Y represents $[Pt^{III}(CN)_4Br]^{2-}$ in 60% of the unit cells and $[Pt^{II}(CN)_4H_2O]^{2-}$ in the remainder of the cells.

This formulation implies a Pt III oxidation state for some of the Pt sites at $z = 0.499$ while the random polymeric mixture of two kinds of sites results in an inability to recognize its distinct presence in the structure. Considering the lack of an octahedrally coordinated Pt(IV) polyion in KCP(Br), although both octahedral $K_2Pt(CN)_4Br_2$ and square-planar $K_2Pt(CN)_4$ are used to synthesize KCP(Br), an extremely reactive $[Pt^{III}(CN)_4Br]^{2-}$ square-pyramidal ion is a possibility during crystallization. In fact, Pt(III) complexes have been invoked to explain the kinetics of redox reactions between Pt(II) and Pt(IV).[22,23] Such an ion would most logically sit down on the *ab* face of a growing crystal of KCP(Br), and this happens to be the most active face with long, needle-shaped crystals resulting. As Br^- ions are accommodated into interstices of the growing crystals, the second Br^- of the Pt(III) complex is ionized into solution to maintain electrical neutrality. A recent EPR study of Magnus' green salt, $Pt(NH_3)_4PtCl_4$, was interpreted in terms of an electronic model formally equivalent to a substitution of Pt(III) for some of the Pt(II) sites due to the presence of Pt(IV) impurities during crystallization.[24]

Acknowledgment. We wish to thank M. Paputa for the TGA experiment, R. Saillant, R. Jaklevic, and S. Werner for valuable discussions, and B. Novak for computational assistance. The x-ray data were taken on a Syntex diffractometer kindly loaned to us by M. Glick and Wayne State University. The neutron data were taken at the Ford Nuclear Reactor at the University of Michigan.

Registry No. $K_2Pt(CN)_4{\cdot}3.2H_2O$, 14323-36-5; Br_2, 7726-95-6.

Supplementary Material Available: Tables V and VI, listing structure factor amplitudes for KCP(Br) (x-ray data at 300 K; neutron data at 8 K) (9 pages). Ordering information is given on any current masthead page.

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Transition Metal σ-Acyls and Related Species. IV.[1-3] Crystal Structure and Molecular Geometry of $\mathrm{MeCH{\cdots}CH{\cdots}CHCHMeOC({=}O)Fe(CO)_3}$, a Molecule Containing an Fe—C(Carboxylate) Linkage in a Ferrelactone Ring

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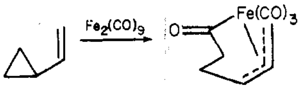
Received September 3, 1975 AIC50653I

The stereochemistry of the species $\mathrm{MeCH{\cdots}CH{\cdots}CHCHMeOC({=}O)Fe(CO)_3}$, prepared by Moriarty et al. from the reaction of iron carbonyl with the monoepoxide of *cis,trans*-hexa-2,4-diene, has been determined unambiguously by means of a single-crystal x-ray diffraction study. The complex crystallizes in the centrosymmetric orthorhombic space group *Pbca* [D_{2h}^{15}; No. 61] with $a = 12.0732$ (16) Å, $b = 15.2272$ (12) Å, $c = 12.2010$ (15) Å, $V = 2243.04$ Å^3, and $Z = 8$. X-ray diffraction data complete to $2\theta = 50°$ (Mo Kα radiation) were collected with a Picker FACS-1 automated diffractometer, and the structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques. All atoms (including hydrogens) were successfully located, the final discrepancy indices being $R_F = 3.21\%$ and $R_{wF} = 3.06\%$ for the 1434 independent reflections (none rejected). The molecule has the skeletal form $\mathrm{MeCH{\cdots}CH{\cdots}CH{-}CHMeOC({=}O)Fe(CO)_3}$ and contains a ferrelactone ring. The iron atom is bonded to three carbonyl ligands (Fe–CO = 1.784 (3), 1.798 (3), and 1.826 (3) Å), to a π-allylic fragment (Fe–C(3) = 2.090 (2), Fe–C(4) = 2.077 (3), Fe–C(5) = 2.209 (3) Å), and to a lactone system, the Fe–C σ-bond distance in the FeC(=O)OR system being 1.985 (2) Å.

Introduction

The vinylcyclopropyl system is known to react with iron carbonyl to yield a species which contains both a (π-allyl)→iron and a (σ-acyl)→iron linkage;[4] see eq 1.



