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, 24× 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 St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC407485.

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Transition Metal σ-Acyls. III.[1,2] Crystal Structure and Molecular Geometry of $[C_5H_4C_6H_6CO]Fe_2(CO)_5$, Including the Location and Refinement of All Hydrogen Atoms

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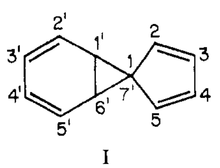
The complex $[C_5H_4C_6H_6CO]Fe_2(CO)_5$, prepared by Moriarty and coworkers by the reaction of $Fe_2(CO)_9$ and spiro-[2,4-cyclopentadiene-1,7'-norcara-2',4'-diene], crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14] with $a = 6.562$ (1) Å, $b = 21.690$ (5) Å, $c = 11.399$ (2) Å, and $\beta = 96.78$ (2)°. The observed density of 1.71 (2) g cm^{-3} is consistent with the value of 1.739 g cm^{-3} calculated for mol wt 421.96 and $Z = 4$. 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 a combination of Patterson, Fourier, and least-squares refinement techniques. All atoms, including hydrogen atoms, have been successfully located. The final discrepancy indices are $R_F = 5.02\%$ and $R_{wF} = 4.24\%$ for the 2852 independent reflections (none rejected). The structural analysis shows that the original spiro[2,4-cyclopentadiene-1,7'-norcara-2',4'-diene] framework has undergone 1,6' bond scission with incorporation of a –C(=O)– moiety at position 6'. The resulting molecule consists of a 5,6-*cis*-disubstituted-1,3-cyclohexadieneiron tricarbonyl residue, where the substituents are defined by the framework $-(\eta^5\text{-}C_5H_4)Fe(CO)_2C(=O)-$. Atom Fe(1) is linked to three terminal carbonyl groups and the η^4-cyclohexadiene fragment, iron–carbon distances around the diene (cyclically) being 2.097 (3), 2.048 (3), 2.049 (3), and 2.098 (3) Å and carbon–carbon distances within the diene system (taken cyclically) being 1.429 (4), 1.387 (5), and 1.428 (4) Å. Atom Fe(2) is linked to two terminal carbonyl ligands, to an η^5-cyclopentadienyl ligand (Fe–C = 2.068 (3)–2.128 (4) Å and C–C = 1.403 (6)–1.436 (5) Å), and to a σ-acyl residue. The iron–σ-acyl bond distance of 1.9596 (30) Å is significantly shorter than the accepted Fe–C (sp^3) distances of 2.0977 (23) Å for an $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ species.

Introduction

The reactions of spironorcaradienes with diiron enneacarbonyl have recently been studied by Moriarty and coworkers.[3] The reaction of $Fe_2(CO)_9$ with spiro[2,4-cyclopentadiene-1,7'-norcara-2',4'-diene], $C_{11}H_{10}$, I, in diethyl ether



I

at 36° for 30 hr produces as its principal product (28% yield) a compound of stoichiometry $(C_{11}H_{10})Fe_2(CO)_6$. This complex has an infrared spectrum which suggests the presence of terminal carbonyl ligands (ν 1965–1985, 2005, 2032 cm^{-1}) and an acyl carbonyl group (ν 1630 cm^{-1}). In order to determine the overall stereochemistry of this new complex and in view of our previous interest in σ-acyl derivatives of the transition metals,[1,2] we decided to subject this material to a single-crystal X-ray structural analysis. Our results are reported below.

Collection of the X-Ray Diffraction Data

Crystals of the complex were provided by Professor R. M. Moriarty of the University of Illinois at Chicago Circle. The crystal used was a platelike parallelepiped having the dimensions $(010)\rightarrow(0\bar{1}0) = 0.12$ mm, $(100)\rightarrow(\bar{1}00) = 0.295$ mm, and $(001)\rightarrow(00\bar{1}) = 0.34$ mm. The crystal was sealed into a Lindemann tube, which was fixed into a brass "pin" on a eucentric goniometer. Preliminary (0–2)*kl* Weissenberg photographs, an *a*-axis rotation photograph, *h*(0–2)*l* and *hk*(0–2) precession photographs, and *b* and *c* cone-axis photographs yielded approximate cell dimensions, indicated C_{2h} (2/*m*) Laue symmetry,

Table I. Experimental Data for the X-Ray Diffraction Study

(A) Crystal Parameters (at 25°)[a]

$a = 6.5621\ (12)$ Å
$b = 21.6899\ (51)$ Å
$c = 11.3989\ (22)$ Å
$\cos\beta = -0.1181\ (2)$
$\beta = 96.78\ (2)°$
$V = 1611.1$ Å^3
Space group $P2_1/c$ [C_{2h}^5; No. 14]
$Z = 4$
Mol wt = 421.96
ρ(calcd) = 1.739 g cm^{-3}
ρ(obsd)[b] = 1.71 (2) g cm^{-3}

