Synthesis and Crystal and Molecular Structure of Dicarbonyl-3-[π-(2-cyclohexadienyl)]-σ-propenoyliron

P. Janse Van Vuuren,[1a] R. J. Fletterick,[1b] J. Meinwald, and R. E. Hughes*

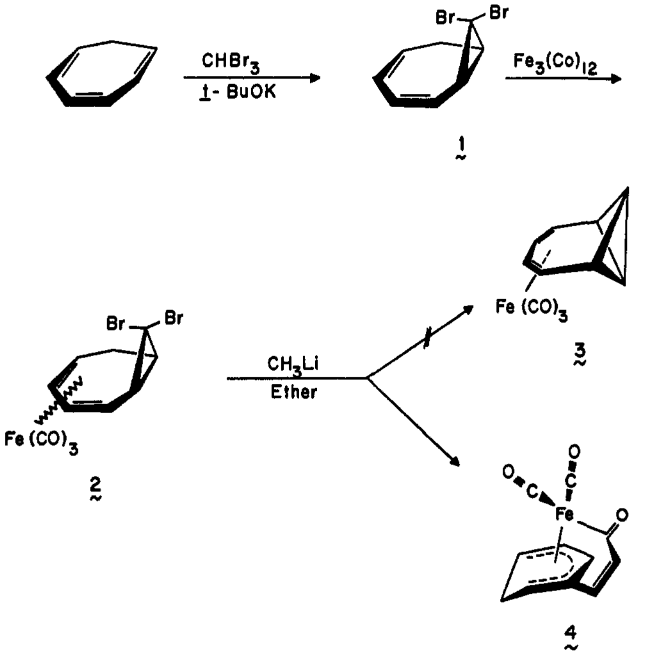
Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. *Received September 8, 1970*

Abstract: The crystal and molecular structure of the iron π complex obtained from the reaction of methyllithium with tricarbonyl-8,8-dibromobicyclo[5.1.0]octa-2,4-dieneiron has been determined by a single-crystal three-dimensional X-ray diffraction study. The complex crystallizes in the monoclinic space group $P2_1/c$ with lattice parameters $a = 10.740 \pm 0.003$, $b = 6.967 \pm 0.002$; $c = 13.154 \pm 0.004$ Å, and $\beta = 97.64 \pm 0.01°$. The intensity data for 2280 reflections were collected on a Picker automatic diffractometer, and the structure was solved from three-dimensional Patterson and Fourier syntheses. Full-matrix least-squares refinement, including anisotropic thermal parameters, gave a final conventional residual $R = 0.052$ for 1836 statistically retained reflections. The structure of the compound reveals an unsymmetrically substituted π-cyclohexadienyl ligand which is linked to the iron atom by means of a propenoyl side chain. The presence of the π-cyclohexadienyl ligand in the product is suggestive of an extensive skeletal rearrangement in the ligand structure of the precursor. The most interesting feature of this intramolecular "head-to-tail" bonded iron σ,π complex is the positional shift of the iron atom out of the pseudomirror plane of the π-cyclohexadienyl ligand. Analysis of the bonding geometry reveals that considerable intramolecular strain accompanies the unusual side-chain linkage to the iron atom.

The reaction of tricarbonyl-8,8-dibromobicyclo[5.1.0]octa-2,4-dieneiron (2) with methyllithium did not afford[2] the expected π complex of the desired cyclooctatetraene valence isomer, tricyclo[5.1.0.0^{2,8}]octa-3,5-diene (3). The molecular structure of the major product, isomeric with 3, was established by means of a single-crystal X-ray structure analysis and found to be dicarbonyl-3-[π-(2-cyclohexadienyl)]-σ-propenoyliron (4).

We report herein the details of the synthesis (outlined in Scheme I) and the X-ray crystallographic study of this unusual metal π complex. This interesting compound involves the relatively rare π-cyclohexadienyl ligand,[3] and provides the second example of an intramolecularly "head-to-tail"-bonded iron σ,π complex;[4] its formation requires a deep-seated reorganization in the ligand structure of the precursor[5] 2. Moreover, the dehalogenated complex displays a significant distortion of the iron–ligand π bond as a result of intramolecular strain.