(1)

Vinyl epoxides (vinyloxiranes) react analogously, resulting in species containing a (π-allyl)→iron linkage and an Fe–C (iron–carboxylate) σ linkage;[5] see eq 2.

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Table I. Experimental Data for the X-Ray Diffraction Study of $Me_2C_4H_4OCOFe(CO)_3$

(A) Crystal Parameters at 22.5 ± 0.5 °C

Crystal system: orthorhombic	Space group: *Pbca* [D_{2h}^{15}; No. 61]
$a = 12.0732$ (16) Å[a]	$Z = 8$
$b = 15.2272$ (22) Å	Mol wt 266.04
$c = 12.2010$ (15) Å	ρ(calcd) = 1.576 g cm^{-3}
$V = 2243.04$ Å^3	

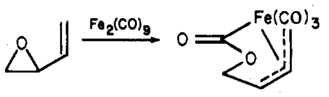
(B) Measurement of Intensity Data

Radiation: Mo Kα
Filter: Nb foil at counter aperture
Attenuators: used if I(peak) > 10^4 counts/s
Takeoff angle: 3.5°
Detector aperture: 4 mm × 4 mm
Crystal–detector distance: 330 mm
Crystal orientation: ca. 5° from [001]
Reflections measured: $+h,+k,+l$
Maximum 2θ: 50°
Scan type: coupled θ(crystal)-2θ(counter)
Scan speed: 1.0°/min
Scan range: $\Delta(2\theta) = (1.40 + 0.692 \tan \theta)°$, starting 0.70° below the Mo Kα_1 peak
Background measurement: stationary crystal, stationary counter; 20 s each at beginning and end of the 2θ scan
Standard reflections: three remeasured after every 48 reflections; rms deviations (after application of an isotropic linear decay correction)[b,c] were 0.92% for 600, 0.61% for 060, and 0.49% for 006
Reflections collected: 1437 independent measurements, 241 systematic absences, and 63 duplicate reflections

(C) Treatment of Data

Conversion to $|F_o|$ and $\sigma(|F_o|)$: as in ref 7, using an ignorance factor of $p = 0.035$
Absorption coefficient: $\mu = 13.82$ cm^{-1}
Transmission factors:[d,e] maximum 0.733, minimum 0.673

[a] Cell parameters are from a least-squares fit to the setting angles of the resolved Mo Kα_1 peaks of 12 reflections in the range $2\theta = 40.8$–$50.5°$ and are based on λ(Mo Kα_1) 0.709300 Å: see J. A. Bearden, *Rev. Mod. Phys.*, 39, 78 (1967). [b] The three standard reflections decreased continuously throughout data collection: 600 by 5.3%, 060 by 6.5%, and 006 by 3.2%. [c] Data reduction (including averaging, Lp correction, linear decay correction) was performed using the Fortran IV program RDUS, by B. G. DeBoer. [d] Data were corrected for the effects of absorption using the Fortran IV program DRABZ, by B. G. DeBoer. [e] The correctness of the absorption correction was checked by realigning the crystal with c^* coincident with the ϕ axis and measuring (via a θ–2θ scan) the intensity of the strong axial 004 reflection at $\chi = 90°$ and at 10° intervals from $\phi = 0°$ to $\phi = 350°$; following correction for absorption, the ϕ dependence of this reflection was essentially eliminated.



(2)

We have now undertaken an x-ray crystallographic study of a ferrelactone derived from the reaction of iron carbonyl with the monoepoxide of *cis,trans*-hexa-2,4-diene. The purposes of this study were twofold: first, to characterize structurally the Fe–C(carboxylate) (FeC(=O)OR) linkage, and, second (as a collaborative enterprise with Professor R. M. Moriarty, the results of which have previously been communicated[6]), to determine the stereochemical course of the reaction of iron carbonyl with diastereomeric vinyloxiranes.

Experimental Section

A preliminary photographic study of the x-ray diffraction pattern showed the crystal to belong to the orthorhombic system (D_{2h} or *mmm* Laue symmetry). The systematic absences $0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$, and $hk0$ for $h = 2n + 1$ uniquely determine the space group to be the centrosymmetric *Pbca* [D_{2h}^{15}; No. 61].

The crystal was transferred to a Picker FACS-1 diffractometer to collect the "intensity data". The apparatus and experimental procedure have been described at length previously.[7] Details pertinent to the present study are given in Table I.