(B) Measurement of Intensity Data

Radiation: Mo Kα
Filter(s): Nb foil at counter aperture (~47% transmission of Mo Kα)
Attenuators: not used
Takeoff angle: 3.0°
Detector aperture: 5 mm × 5 mm
Crystal–detector distance: 330 mm
Crystal orientation: mounted on [100]
Reflections measured: $+h,+k,\pm l$
Maximum 2θ: 50°
Scan type: coupled θ(crystal)–2θ(counter)
Scan speed: 1.0°/min
Scan length: $\Delta(2\theta) = (1.40 + 0.692 \tan\theta)°$, starting 0.70° below the Mo Kα_1 peak
Background measurement: stationary-crystal, stationary-counter; 40 sec each at beginning and end of 2θ scan
Standard reflections: three remeasured after every 48 reflections; rms deviations (after application of an isotropic linear decay correction)[c] were 0.55% for 200, 0.71% for 040, and 0.32% for $\bar{1}04$
Reflections collected: 2852 independent measurements, 259 duplicate or equivalent measurements (averaged into primary data set), and 102 systematic absences

(C) Treatment of Intensity Data

Conversion to $|F_o|$ and $\sigma(|F_o|)$: as in ref 4, using an "ignorance factor" of $p = 0.04$
Absorption coefficient: $\mu = 10.80$ cm^{-1}; maximum and minimum transmission factors were 0.901 and 0.709, respectively[d]

[a] Based on λ(Mo Kα_1) = 0.709300 Å: J. A. Bearden, *Rev. Mod. Phys.*, 39, 78 (1967). [b] By neutral buoyancy. [c] Data reduction (including averaging, linear decay correction, etc.) was performed using the Fortran IV program RDUS, by B. G. DeBoer. [d] Absorption corrections were carried out using the Fortran IV program DRAB, by B. G. DeBoer.

and showed systematic absences [$h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$] which are characteristic only of the centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14].

The crystal was transferred to a Picker FACS-1 computer-controlled diffractometer, was accurately centered, and was orientated so as to place a^* precisely coincident with the instrumental ϕ axis. The apparatus and experimental procedure have been described at length previously.[4] Details pertinent to the present study are given in Table I.

As a check on absorption, the intensity of the strong axial 200 reflection was measured (by a θ–2θ scan) at $\chi = 90°$ and at 10° intervals from $\phi = 0°$ to $\phi = 350°$. The observed variation in intensity as a function of ϕ was sufficiently large [(maximum − minimum)/mean = 20%] as to indicate that an absorption correction would be required. These ("ϕ-scan") data were processed along with the primary data set; following correction for absorption, the ϕ dependence of this reflection was essentially eliminated, thereby providing independent confirmation of the validity of the absorption correction applied.

Solution and Refinement of the Structure

Scattering factors for neutral iron, oxygen, and carbon were taken from the compilation of Cromer and Waber;[5] those for neutral hydrogen are the "best floated spherical H atom" values of Stewart et al.[6] For nonhydrogen atoms, both the real and imaginary components of anomalous dispersion were included, using the values of Cromer and Liberman.[7]

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

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

and

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

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), PLOD (least-squares planes and lines, by B. G. DeBoer), and ORTEP (thermal ellipsoid drawings, by C. K. Johnson).

The positions of the two iron atoms were quickly and unambiguously established from a three-dimensional Patterson map. A Fourier synthesis, phased by these two atoms (R_F = 43.4%, R_{wF} = 48.6%) led to the location of five carbonyl ligands. A second Fourier synthesis, phased now by 12 atoms (R_F = 37.4%, R_{wF} = 40.8%), yielded the positions of all remaining nonhydrogen atoms. Several cycles of full-matrix least-squares refinement of the scale factor and individual positional and isotropic thermal parameters for all 25 nonhydrogen atoms (101 parameters in all) led to convergence with R_F = 10.62% and R_{wF} = 11.01%. Continued refinement, now using anisotropic thermal parameters for all nonhydrogen atoms (226 parameters), converged with R_F = 6.23% and R_{wF} = 6.36%. A difference-Fourier synthesis now revealed the positions of all 10 hydrogen atoms, with peak heights ranging from 0.76 to 0.48 e Å^{-3}. The inclusion of these ten atoms with isotropic thermal parameters of 5.0 Å^2 led to an improvement of the discrepancy indices to R_F = 5.53% and R_{wF} = 4.82% even before refinement. Four cycles of full-matrix least-squares refinement of all positional parameters, anisotropic thermal parameters for all nonhydrogen atoms, isotropic thermal parameters for all hydrogen atoms, and the scale factor (266 parameters in all) led to final convergence with R_F = 5.02% and R_{wF} = 4.24% for the 2852 independent reflections. (None rejected as "not significantly above background".) Maximum shifts during the final cycle of refinement were 0.08σ for a thermal parameter and 0.03σ for a positional parameter. The "goodness of fit", defined by $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 1.145, where m (the number of observations) was 2852 and n (the number of variables) was 266; the ratio m:n was 10.72:1. The 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.

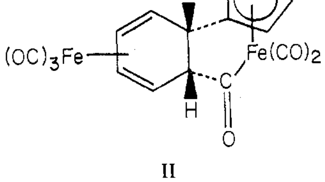
A final difference-Fourier map was devoid of significant features, thereby providing independent confirmation that the structure was both correct and complete. [The two highest peaks were of height 0.53 e Å^{-3} at 0.72, 0.09, 0.20 and 0.52 e Å^{-3} at 0.93, 0.07, 0.36; all other features were below 0.47 e Å^{-3}.]

A table of observed and calculated structure factor amplitudes is available. [See paragraph at end of paper regarding supplementary material.] Positional parameters are given in Table II; anisotropic thermal parameters are listed in Table III.

The Molecular Structure

The crystals consist of discrete molecular units of stoichiometry [$C_5H_4C_6H_6CO$]$Fe_2(CO)_5$, which are mutually separated by normal van der Waals distances.

