)	121 (22)	39 (5)	2 (10)	−5 (5)	−9 (9)	3.20
O(1)	102 (8)	169 (19)	67 (6)	7 (10)	−5 (5)	−48 (9)	5.65
O(2)	36 (6)	334 (28)	143 (10)	19 (10)	0 (5)	−10 (13)	7.44
O(3)	101 (8)	263 (25)	115 (8)	−57 (12)	32 (7)	53 (12)	7.56
O(4)	100 (8)	308 (25)	46 (5)	66 (11)	3 (5)	−54 (9)	6.10
O(5)	73 (6)	327 (26)	59 (5)	26 (11)	−11 (5)	35 (10)	6.01
O(6)	85 (7)	222 (21)	61 (5)	−26 (10)	20 (5)	40 (9)	5.44

[a] These are the β_{ij}'s in the expression $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Standard deviations in parentheses are in the last significant figure listed.

Table VI. Selected Intermolecular Contacts, Ångströms

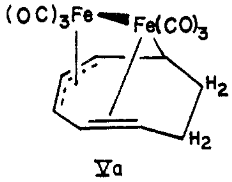
Atom I	Atom J	Vector from molecule containing I to molecule containing J	Contact
O(5)	C(2)	$\bar{x}, {}^1/_2 + y, {}^1/_2 - z$	3.38
O(2)	C(3)	$\bar{x}, \bar{y}, \bar{z}$	3.45
O(6)	C(4)	$\bar{x}, {}^1/_2 + y, {}^1/_2 - z$	3.37
O(4)	C(7)	$\bar{x}, {}^1/_2 + y, {}^1/_2 - z$	3.45
O(6)	C(7)	$\bar{x}, {}^1/_2 + y, {}^1/_2 - z$	3.48
O(5)	C(11)	$x, {}^1/_2 - y, {}^1/_2 + z$	3.43
O(2)	O(1)	$\bar{x}, {}^1/_2 + y, {}^1/_2 - z$	2.97
O(5)	O(2)	$\bar{x}, {}^1/_2 + y, {}^1/_2 - z$	3.45
O(3)	O(2)	$\bar{x}, \bar{y}, \bar{z}$	3.32
O(3)	O(3)	$\bar{x}, \bar{y}, \bar{z}$	3.16
O(3)	O(5)	$x, {}^1/_2 - y, {}^1/_2 + z$	3.47
O(4)	O(6)	$\bar{x}, {}^1/_2 + y, {}^1/_2 - z$	3.21

CO groups the legs. The Fe–Fe distance is one of the longest known. Such long bonds are generally to be found[13,14] in the absence of bridging CO groups which tend to shorten metal–metal distances.[15–18]

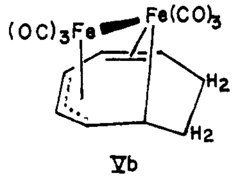
Each iron atom lies within bonding distance of three ring carbon atoms. Thus, Fe(1) lies 2.18, 2.22, and 2.08 Å from carbon atoms 7, 8, and 12, respectively, while Fe(2) is 2.12, 2.06, and 2.17 Å from carbon atoms 9, 10, and 11, respectively. Employing the same reasoning and comparisons with other structures as we used in the case of $(C_8H_8)Ru_2(CO)_6$, we can say that Fe(2) and carbon atoms 9, 10, and 11 constitute a π-allyl- (or *trihapto*allyl-) metal complex, whereas Fe(1) can be considered to form a σ bond to carbon atom 12 and an olefin–metal complex to the C_7–C_8 pair. For each iron atom, there are no Fe–C distances other than those just discussed which are short enough to justify the assumption of significant Fe–C bonding. All of these other ten Fe–C distances are ≥2.8 Å.

Now that the structure of $(C_8H_{10})Fe_2(CO)_6$ is known, it can be named systematically so as to indicate its true constitution, without at the same time introducing any assumptions about the finer details of bonding. Using the scheme recently proposed,[2] the name of this compound is (1,2,6-*trihapto*:3,4,5-*trihapto*cycloocta-1,3,5-triene)hexacarbonyldiiron. The less explicit systematic name, (*hexahapto*cycloocta-1,3,5-triene)hexacarbonyldiiron would also be correct, but would not distinguish between II and the correct structure.

As in the case of $(C_8H_8)Fe_2(CO)_6$ and $(C_8H_8)Ru_2(CO)_6$, there still remains the question of how to account for the nmr spectrum which indicates that in solution the protons appear to form four equivalent pairs. Since the same type of structure has now been found in crystals of both $(C_8H_8)Ru_2(CO)_6$ and $(C_8H_{10})Fe_2(CO)_6$, it appears quite likely that this kind of unsymmetrical structure is indeed the intrinsically preferred structure and, conversely, unlikely that in solution these molecules would rearrange to structures such as II and III, or even to symmetrical structures of the type I. We believe it to be most likely that these are fluxional molecules oscillating rapidly between the two oppositely skewed structures Va and Vb, which are enantiomorphs, with the symmetrical structure of type I representing the activated complex for this rearrangement or a very short-lived intermediate. Another possibility, but one which we think is considerably less likely, is that a structure of type II or III could be the transition state (or unstable intermediate) for interconversion of Va and Vb.