Table II. Final Positional Parameters, with Esd's, for $Me_2C_4H_4OCOFe(CO)_3$[a]

Atom	x	y	z	B,[b] Å^2
Fe	0.547 484 (27)	0.175 882 (22)	0.333 578 (25)	3.527
C(1)	0.405 36 (34)	0.397 33 (23)	0.415 27 (33)	6.24
C(2)	0.375 04 (23)	0.301 86 (19)	0.406 55 (22)	4.69
C(3)	0.415 56 (20)	0.260 89 (18)	0.301 19 (21)	4.08
C(4)	0.389 25 (20)	0.175 25 (18)	0.266 82 (21)	4.07
C(5)	0.389 70 (21)	0.102 50 (18)	0.335 45 (21)	4.24
C(6)	0.379 64 (31)	0.011 26 (22)	0.290 53 (30)	5.60
C(7)	0.505 67 (24)	0.202 98 (16)	0.487 22 (20)	4.27
C(11)	0.619 54 (21)	0.082 74 (19)	0.389 43 (20)	4.73
C(12)	0.642 87 (22)	0.264 78 (19)	0.346 67 (19)	4.46
C(13)	0.594 25 (21)	0.148 84 (17)	0.195 33 (21)	4.05
O(2)	0.417 36 (14)	0.257 55 (12)	0.501 85 (14)	5.03
O(7)	0.549 09 (7)	0.175 56 (11)	0.569 91 (14)	5.91
O(11)	0.661 01 (19)	0.022 74 (15)	0.425 39 (17)	7.39
O(12)	0.700 55 (18)	0.323 19 (14)	0.354 87 (17)	6.52
O(13)	0.627 03 (15)	0.129 08 (13)	0.111 96 (15)	5.62
H(1A)	0.372 2 (28)	0.423 6 (22)	0.474 9 (29)	9.3 (11)
H(1B)	0.493 3 (29)	0.406 2 (19)	0.412 3 (24)	7.8 (8)
H(1C)	0.377 0 (26)	0.431 2 (20)	0.357 8 (25)	6.9 (9)
H(2)	0.295 6 (21)	0.298 6 (14)	0.411 7 (17)	3.6 (5)
H(3)	0.428 3 (17)	0.306 1 (14)	0.241 5 (19)	3.2 (5)
H(4)	0.387 1 (20)	0.161 9 (14)	0.190 7 (21)	4.0 (6)
H(5)	0.370 6 (17)	0.107 8 (15)	0.413 0 (20)	3.9 (5)
H(6A)	0.409 6 (21)	0.008 7 (16)	0.214 9 (24)	5.1 (6)
H(6B)	0.428 5 (24)	−0.031 0 (19)	0.329 9 (21)	5.4 (7)
H(6C)	0.303 4 (27)	−0.005 5 (22)	0.282 3 (25)	8.7 (10)

[a] Esd's, shown in parentheses, are right-adjusted to the last digit of the preceding number. They are derived from the inverse of the least-squares matrix from the last cycle of refinement. [b] For anisotropic thermal parameters of the nonhydrogen atoms, see Table III.

Solution and Refinement of the Structure

Computer programs used during the structural analysis were FORDAP (Fourier synthesis, by A. Zalkin), LSHF (structure factor calculations and full-matrix least-squares refinement, by B. G. DeBoer), STAN1 (distances, angles, and their esd's, by B. G. DeBoer), and ORTEP (thermal ellipsoid drawings, by C. K. Johnson).

Scattering factors for neutral iron, oxygen, and carbon were taken from the compilation of Cromer and Waber;[8] those for neutral hydrogen are the "best floated spherical H atom" values of Stewart et al.[9] For nonhydrogen atoms, both the real and imaginary components of anomalous dispersion were included, using the values of Cromer and Liberman.[10]

The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w[|F(hkl)|] = \sigma^{-2}[|F(hkl)|]$

Discrepancy indices used below are defined as

$$R_F = \left[\frac{\sum ||F_o| - |F_c||}{\sum |F_o|}\right] \times 100\ (\%)$$

$$R_{wF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2}\right]^{1/2} \times 100\ (\%)$$