Interatomic distances with their estimated standard deviations (esd's) are shown in Table IV; bond angles, with esd's, are collected in Table V. The labeling of all nonhydrogen atoms and the overall molecular geometry are shown in Figure 1. Hydrogen atoms, the labels of which are omitted from this diagram for the sake of clarity, are numbered identically with their attached carbon atoms. The molecule may formally be represented by structure II. [Note, however, that the crystal is racemic and that II *and its mirror image* are present in equal amounts, being mutually related by crystallographic operations of the second kind.]



II

Table II. Final Atomic Coordinates with Esd's[a,b]

Atom	*x*	*y*	*z*	*B*, Å^2
Fe(1)	0.171866 (67)	0.576885 (18)	0.226004 (35)	3.01
Fe(2)	0.284252 (71)	0.334818 (20)	0.312949 (37)	3.33
O(1)	0.37831 (46)	0.58415 (13)	0.01343 (23)	6.52
O(2)	−0.21270 (44)	0.64267 (14)	0.15744 (24)	6.62
O(3)	0.36684 (48)	0.68172 (11)	0.35700 (23)	6.10
O(4)	0.17760 (49)	0.37479 (14)	0.54080 (22)	6.81
O(5)	0.60238 (51)	0.24926 (13)	0.40583 (25)	6.96
O(6)	0.63769 (36)	0.40839 (11)	0.38387 (20)	4.75
C(1)	0.29585 (54)	0.58268 (15)	0.09649 (28)	4.15
C(2)	−0.06387 (58)	0.61772 (16)	0.18346 (27)	4.41
C(3)	0.28636 (53)	0.64162 (15)	0.30741 (27)	3.94
C(4)	0.21836 (56)	0.35798 (15)	0.45088 (29)	4.34
C(5)	0.47884 (59)	0.28352 (16)	0.37087 (30)	4.57
C(6)	0.47711 (45)	0.40409 (13)	0.32094 (25)	3.18
C(11)	0.15469 (47)	0.37998 (14)	0.16260 (24)	3.36
C(12)	−0.00461 (56)	0.35713 (16)	0.22417 (32)	4.56
C(13)	0.01486 (65)	0.29121 (17)	0.22948 (38)	5.52
C(14)	0.18376 (63)	0.27436 (17)	0.17178 (32)	4.96
C(15)	0.26968 (60)	0.32871 (15)	0.12950 (28)	4.26
C(21)	0.21621 (46)	0.44655 (13)	0.15189 (24)	3.10
C(22)	0.04705 (48)	0.49029 (14)	0.17740 (26)	3.39
C(23)	0.02053 (51)	0.50583 (14)	0.29642 (27)	3.79
C(24)	0.19927 (49)	0.51933 (14)	0.36948 (24)	3.37
C(25)	0.38258 (49)	0.51481 (14)	0.31389 (25)	3.25
C(26)	0.41307 (45)	0.45907 (13)	0.23715 (24)	3.04
H(12)	−0.1091 (51)	0.3823 (15)	0.2657 (28)	5.60 (75)
H(13)	−0.0891 (58)	0.2670 (17)	0.2646 (31)	6.49 (88)
H(14)	0.2077 (51)	0.2323 (17)	0.1552 (29)	6.01 (85)
H(15)	0.4189 (58)	0.3328 (16)	0.0957 (31)	6.18 (83)
H(21)	0.2196 (40)	0.4506 (12)	0.0683 (23)	3.74 (60)
H(22)	−0.0818 (44)	0.4896 (12)	0.1190 (23)	3.99 (60)
H(23)	−0.1222 (49)	0.5101 (14)	0.3279 (26)	4.98 (66)
H(24)	0.1882 (45)	0.5337 (13)	0.4474 (25)	4.44 (61)
H(25)	0.5036 (45)	0.5311 (13)	0.3561 (24)	4.31 (68)
H(26)	0.5240 (41)	0.4656 (12)	0.1946 (22)	3.50 (57)

[a] Estimated standard deviations, shown in parentheses, are right-adjusted to the last digit of the preceding number and are those derived from the inverse of the least-squares matrix. [b] For nonhydrogen atoms, the "equivalent isotropic thermal parameters" are listed. They correspond to the average of the mean-square displacements along the three principal axes of the anisotropic thermal ellipsoid.

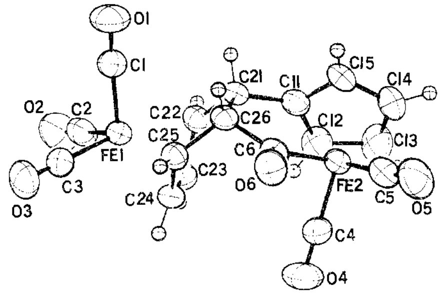


Figure 1. Labeling of atoms in the $[C_5H_4C_6H_6CO]Fe_2(CO)_5$ molecule [ORTEP drawing; hydrogen atoms artificially reduced].

As can clearly be seen both from Figure 1 and structure II, the spiro[2,4-cyclopentadiene-1,7'-norcara-2',4'-diene] moiety has suffered some disruption and modification. The modified ligand still contains a five-membered and a six-membered ring, but the three-membered ring has now opened up as a result of 1,6' bond scission with a keto group now acting as a substituent at position 6' (using the numbering scheme of structure I).