Va



Vb

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(13) F. A. Cotton and J. Takats, *J. Am. Chem. Soc.*, 90, 2031 (1968).
(14) M. R. Churchill, *Inorg. Chem.*, 6, 185 (1967).
(15) L. F. Dahl and J. F. Blount, *ibid.*, 4, 1373 (1965).
(16) C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, 88, 1821 (1966).
(17) O. S. Mills, *Acta Cryst.*, 11, 620 (1958).
(18) H. M. Powell and R. V. G. Ewens, *J. Chem. Soc.*, 286 (1939).

The structure of $(C_8H_{10})Fe_2(CO)_6$ in the solid state is of very particular interest because this is precisely the compound which initiated the postulation of structures such as II and III on the basis of Mössbauer data.[5] We thus have a direct and irrefutable invalidation of the Mössbauer criterion as applied to the case of $(C_8H_{10})Fe_2(CO)_6$ and, by direct implication, in the case of $(C_8H_8)Fe_2(CO)_6$. It is perhaps a little less certain that the structure postulated for $(C_7H_8)Fe_2(CO)_6$ is also incorrect, because the change in ring size *could* lead to significantly different bonding proclivities in the C_7 system as compared to the C_8 systems. However, it seems to us that the correct structure of $(C_7H_8)Fe_2(CO)_6$ is likely to be similar to those we have found for $(C_8H_8)Ru_2(CO)_6$ and $(C_8H_{10})Fe_2(CO)_6$.

It is now abundantly clear, if indeed it was not already so, that in Mössbauer spectroscopy as in all other types of spectroscopy there is great danger in using negative evidence (absence of bands, failure to observe splittings, etc.) to infer structures.

We know of at least one instance[19] in which a structure has been assigned by analogy with II. Presumably a structure analogous to V should be assigned instead.

[19] G. N. Schrauzer and P. W. Glockner, *J. Am. Chem. Soc.*, 90, 2800 (1968).

Stereochemically Nonrigid Organometallic Molecules. XIX.[1a] (1,2,3-*Trihapto*:4,5,6,7-*tetrahapto*cycloheptatrienyl)-[(*pentahapto*cyclopentadienyl)dicarbonylmolybdenum]-[tricarbonyliron].[1b] Preparation, Structure, and Temperature-Dependent Proton Magnetic Resonance Spectrum[2]

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Abstract: A compound containing both the $C_5H_5)(CO)_2Mo$ and $Fe(CO)_3$ groups bound to a cycloheptatrienyl ring, C_7H_7, has been prepared by photochemical reaction of $(C_7H_7)(C_5H_5)Mo(CO)_2$ with$Fe(CO)_5$ and/or $Fe_2(CO)_9$. This red crystalline compound, $(C_5H_5)(CO)_2Mo(C_7H_7)Fe(CO)_3$, appears to have a structure in which the $(C_5H_5)(CO)_2Mo$ group lies over one face of the C_7H_7 ring and interacts wth a sequence of three carbon atoms (a π-allyl-type complex) of the C_7H_7 ring, while the $Fe(CO)_3$ lies over the other face and interacts with a butadiene-like sequence of four carbon atoms. The molecule is fluxional and gives a pmr spectrum consistent with this structure only at temperatures below about $-50°$. Above this temperature the complex pattern of resonances due to the C_7H_7 ring collapses, and at room temperature and above these seven protons give only a single resonance. The Arrhenius activation energy for the rearrangement (in 4:1 $CDCl_3/CD_3C_6D_5$) is 13 ± 1 kcal/mol. The low-temperature spectrum collapses unsymmetrically and detailed analysis, including comparison with computer-simulated spectra, permits us to exclude all rearrangement pathways except 1,2 shifts or a mixture of 1,2 and 1,3 shifts.

One way of classifying fluxional organometallic molecules[4] is according to the number of metal atoms bonded to the organic moiety, usually a cyclic olefin, which is intramolecularly mobile. There are a number of molecules known with two such metal atoms, but in all cases in which fluxional character is definitely established, these two metal atoms are on the same side of the ring and are connected to each other.

It was the objective of the investigation reported here to prepare and characterize a fluxional compound with two separate, unconnected metal atoms lying on opposite sides of a cyclic polyolefin.[5] In fact, the molecule we have studied, shown schematically as I, contains two different metal atoms in different environments. It is of particular interest because it combines two mononuclear systems, *viz.*, II[8] and III,[9] each of which is already known to be fluxional.

A point of particular interest is how the simultaneous attachment of both metal-containing moieties will affect the rate of rotation of the cycloheptatrienyl ring, as

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[1] (a) Part XVIII: F. A. Cotton and P. Legzdins, *J. Am. Chem. Soc.*, 90, 6232 (1968). (b) For an explanation of the nomenclature see F. A. Cotton, *ibid.*, 90, 6230 (1968).

[2] This study was supported in part by Grant No. GP 7034X from the National Science Foundation.

[3] National Institutes of Health Postdoctoral Fellow, 1968.

[4] F. A. Cotton, *Accounts Chem. Res.*, 1, 257 (1968).

[5] The only well-characterized[6,7] molecule of this type which has been previously reported is *trans*-$C_8H_8[Fe(CO)_3]_2$, but this does not show fluxional character,[7] at least up to room temperature.

[6] B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, 37, 2084 (1962).

[7] C. E. Keller, G. F. Emerson, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 1388 (1965).

[8] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 3, 785 (1964). In this paper an unsuccessful attempt to prepare I from II is mentioned.

[9] J. E. Mahler, D. A. K. Jones, and R. Pettit, *J. Am. Chem. Soc.*, **86**, 3589 (1964).