The position of the iron atom was quickly and unambiguously determined from a three-dimensional Patterson map. A Fourier synthesis, phased by this atom, yielded the coordinates of the remaining 15 nonhydrogen atoms. Refinement of positional and isotropic thermal parameters along with the scale factor (65 variables) led to convergence with $R_F = 11.12\%$ and $R_{wF} = 14.06\%$. Continued refinement, now using anisotropic thermal parameters (145 variables), led to $R_F = 6.11\%$ and $R_{wF} = 8.65\%$. A difference-Fourier synthesis now revealed the locations of each of the 10 hydrogen atoms. Six cycles of full-matrix least-squares refinement of all positional parameters, anisotropic thermal parameters for all nonhydrogen atoms, isotropic thermal parameters for the hydrogen atoms, and the scale factor (185 variables in all) led to final convergence with $R_F = 3.21\%$ and $R_{wF} = 3.06\%$ for the 1434 independent reflections (none rejected as "not significantly above background"). Maximum shifts during the final cycle of refinement were $\Delta/\sigma = 0.010$ for a nonhydrogen parameter and $\Delta/\sigma = 0.018$ for a hydrogen atom parameter.

The "goodness of fit", defined by $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 1.185, where m (the number of observations) was 1434 and n (the number of variables) was 185; the ratio $m{:}n$ was 7.75:1. The

Table III. Anisotropic Thermal Parameters for $Me_2C_4H_4OCOFe(CO)_3$[a,b]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U\rangle$[c]
Fe	3.603 (20)	4.445 (20)	2.534 (18)	0.382 (13)	0.179 (11)	0.452 (12)	0.175, 0.209, 0.244
C(1)	7.19 (21)	5.34 (17)	6.20 (18)	1.72 (16)	0.43 (16)	0.08 (14)	0.233, 0.279, 0.324
C(2)	4.08 (15)	5.56 (16)	4.41 (14)	0.67 (11)	0.61 (10)	0.26 (11)	0.212, 0.240, 0.275
C(3)	3.88 (12)	4.96 (14)	3.41 (11)	0.75 (11)	0.39 (9)	0.92 (11)	0.194, 0.211, 0.270
C(4)	3.37 (12)	5.79 (15)	3.03 (12)	0.38 (10)	0.02 (9)	0.23 (11)	0.195, 0.205, 0.273
C(5)	3.88 (12)	5.46 (15)	3.38 (12)	−0.19 (10)	0.36 (9)	0.26 (11)	0.200, 0.227, 0.264
C(6)	5.79 (20)	5.61 (18)	5.40 (17)	−0.46 (14)	−0.01 (14)	−0.29 (13)	0.253, 0.265, 0.280
C(7)	5.44 (13)	4.29 (11)	3.07 (12)	0.02 (11)	0.43 (10)	0.06 (10)	0.195, 0.233, 0.264
C(11)	4.99 (14)	5.77 (15)	3.41 (12)	0.71 (12)	0.28 (10)	0.33 (11)	0.206, 0.241, 0.282
C(12)	4.08 (13)	5.20 (15)	4.09 (13)	0.72 (12)	0.67 (10)	0.21 (10)	0.205, 0.234, 0.269
C(13)	3.79 (12)	5.14 (13)	3.21 (12)	0.50 (10)	0.03 (9)	0.53 (10)	0.197, 0.215, 0.262
O(2)	6.33 (10)	5.49 (9)	3.27 (7)	0.83 (8)	1.17 (7)	0.23 (7)	0.191, 0.253, 0.301
O(7)	8.83 (13)	6.16 (11)	2.75 (8)	1.12 (9)	−0.65 (7)	0.33 (7)	0.182, 0.272, 0.343
O(11)	9.13 (15)	7.07 (12)	5.97 (11)	3.48 (11)	−0.31 (10)	1.47 (9)	0.215, 0.291, 0.387
O(12)	5.34 (11)	6.28 (12)	7.94 (13)	−0.92 (9)	0.94 (9)	−0.38 (9)	0.243, 0.286, 0.327
O(13)	5.68 (10)	7.78 (12)	3.46 (8)	1.08 (9)	0.68 (7)	−0.35 (8)	0.201, 0.264, 0.323

[a] These anisotropic thermal parameters are analogous to the usual form of the isotropic thermal parameter and have units of Å^2. They enter the expression for the structure factor in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] See footnote *a* to Table II. [c] 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 Figure 1.