The resulting molecule consists of a 5,6-*cis*-disubstituted-1,3-cyclohexadieneiron tricarbonyl residue, with the substituents defined by the framework $-(\eta^5\text{-}C_5H_4)Fe(CO)_2C(=O)-$. [N.B. The numbering scheme used here is now that of the cyclohexadiene framework and not that of the spiro compound.]

The Cyclohexadieneiron Tricarbonyl Moiety

Atom Fe(1) is linked to three terminal carbonyl ligands and to a conjugated cis 1,3-diene ligand. The iron atom is best regarded as in a formal oxidation state of zero and has a d^8 configuration; the appropriate inert-gas configuration is reached by the donation of two electrons from each carbonyl ligand and four electrons from the diene. [Note that the bonding of conjugated diolefins to transition metals is necessarily complex and is best handled via a molecular orbital scheme. This has been discussed in detail by Churchill and Mason[8] and will not be commented on here.]

Table III. Anisotropic Thermal Parameters (with Esd's) For Nonhydrogen Atoms[a,b]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	⟨*U*⟩[c]
Fe(1)	3.467 (21)	2.943 (20)	2.690 (19)	−0.060 (16)	0.650 (15)	−0.244 (14)	0.176, 0.195, 0.212
Fe(2)	4.042 (23)	2.930 (20)	3.192 (21)	−0.105 (17)	1.223 (17)	−0.350 (15)	0.177, 0.196, 0.238
O(1)	8.13 (19)	7.37 (17)	4.65 (13)	−2.17 (14)	3.17 (13)	−0.76 (11)	0.196, 0.274, 0.366
O(2)	5.82 (16)	7.20 (17)	6.48 (16)	2.69 (14)	−0.72 (13)	−0.58 (13)	0.214, 0.279, 0.357
O(3)	8.48 (18)	3.92 (12)	5.51 (13)	−0.96 (13)	−0.81 (13)	−0.95 (11)	0.199, 0.269, 0.346
O(4)	8.99 (20)	7.59 (18)	4.40 (13)	1.80 (15)	3.09 (13)	−0.02 (12)	0.194, 0.294, 0.366
O(5)	8.65 (20)	5.53 (15)	6.46 (16)	2.89 (15)	−0.13 (14)	−0.47 (12)	0.219, 0.281, 0.371
O(6)	4.43 (12)	4.51 (12)	5.07 (12)	0.10 (10)	−0.50 (10)	−0.37 (09)	0.218, 0.237, 0.278
C(1)	5.14 (18)	3.80 (16)	3.64 (15)	−0.69 (14)	1.03 (14)	−0.27 (12)	0.208, 0.211, 0.265
C(2)	5.68 (21)	4.14 (17)	3.30 (15)	0.61 (16)	0.05 (14)	−0.65 (12)	0.193, 0.229, 0.279
C(3)	4.90 (18)	3.32 (15)	3.60 (15)	0.29 (14)	0.46 (13)	0.08 (12)	0.203, 0.214, 0.251
C(4)	5.44 (19)	3.88 (16)	3.99 (16)	0.43 (14)	1.76 (15)	0.33 (13)	0.199, 0.219, 0.278
C(5)	5.72 (20)	3.96 (17)	4.12 (17)	0.49 (16)	1.02 (15)	−0.65 (13)	0.199, 0.244, 0.272
C(6)	3.26 (14)	3.38 (14)	3.00 (13)	0.27 (11)	0.75 (11)	−0.73 (11)	0.165, 0.209, 0.224
C(11)	3.57 (14)	3.52 (14)	2.96 (13)	−0.30 (12)	0.25 (11)	−0.60 (11)	0.179, 0.213, 0.224
C(12)	3.92 (17)	4.36 (18)	5.45 (19)	−0.68 (14)	0.78 (15)	−0.36 (15)	0.208, 0.242, 0.267
C(13)	5.16 (21)	4.23 (19)	7.22 (25)	−1.95 (17)	0.96 (19)	−0.39 (17)	0.184, 0.287, 0.306
C(14)	6.48 (23)	3.42 (17)	4.94 (19)	−0.78 (16)	0.55 (17)	−1.15 (14)	0.185, 0.264, 0.291
C(15)	5.96 (21)	3.49 (16)	3.36 (15)	−0.07 (14)	0.67 (14)	−1.10 (12)	0.171, 0.239, 0.275
C(21)	3.85 (15)	3.04 (13)	2.49 (12)	−0.04 (11)	0.66 (11)	−0.35 (10)	0.169, 0.200, 0.222
C(22)	3.44 (15)	3.32 (14)	3.38 (14)	−0.34 (12)	0.29 (12)	−0.51 (11)	0.186, 0.212, 0.222
C(23)	4.04 (16)	3.57 (15)	4.06 (16)	−0.41 (12)	1.72 (13)	−0.06 (12)	0.181, 0.213, 0.257
C(24)	4.50 (17)	3.24 (14)	2.49 (13)	0.14 (12)	0.89 (12)	−0.21 (10)	0.169, 0.204, 0.241
C(25)	3.53 (14)	3.00 (14)	3.12 (13)	−0.15 (12)	0.00 (11)	−0.33 (10)	0.182, 0.205, 0.220
C(26)	2.77 (13)	3.37 (14)	3.14 (13)	−0.20 (11)	1.06 (11)	−0.30 (10)	0.164, 0.199, 0.221

[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 figures.

Table IV. Interatomic Distances (Å), with Esd's

Atoms	Dist	Atoms	Dist
(A) Fe-C(carbonyl) Bond Lengths			
Fe(1)-C(1)	1.772 (3)	Fe(2)-C(4)	1.753 (3)
Fe(1)-C(2)	1.799 (4)	Fe(2)-C(5)	1.762 (4)
Fe(1)-C(3)	1.798 (3)		
(B) Fe-C(acyl) σ-Bond Length			
Fe(2)-C(6)	1.9596 (30)		
(C) Fe-C(π-cyclopentadienyl) Distances			
Fe(2)-C(11)	2.068 (3)	Fe(2)-C(14)	2.120 (4)
Fe(2)-C(12)	2.097 (4)	Fe(2)-C(15)	2.086 (3)
Fe(2)-C(13)	2.128 (4)		
(D) Fe-C(cyclohexadiene) Distances			
Fe(1)· · ·C(21)	2.975 (3)	Fe(1)-C(24)	2.049 (3)
Fe(1)-C(22)	2.097 (3)	Fe(1)-C(25)	2.098 (3)
Fe(1)-C(23)	2.048 (3)	Fe(1)· · ·C(26)	3.001 (3)
(E) C-O(carbonyl) Distances			
C(1)-O(1)	1.145 (4)	C(4)-O(4)	1.149 (4)
C(2)-O(2)	1.125 (5)	C(5)-O(5)	1.137 (5)
C(3)-O(3)	1.133 (4)		
(F) C-O(acyl) Distance			
C(6)-O(6)	1.206 (4)		
(G) Distances around π-Cyclopentadienyl System			
C(11)-C(12)	1.416 (5)	C(11)-C(21)	1.508 (4)
C(12)-C(13)	1.436 (5)	C(12)-H(12)	1.04 (3)
C(13)-C(14)	1.403 (6)	C(13)-H(13)	0.98 (4)
C(14)-C(15)	1.416 (5)	C(14)-H(14)	0.95 (4)
C(15)-C(11)	1.420 (5)	C(15)-H(15)	1.10 (4)
(H) Distances around Cyclohexadiene System			
		C(21)-C(11)	1.508 (4)
C(21)-C(22)	1.514 (4)	C(21)-H(21)	0.96 (3)
C(22)-C(23)	1.429 (4)	C(22)-H(22)	1.01 (3)
C(23)-C(24)	1.387 (5)	C(23)-H(23)	1.05 (3)
C(24)-C(25)	1.428 (4)	C(24)-H(24)	0.95 (3)
C(25)-C(26)	1.519 (4)	C(25)-H(25)	0.95 (3)
C(26)-C(21)	1.546 (4)	C(26)-H(26)	0.93 (3)
		C(26)-C(6)	1.554 (4)

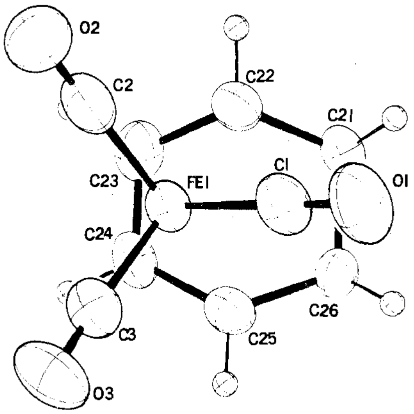


Figure 2. Geometry of the (1,3-cyclohexadiene)Fe(CO)$_3$ portion of the molecule.

The cyclohexadiene ligand and the Fe(CO)$_3$ group are present in a rotomeric conformation such that the entire (diene)Fe(CO)$_3$ system has approximately C_s (*m*) symmetry. As can clearly be seen in Figure 2, the carbonyl ligand C(1)–O(1) passes over the center of the C(21)–C(26) bond, while the ligands C(2)–O(2) and C(3)–O(3) pass essentially above atoms C(23) and C(24). The Fe(CO)$_3$ system deviates systematically from its possible C_{3v} symmetry toward the C_s symmetry of the entire (diene)Fe(CO)$_3$ assembly. Thus, the bond angle C(2)–Fe(1)–C(3) is 92.77 (15)° whereas the angles C(1)–Fe(1)–C(2) and C(1)–Fe(1)–C(3) are significantly greater with values of 101.84 (15) and 99.76 (15)°, respectively. Similarly (but at a lower level of significance), the bond length Fe(1)–C(1) is 1.772 (3) and is 0.02 Å (or more than 5σ) shorter than found in the bonds Fe(1)–C(2) and Fe(1)–C(3), which have values of 1.799 (4) and 1.798 (3) Å. Carbon–oxygen distances show a similar systematic variation with that for C(1)–O(1) being 1.145 (4) Å, while those for C(2)–O(2) and C(3)–O(3) are 1.125 (5) and 1.133 (4) Å, respectively.