Table IV. Interatomic Distances (A), with Esd's[a]

	(A) Distances from Iron Atom		
Fe···C(2)	2.9677 (27)	Fe–C(11)	1.7980 (29)
Fe–C(3)	2.0901 (24)	Fe–C(12)	1.7844 (31)
Fe–C(4)	2.0768 (25)	Fe–C(13)	1.8258 (26)
Fe–C(5)	2.2086 (26)	Fe···O(11)	2.9276 (21)
Fe–C(7)	1.9848 (24)	Fe···O(12)	2.9179 (23)
Fe···O(2)	2.8687 (16)	Fe···O(13)	2.9567 (19)
	(B) Distances within $Me_2C_4H_4OCO$ System		
C(1)–C(2)	1.5030 (45)	C(5)–C(6)	1.4984 (41)
C(2)–C(3)	1.5104 (36)	C(2)–O(2)	1.4381 (30)
C(3)–C(4)	1.4061 (34)	O(2)–C(7)	1.3635 (29)
C(4)–C(5)	1.3887 (35)	C(7)–O(7)	1.2112 (29)
	(C) Carbon–Hydrogen Distances		
C(1)–H(1A)	0.92 (3)	C(4)–H(4)	0.95 (2)
C(1)–H(1B)	1.07 (3)	C(5)–H(5)	0.98 (2)
C(1)–H(1C)	0.94 (3)	C(6)–H(6A)	0.99 (3)
C(2)–H(2)	0.96 (2)	C(6)–H(6B)	1.00 (3)
C(3)–H(3)	1.01 (2)	C(6)–H(6C)	0.96 (3)
	(D) C–O Distances within Carbonyl Groups		
C(11)–O(11)	1.1304 (29)	C(13)–O(13)	1.1322 (28)
C(12)–O(12)	1.1341 (30)		

[a] Esd's, shown in parentheses, are right-adjusted to the last digit of the preceding number. They were calculated using the Fortran IV program STAN1 by B. G. Deboer and include the effects of uncertainties in unit cell parameters, as well as all correlation coefficients. No corrections have been applied for the effects of thermal motion.

Table V. Angles (deg), with Esd's[a]

	(A) Angles around Iron Atom		
C(7)–Fe–C(11)	85.93 (11)	C(3)–Fe–C(4)	39.44 (09)
C(7)–Fe–C(12)	85.52 (10)	C(4)–Fe–C(5)	37.66 (09)
C(7)–Fe–C(13)	176.49 (12)	C(3)–Fe–C(5)	70.00 (11)
C(11)–Fe–C(12)	104.61 (12)	C(3)–Fe–C(11)	158.26 (11)
C(11)–Fe–C(13)	91.30 (11)	C(5)–Fe–C(12)	159.97 (11)
C(12)–Fe–C(13)	93.11 (13)		
	(B) Angles within $Me_2C_4H_4OCO$ Ligand		
C(1)–C(2)–C(3)	112.39 (26)	C(1)–C(2)–O(2)	108.06 (25)
C(2)–C(3)–C(4)	124.32 (25)	C(2)–O(2)–C(7)	117.25 (18)
C(3)–C(4)–C(5)	123.99 (25)	O(2)–C(7)–O(7)	116.08 (21)
C(4)–C(5)–C(6)	121.25 (26)	O(2)–C(7)–Fe	116.69 (17)
C(3)–C(2)–O(2)	112.29 (22)	O(7)–C(7)–Fe	127.23 (20)
	(C) Angles Involving Methyl Hydrogens		
C(2)–C(1)–H(1A)	111.7 (22)	C(5)–C(6)–H(6A)	110.3 (15)
C(2)–C(1)–H(1B)	111.2 (17)	C(5)–C(6)–H(6B)	112.0 (16)
C(2)–C(1)–H(1C)	113.1 (19)	C(5)–C(6)–H(6C)	111.3 (20)
H(1A)–C(1)–H(1B)	113.8 (26)	H(6A)–C(6)–H(6B)	102.0 (21)
H(1A)–C(1)–H(1C)	101.1 (27)	H(6A)–C(6)–H(6C)	104.0 (23)
H(1B)–C(1)–H(1C)	105.6 (26)	H(6B)–C(6)–H(6C)	116.5 (25)
	(D) Angles Involving Other Hydrogens		
H(2)–C(2)–C(1)	106.7 (14)	H(4)–C(4)–C(3)	119.7 (14)
H(2)–C(2)–C(3)	111.0 (13)	H(4)–C(4)–C(5)	114.8 (14)
H(2)–C(2)–O(2)	106.1 (13)	H(5)–C(5)–C(4)	121.1 (14)
H(3)–C(3)–C(2)	112.4 (12)	H(5)–C(5)–C(6)	114.3 (14)
H(3)–C(3)–C(4)	116.7 (12)		
	(E) Angles within Carbonyl Ligands		
Fe–C(11)–O(11)	177.35 (27)	Fe–C(13)–O(13)	176.43 (23)
Fe–C(12)–O(12)	177.68 (24)		

[a] See footnote to Table IV.