All of these distortions simply reflect the perturbation of the Fe(CO)$_3$ group by the low symmetry of the diene–metal bonding and are expected.[9]

Bond lengths around the 1,3-diene system (taken cyclically) are C(22)–C(23) = 1.429 (4) Å, C(23)–C(24) = 1.387 (5) Å, and C(24)–C(25) = 1.428 (4) Å. This pattern of distances is appreciably different from that found in a free (i.e., uncoordinated) 1,3-diene and is common to all (1,3-diene)Fe(CO)$_3$ species that have been examined. Compilations of carbon–carbon distances in known (1,3-diene)Fe(CO)$_3$ complexes have been presented previously both by Churchill and Bird[10] and by Cotton et al.[11]

The iron atom, Fe(1), is appreciably closer to the central atoms of the 1,3-diene system [Fe(1)–C(23) = 2.048 (3) Å and Fe(1)–C(24) = 2.049 (3) Å] than it is to the terminal atoms [Fe(1)–C(22) = 2.097 (3) Å and Fe(1)–C(25) = 2.098 (3) Å]. The nonbonding contacts Fe(1)···C(21) and Fe(1)···C(26) are considerably longer, with individual values of 2.975 (3) and 3.001 (3) Å, respectively.

As shown in Table VI, the cis 1,3-diene system is planar within the limits of experimental error, the root-mean-square (rms) deviation from planarity being only 0.0030 Å. The iron atom, Fe(1), lies +1.627 Å from this plane and *all* hydrogen atoms of the diene system are displaced out of the plane of the four carbon atoms and toward the iron atom. The central hydrogen atoms, H(23) and H(24), lie +0.05 and +0.09 Å from the plane, while the terminal hydrogen atoms, H(22) and H(25), lie +0.20 and +0.17 Å from the diene plane. Carbon–hydrogen bond lengths within the diene system are (cyclically) C(22)–H(22) = 1.01 (3) Å, C(23)–H(23) = 1.05 (3) Å, C(24)–H(24) = 0.95 (3) Å, and C(25)–H(25) = 0.95 (3) Å. [The normal value from an X-ray crystallographic study is approximately 0.95 Å.[12]]

The system C(22)–C(21)–C(26)–C(25) is slightly perturbed from being perfectly planar, with the rms deviation from planarity being 0.024 Å. The dihedral angle between this system and the diene plane is 40.94°. It is interesting to note that the corresponding angle in the perfluorinated species octafluorocyclohexa-1,3-dieneiron tricarbonyl, $C_6F_8Fe(CO)_3$, is increased to a value of 47.3°.[13,14]

The saturated portion of the cyclohexadiene system is characterized by the carbon–carbon bond length C(26)–C(21) = 1.546 (4) Å—a distance in agreement with that expected for a normal C(sp^3)–C(sp^3) linkage. This portion of the ring is bonded to the 1,3-diene system via the bonds C(21)–C(22) and C(26)–C(25), which have lengths of 1.514 (4) and 1.519 (4) Å (respectively); the recognized C(sp^3)–C(sp^2) bond length is 1.51 Å.

The Cyclopentadienyliron Dicarbonyl System

Atom Fe(2) is in a coordination environment consistent with its being assigned an oxidation state of +II, thereby having a d^6 electronic configuration. The noble gas configuration is achieved by the donation of six electrons from the η^5-cyclopentadienyl anion, two electrons from each of the two terminal carbonyl ligands, and two electrons from the σ-acyl residue. The geometry of the coordination sphere of Fe(2) resembles a "three-legged piano stool". Angles between the monodentate ligands are all close to 90°, individual values being C(4)–Fe(2)–C(5) = 95.13 (16)°, C(4)–Fe(2)–C(6) = 87.99 (14)°, and C(5)–Fe(2)–C(6) = 91.80 (15)°. The geometry about Fe(2) is shown pictorially in Figure 3. Iron–carbon distances within the carbonyl ligands are Fe(2)–C(4) = 1.753 (3) Å and

Table V. Interatomic Angles (deg) with Esd's

Atoms	Angle	Atoms	Angle
(A) Angles Involving Iron Atoms			
C(1)-Fe(1)-C(2)	101.84 (15)	C(4)-Fe(2)-C(5)	95.13 (16)
C(1)-Fe(1)-C(3)	99.76 (15)	C(4)-Fe(2)-C(6)	87.99 (14)
C(2)-Fe(1)-C(3)	92.77 (15)	C(5)-Fe(2)-C(6)	91.80 (15)
C(22)-Fe(1)-C(23)	40.29 (12)	C(11)-Fe(2)-C(12)	39.74 (13)
C(23)-Fe(1)-C(24)	39.59 (13)	C(12)-Fe(2)-C(13)	39.74 (14)
C(24)-Fe(1)-C(25)	40.26 (12)	C(13)-Fe(2)-C(14)	38.56 (16)
C(25)-Fe(1)-C(22)	76.48 (12)	C(14)-Fe(2)-C(15)	39.33 (14)
		C(15)-Fe(2)-C(11)	39.97 (13)
(B) Angles within Carbonyl Groups			
Fe(1)-C(1)-O(1)	177.40 (32)	Fe(2)-C(4)-O(4)	178.03 (35)
Fe(1)-C(2)-O(2)	179.11 (42)	Fe(2)-C(5)-O(5)	178.07 (35)
Fe(1)-C(3)-O(3)	176.86 (34)		
(C) Angles around Acyl Carbon			
Fe(2)-C(6)-O(6)	126.94 (23)	O(6)-C(6)-C(26)	117.37 (26)
Fe(2)-C(6)-C(26)	115.68 (20)		
(D) C-C-C Angles within π-Cyclopentadienyl Ring			
C(15)-C(11)-C(12)	107.71 (28)	C(13)-C(14)-C(15)	108.13 (32)
C(11)-C(12)-C(13)	107.59 (32)	C(14)-C(15)-C(11)	108.44 (31)
C(12)-C(13)-C(14)	108.12 (34)		
(E) External Angles of π-Cyclopentadienyl Ring			
C(21)-C(11)-C(15)	124.94 (28)	H(13)-C(13)-C(14)	132.6 (22)
C(21)-C(11)-C(12)	126.56 (28)	H(14)-C(14)-C(13)	120.2 (21)
H(12)-C(12)-C(11)	126.7 (19)	H(14)-C(14)-C(15)	130.6 (21)
H(12)-C(12)-C(13)	125.5 (19)	H(15)-C(15)-C(14)	126.5 (18)
H(13)-C(13)-C(12)	119.1 (22)	H(15)-C(15)-C(11)	123.7 (18)
(F) C-C-C Angles in Cyclohexadiene Ring			
C(26)-C(21)-C(22)	110.26 (23)	C(23)-C(24)-C(25)	114.58 (26)
C(21)-C(22)-C(23)	120.30 (26)	C(24)-C(25)-C(26)	119.04 (26)
C(22)-C(23)-C(24)	115.52 (29)	C(25)-C(26)-C(21)	110.16 (24)
(G) External Angles of Cyclohexadiene Ring			
C(11)-C(21)-C(26)	109.22 (23)	C(6)-C(26)-C(21)	113.37 (23)
C(11)-C(21)-C(22)	112.03 (25)	C(6)-C(26)-C(25)	107.53 (22)
C(11)-C(21)-H(21)	101.9 (16)	C(6)-C(26)-H(26)	105.4 (16)
C(22)-C(21)-H(21)	103.7 (16)	C(21)-C(26)-H(26)	110.2 (16)
C(26)-C(21)-H(21)	119.5 (16)	C(25)-C(26)-H(26)	110.0 (16)
H(22)-C(22)-C(21)	116.0 (16)	H(24)-C(24)-C(23)	118.5 (18)
H(22)-C(22)-C(23)	116.2 (16)	H(24)-C(24)-C(25)	126.7 (18)
H(23)-C(23)-C(22)	124.1 (17)	H(25)-C(25)-C(24)	116.7 (17)
H(23)-C(23)-C(24)	120.3 (17)	H(25)-C(25)-C(26)	115.5 (18)

Fe(2)–C(5) = 1.762 (4) Å; these distances are each slightly, but significantly, shorter than those in the (1,3-diene)Fe(CO)$_3$ portion of this molecule (vide supra). Carbon–oxygen distances are C(4)–O(4) = 1.149 (4) Å and C(5)–O(5) = 1.137 (5) Å.

The five carbon atoms of the η^5-cyclopentadienyl ligand have a rms deviation of only 0.0036 Å from their least-squares plane (see Table VI); atom Fe(2) lies +1.718 Å from this plane. The substituent, C(21), lies +0.223 Å from the carbocyclic plane (i.e., is bent toward Fe(2)). Deviations of hydrogen atoms from the plane of the five carbon atoms range from +0.19 to –0.14 Å (average +0.01 Å). However, it should be emphasized that hydrogen atoms in this portion of the molecule seem to be less well defined than those in the diene system; thus, the carbon–hydrogen distances range from 0.95 (4) to 1.10 (4) Å, averaging 1.02 Å. (Cf. the accepted value of ca. 0.95 Å.[12])

Although iron–carbon distances vary significantly (individual values ranging from 2.068 (3) to 2.128 (4) Å), the pentaatomic carbocyclic ring has D_{5h} symmetry within the limits of experimental error. Carbon–carbon distances vary from C(13)–C(14) = 1.403 (6) Å to C(12)–C(13) = 1.436 (5) Å, the average value being 1.418 Å. [Note that this is consistent with the expected C–C(cyclopentadienyl) bond length of ca. 1.42–1.43 Å; artificial contraction due to libration, which often occurs in unsubstituted η^5-cyclopentadienyl rings,[15] plays no part here because the five-membered ring is rendered rigid via the C(11)–C(21) linkage.]

Angles within the ring range from C(11)–C(12)–C(13) = 107.59 (32)° to C(14)–C(15)–C(11) = 108.44 (31)°, averaging 108.00° as expected for a planar pentagon. External angles at C(11) are C(21)–C(11)–C(15) = 124.94 (28)° and C(21)–C(11)–C(12) = 126.56 (28)°; external angles involving the hydrogen atoms range from 119.1 (22) to 132.6 (22)°, averaging 125.6°. (The exterior half-angle for a regular planar pentagon is 126.0°.)

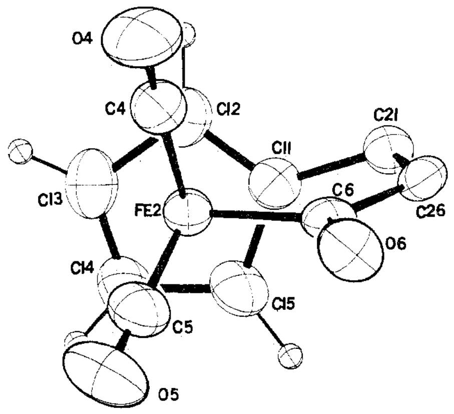


Figure 3. Geometry about Fe(2), showing the σ-acyl ligand.