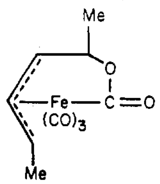
function $\sum w(|F_o| - |F_c|)^2$ was not markedly dependent upon $|F_o|$ or $(\sin\theta)/\lambda$, thereby suggesting that the weighting scheme was appropriate. There was no evidence suggesting secondary extinction.

A final difference-Fourier map was devoid of significant features, thereby providing independent confirmation that the structure was both correct and complete. [The three highest peaks were of height 0.29 e/Å^3 (at 0.120, 0.210, 0.160), 0.23 e/Å^3 (at 0.020, 0.255, 0.160), and 0.22 e/Å^3 (at 0.120, 0.135, 0.160). All other features were below 0.20 e/Å^3 in height.]

A table of observed and calculated structure factor amplitudes is available as supplementary material. Positional parameters are given in Table II; anisotropic thermal parameters are listed in Table III.

The Molecular Structure

The crystals contain discrete molecular units of $MeCH{\cdots}CH{\cdots}CHCHMeOC(=O)Fe(CO)_3$ which are separated by normal van der Waals distances. Interatomic distances and angles are shown in Tables IV and V, respectively. The molecular geometry and the scheme for labeling atoms are shown in Figure 1. [Note that the complex crystallizes in a space group containing operations of the second kind (i.e., inversion centers and glide planes) and that the crystals therefore contain an ordered racemic array of enantiomers **1** and **2**.]



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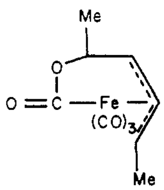

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The central iron atom has a quasioctahedral coordination geometry, being linked to three carbonyl ligands, being C bonded to a carboxylate group, and interacting with a (formally bidentate) π-allyl group. The molecule is thus a member of the $(\pi\text{-}C_3H_5)Fe(CO)_3R$ family.

The geometry of the $Fe(CO)_3$ moiety is distorted considerably from the possible C_{3v} symmetry and *approximates* to

Table VI. Distances (Å) within Selected π-Allyl→Iron Systems

Molecule	Fe-C(terminal)	Fe-C(central)	Δ[a]	C-C	Ref
(azulene)$Fe_2(CO)_5$ (3)	2.200 (8) 2.142 (8)	2.050 (8)	+0.121	1.432 (12) 1.391 (12)	12
$C_4H_6Fe(CO)_3SO_2BF_3$ (4)	2.194 (18) 2.202 (17)	2.091 (16)	+0.107	1.440 (24) 1.420 (23)	13
(acenaphthylene)$Fe_2(CO)_5$ (5)	2.241 (8) 2.242 (8)	2.051 (7)	+0.191	1.431 (11) 1.431 (11)	14
$Me_2C_4H_4OCOFe(CO)_3$ (1)	2.090 (2) 2.209 (3)	2.077 (3)	+0.073	1.406 (3) 1.389 (4)	This work

[a] Δ = [Fe-C(terminal)]$_{av}$ − [Fe-C(central)].

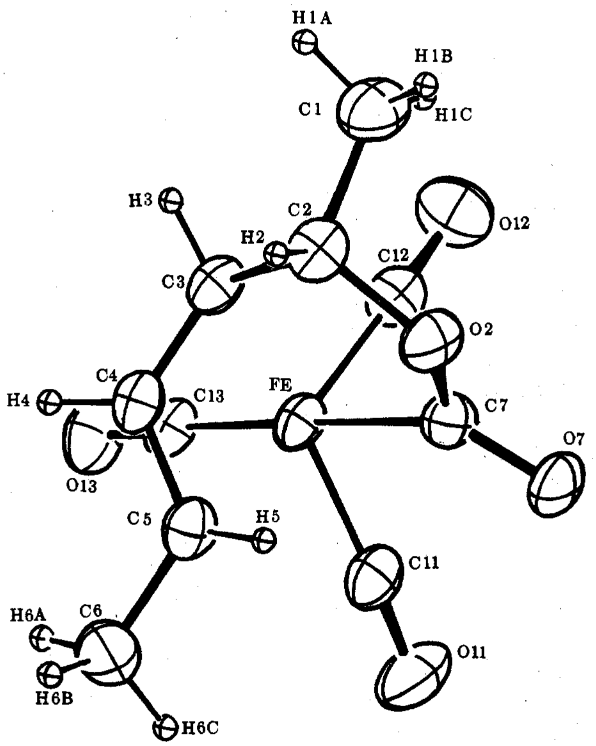
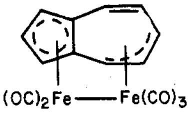


Figure 1. Geometry and labeling for the MeCH⋯CH⋯CHCHMe-OC(=O)Fe(CO)$_3$ molecule [ORTEP diagram, 50% probability ellipsoids for all atoms except hydrogens, which are shown artificially reduced to spheres of radius 0.10 Å].

C_s symmetry (the ligand C(13)-O(13) being unique). Thus, the angle C(11)-Fe-C(12) has a value of 104.61 (12)° and is more than 10° greater than the angles C(11)-Fe-C(13) = 91.30 (11)° and C(12)-Fe-C(13) = 93.11 (13)°. Similarly, the Fe-C(13) bond [1.8258 (26) Å] is significantly longer than the pseudomirror-related linkages Fe-C(11) and Fe-C(12), which have values of 1.7980 (29) and 1.7844 (31) Å, respectively. As might be anticipated from the known low sensitivity of bonds of high bond order to small changes in bond order, there is no distinction in distances within the two sets of C≡O ligands. Individual values are as follows: C(11)-O(11) = 1.1304 (29) Å, C(12)-O(12) = 1.1341 (30) Å, and C(13)-(13) = 1.1322 (28) Å. The Fe-C-O bond angles are all close to 180°, but that for the Fe-C(13)-O(13) system [176.43 (23)°] is bent slightly more than the remaining two [Fe-C(11)-O(11) = 177.35 (27)° and Fe-C(12)-O(12) = 177.68 (24)°].

The above pattern of distortions suggests that the carboxylate ligand competes more effectively with the carbonyl ligands for π-electron density than does the π-allyl system. However, it should be noted that the angle C(7)-Fe-C(13) is extremely close to 180°, having a value of 176.49 (12)°, whereas the "bidentate" π-allyl ligand is not strictly trans to the carbonyl ligands C(11)-O(11) and C(12)-O(12). [The angles C(3)-Fe-C(11) and C(5)-Fe-C(12) are 158.26 (11) and 159.97 (11)°, respectively.]

Distances within the π-allyl system are C(3)-C(4) = 1.406 (3) Å and C(4)-C(5) = 1.389 (4) Å [average 1.397 ± 0.011 Å],[11] and the angle C(3)-C(4)-C(5) is 123.99 (25)°. The π-allyl→iron bonding is slightly asymmetric, with one "terminal" carbon atom [C(3)] being closer to the metal than is usual. This is probably a result of strain in the molecule caused by the presence of the ferrelactone ring. Distances within the π-allyl→iron fragment are compared in Table VI with those in (azulene)$Fe_2(CO)_5$ (3),[12] $C_4H_6Fe(CO)_3SO_2BF_3$ (4),[13] and (acenaphthylene)$Fe_2(CO)_5$ (5).[14]



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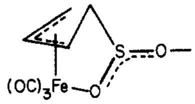

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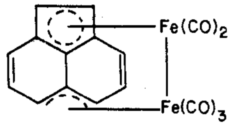

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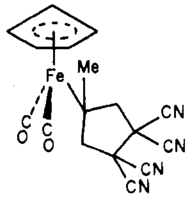
The following points may be made. (i) The central carbon atom of the π-allyl system is always closer to the iron atom than are (on the average) the two terminal carbon atoms. The difference (Δ) ranges from ca. 0.07 Å in the present compound to ca. 0.19 Å in (acenaphthylene)$Fe_2(CO)_5$. (ii) The two terminal carbon atoms are equidistant from the iron atom except when strain within the molecule causes a perturbation. The perturbation in the present molecule is represented by a difference of 0.1185 ± 0.0035 Å[11] (approximately 34σ) and is such that atom C(3) is pulled closer than normal to the iron atom by virtue of the ferrelactone ring. (iii) The average carbon-carbon distance in these π-allyl systems ranges from 1.397 Å in the present molecule to 1.431 Å in (acenaphthylene)$Fe_2(CO)_5$; the overall mean value is 1.418 Å for these four molecules.