The Iron–σ-Acyl Linkage

Angles around C(6), the acyl carbon atom, show slight deviations from a regular trigonal geometry. Thus,

Table VI. Least-Squares Planes and Deviations of Atoms Therefrom (in Å)[a,b]

Atom	Dev	Atom	Dev
Plane I: $0.50232X + 0.07828Y + 0.86113Z = 2.6263$ [The η^5-C_5H_5 Ring]			
C(11)*	0.0038	C(21)	0.223
C(12)*	−0.0016	H(12)	0.07
C(13)*	−0.0012	H(13)	−0.07
C(14)*	0.0035	H(14)	−0.14
C(15)*	−0.0045	H(15)	0.19
C(4)	2.791	C(6)	2.544
C(5)	2.798	O(6)	3.651
Fe(2)	1.718		
Plane II: $-0.05737X + 0.96415Y - 0.25908Z = 9.7272$ [The "Diene" Plane]			
C(22)*	0.0017	Fe(1)	1.627
C(23)*	−0.0032	H(22)	0.20
C(24)*	0.0032	H(23)	0.05
C(25)*	−0.0017	H(24)	0.09
C(1)	2.071	H(25)	0.17
C(2)	2.691	C(21)	−0.904
C(3)	2.705	C(26)	−0.960
Plane III: $-0.37704X - 0.62130Y + 0.68690Z = -5.2692$			
C(22)*	0.0150	H(22)	−0.14
C(21)*	−0.0252	H(21)	−0.78
C(26)*	0.0252	C(11)	1.113
C(25)*	−0.0150	H(26)	−0.69
C(23)	0.857	C(6)	1.302
C(24)	0.838	H(25)	−0.18
Dihedral Angles, Deg			
I–II	79.84	II–III	40.94
I–III	110.70		

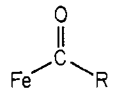
[a] Planes are in cartesian coordinates such that $[X, Y, Z] = [xa + zc \cos\beta, yb, zc \sin\beta]$. [b] Planes are derived using unit weights for atoms marked with an asterisk and zero weight for all other atoms.

Fe(2)–C(6)–O(6) = 126.94 (23)°, whereas Fe(2)–C(6)–C(26) = 115.68 (20)° and O(6)–C(6)–C(26) = 117.37 (26)°. The bond length within the keto group, C(6)–O(6), is 1.206 (4) Å.

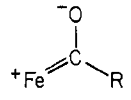
The iron–σ-acyl bond length is Fe(2)–C(6) = 1.9596 (30) Å. This is 0.1381 ± 0.0038 Å (or some 36.5σ) shorter than the "best" (i.e., most accurately determined) Fe–C(sp^3) distance in an (η^5-C_5H_5)Fe$(CO)_2$R species [2.0977 (23) Å, found as the average of iron–alkyl bond lengths in the two crystallographically independent molecules of (η^5-C_5H_5)Fe$(CO)_2(C_4H_7(CN)_4)$].[16]

It is interesting to note that the Fe–σ-acyl linkage in (HB$(pz)_3$)Fe$(CO)_2$(σ-$COCH_3$)[17] is 1.968 (5) Å in length—i.e., is not significantly different from that determined in the present study. This adds further support for the viewpoint that the HB$(pz)_3^-$ ligand is very similar in electronic properties to the η^5-$C_5H_5^-$ ligand.

The present Fe–σ-acyl linkage is compared with Fe–σ-alkyl,[16,18,19] Fe–σ-alkenyl,[20–22] and Fe–σ-alkynyl[23,24] linkages in Table VII. The Fe–σ-acyl linkage is clearly shorter than an Fe–σ-alkyl bond (vide supra), is slightly shorter than an Fe–σ-alkenyl bond, but is longer than an Fe–σ-alkynyl bond. The slight contraction in the Fe–σ-acyl relative to the Fe–σ-alkenyl linkage is consistent with the representation of the former (in valence-bond terms) as a resonance hybrid of the canonical forms III and (the polar form) IV.



III



IV

Table VII. Iron–Carbon σ-Bond Distances in (η^5-C_5H_5)Fe$(CO)_2$-Containing Species

Molecule	Bond	Bond length, Å	Ref
(η^5-C_5H_5)Fe$(CO)_2$(σ-C_5H_5)	Fe–C(sp^3)	2.11 (2)	18
(η^5-C_5H_5)Fe$(CO)_2$($C_4H_7C_2$-$(CN)_4$)	Fe–C(sp^3)	2.0977 (23)	16
(η^5-C_5H_5)Fe$(CO)_2$(σ-CH_2-CO_2H)	Fe-C(sp^3)	2.06 (2)	19
[(η^5-C_5H_5)Fe$(CO)_2$]$_2C_4H_4$	Fe–(CH=)	1.987 (5)	20
(η^5-C_5H_5)Fe$(CO)_2$($C_4H_5SO_2$)	Fe–(C⟨)	1.996 (8)	21
$(PhC_2CO_2Me)_3Fe(CO)_3$	Fe–(C⟨)	1.99 (2)	22
[$C_5H_4C_6H_6CO$]$Fe_2(CO)_5$	Fe–(C$\overset{O}{⟨}$)	1.9596 (30)	This work
(η^5-C_5H_5)Fe$(CO)_2$(σ-C≡CPh)	Fe–(C≡C)	1.920 (6)	23
[(η^5-C_5H_5)Fe$(CO)_2$-(σ-C≡CPh)CuCl]$_2$	Fe–(C≡C) ⋮ Cu	1.906 (10)	24

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Registry No. [$C_5H_4C_6H_6CO$]$Fe_2(CO)_5$, 53337-46-5.

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, 24× 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 St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC408401.

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