Other bond lengths within the organic ligand are in reasonable agreement with accepted values.[15] Thus, C(1)-C(2) = 1.503 (5) Å [accepted C(sp^3)-C(sp^3) distance is 1.537 ± 0.005 Å], C(2)-C(3) = 1.510 (4) Å and C(6)-C(5) = 1.498 (4) Å [accepted C(sp^3)-C(sp^2) distance is 1.510 ± 0.005 Å], C(2)-O(2) = 1.438 (3) Å [accepted C(sp^3)-O distance is 1.426 ± 0.005 Å], C(7)-O(2) = 1.364 (3) Å [accepted value for the longer bond in carboxylic acids and esters is 1.358 ± 0.005 Å], and C(7)-O(7) = 1.211 (3) Å [accepted value for the shorter bond in carboxylic acids and esters is 1.233 ± 0.005 Å].

Hydrogen atoms have been located within reasonable tolerances. Thus, C-C-H angles about sp^2-hybridized carbon atoms range from 112.4 (12) to 121.1 (14)°, while C-C-H angles involving the sp^3-hybridized carbon atom C(2) lie in the range 106.1 (13)-111.0 (13)°. Angles within the methyl groups are C-C-H = 110.3 (15)-113.1 (19)° and H-C-H = 101.1 (27)-116.5 (25)°.

As is always found in x-ray crystallographic studies,[16] the carbon–hydrogen bond lengths are reduced from the true internuclear distance of ~1.08 Å, values for the present complex being C–H(methyl) = 0.92 (3)–1.07 (3) Å, C(sp^3)–H(nonmethyl) = 0.96 (2) Å, and C(sp^2)–H = 0.95 (2)–1.01 (2) Å. The average of the ten independent C–H distances is 0.978 Å.

Finally, we note that the iron–(C-bonded carboxylate) linkage, Fe–C(7), is 1.9848 (24) Å. There are, to our knowledge, no published data concerning the Fe–C(sp^3) distance in (π-C_3H_5)Fe$(CO)_3$R species. There are, however, a number of measurements of the Fe–C(sp^3) linkage in the related (π-C_5H_5)Fe$(CO)_2$R family of compounds; the most precise of these is the value of 2.0977 (23) Å found by Churchill and Chang[17] as the average of two independent measurements from a structural study of (π-C_5H_5)Fe$(CO)_2(C_4H_7C_2(CN)_4)$, **6**. The present Fe–C bond length in FeC(=O)OR of 1.9848 (24) Å is contracted by 0.1129 ± 0.0033 Å (i.e., 34σ) from the above Fe–C(sp^3) distance. This is probably due to resonance stabilization of **7** by form **8** which leads to partial multiple-bond character in the Fe–C bond. The present Fe–C(carboxylate) linkage may be compared with iron–(σ-acyl) distances of 1.9596 (30) Å in [$C_5H_4C_6H_6C$-O]$Fe_2(CO)_5$ (**9**)[3] and 1.968 (5) Å in [HB$(pz)_3$]Fe$(CO)_2$-(σ-$COCH_3$) (**10**).[18]



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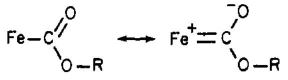
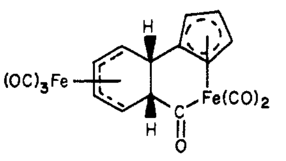


7 **8**



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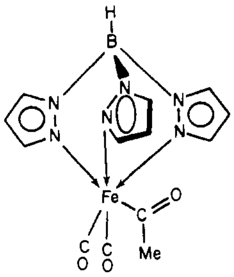

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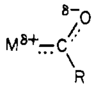
It is difficult to assess whether the increase of ~0.02 Å in the FeC(=O)OR Fe–C distance in our present complex relative to the FeC(=O)R Fe–C linkages in **9** and **10** is an indirect result of the replacement of the π-cyclopentadienyl or hydrotris(1-pyrazolyl)borate ligand by a π-allyl and carbonyl ligand or whether it is an intrinsic effect of the replacement of an alkyl by an alkoxy substituent at the metal-bonded carbon atom. The former seems more likely, however, since the (rather electronegative) second oxygen might be expected to enhance the drift of π electrons from the metal onto the α-carbon atom (cf. **11** and **12**).



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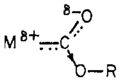

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Acknowledgment. We thank Professor R. M. Moriarty and Dr. B. G. DeBoer for helpful discussions. This work was generously supported by the National Science Foundation (Grant No. GP-42724X, to M.R.C.). Computing services were provided by the Computer Center of the University of Illinois at Chicago Circle; their assistance is gratefully acknowledged.

Registry No. $Me_2C_4H_4OCOFe(CO)_3$, 57378-04-8.

Supplementary Material Available: Listing of structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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