Scheme I



Experimental Section

8,8-Dibromobicyclo[5.1.0]octa-2,4-diene (1). A solution of potassium *tert*-butoxide in *tert*-butyl alcohol was prepared by dissolving potassium (21.7 g, 0.055 g-atom) in 750 ml of dry *tert*-butyl alcohol in a 1-l. Morton flask with a stopcock outlet. In a second 3-l. Morton flask, a solution of freshly distilled bromoform (254 g, 1 mol) and excess distilled cycloheptatriene (300 g, 3.3 mol, J. T. Baker Chemical Co.) was cooled to −10° in an ice-salt bath. To the vigorously stirred solution the previously prepared potassium *tert*-butoxide solution was added dropwise at such a rate that the temperature of the reaction mixture could be maintained between −5 and 0°. After addition (*ca.* 2 hr), the reaction mixture was stirred for an additional 2 hr, allowing it to warm up to room temperature, and was then poured into 2 l. of water. The dark-brown organic layer (lower phase) was separated and washed twice with 500-ml portions of distilled water. The aqueous layer was extracted twice with 250 ml of methylene chloride; these extracts and the organic layer were combined and dried overnight ($MgSO_4$). Solvent and excess cycloheptatriene were removed under reduced pressure (room temperature, 0.1 mm); the vacuum was lowered and the residual liquid rapidly distilled into a trap at −78° (steam bath, 0.002 mm). Vacuum distillation of the crude trap contents through a 6 in. Vigreux column afforded 65.5 g (46% based on potassium) of the dibromide 1 as a light yellow, viscous liquid: bp 42–46° (0.02 mm); ir (neat) 3020 (=C—H), 1620 (C=C), 800, 740, 680, and 645 cm^{-1} (C—Br); uv$_{max}$ (cyclohexane) 263 (ϵ 2800) and 236 nm (ϵ 3650); nmr, 60 MHz (C_6D_6), complex multiplet at δ 5.1–6.3 (4 H, olefinic protons), multiplet at 2.25 (2 H, cyclopropyl or methylene protons), and complex multiplet at 2.05 (2 H, cyclopropyl or methylene protons);

---

[1] (a) Council for Scientific and Industrial Research (South Africa) Graduate Scholar, 1967–1970; (b) National Institutes of Health Predoctoral Trainee.

[2] P. J. Van Vuuren, R. J. Fletterick, J. Meinwald, and R. E. Hughes, *Chem. Commun.*, 883 (1970).

[3] M. R. Churchill and F. R. Scholer, *Inorg. Chem.*, 8, 1950 (1969).

[4] An analogous cyclopentadienyl system involving an oxyvinyl side chain has been reported: L. F. Dahl, R. J. Doedens, W. Hübel, and J. Nielsen, *J. Amer. Chem. Soc.*, 88, 446 (1966). Dare we suggest the common name "Scorpenes" for this class of metal-dicarbonyl complexes?

[5] In view of the unexpected rearrangement reaction observed, we have initiated an X-ray structure determination of this complex to determine the orientation of the $Fe(CO)_3$ moiety relative to the cyclopropane ring.

mass spectrum (70 eV, *m/e*) 264 (center of molecular ion triplet, $C_8H_8Br_2^+$) and 103 (base peak, $C_8H_7^+$).

When, in the above method, the potassium *tert*-butoxide was added as a crystalline solid[6] instead of as a solution in *tert*-butyl alcohol, a yield of 50% could be obtained. Alternatively, the same dibromide was obtained by the reaction of cycloheptatriene with phenyl(tribromomethyl)mercury.[7] The purity of the dibromide as obtained by distillation was estimated by nmr spectroscopy to be approximately 92%; it was not possible to improve it either by redistillation or preparative glpc, and the compound was used as such in the subsequent experiment. The dibromide is stable for weeks under an inert atmosphere if stored in a refrigerator.

Tricarbonyl-8,8-dibromobicyclo[5.1.0]octa-2,4-dieneiron (2). Under an argon atmosphere, excess 8,8-dibromobicyclo[5.1.0]octa-2,4-diene (20.0 g, 0.077 mol) was added to a stirred suspension of triiron dodecacarbonyl[8] (14.6 g, 0.029 mol) in 100 ml of dry *n*-heptane. The reaction mixture was heated under reflux for 6 hr and a dark brown precipitate was removed by filtration; the greenish yellow filtrate was concentrated *in vacuo* and then divided into two fractions, each of which was separately chromatographed on 150 g of dry silica gel. Elution of the columns with pentane yielded a yellow fraction in each case; these were combined and concentrated to approximately 100 ml and allowed to crystallize overnight. The crystalline product was filtered off and, after further concentration of the mother liquor, second and third crops of crystals were obtained. The dibromoiron π complex was eventually obtained in a yield of 5.4 g (15%) as yellow needles: mp 101–103° dec (uncorr); ir (CS_2) 2040, 1985, and 1945 cm^{-1} ($-C \equiv O$); nmr, 60 MHz (CS_2), multiplet at δ 5.25 (2 H, internal olefinic protons), multiplet at 3.25 (1 H, terminal olefinic proton), broad multiplet at 2.95 (1 H, terminal olefinic proton), and multiplets at 2.6–1.6 (4 H, methylene and cyclopropyl protons); mass spectrum (50 eV, *m/e*) 404 (center of molecular ion triplet, $FeC_8H_8Br_2(CO)_3^+$) and 104 (base peak, $C_8H_8^+$).

Anal. Calcd for $C_{11}H_8O_3Br_2Fe$: C, 32.70; H, 1.98; Br, 39.60; Fe, 13.86. Found:[10] C, 32.79; H, 2.0; Br, 39.43; Fe, 13.93.

Dicarbonyl-3-[π-(2-cyclohexadienyl)]-σ-propenoyliron (4). A solution of **2** (5.5 g, 0.0137 mol) in 150 ml of absolute ether under an argon atmosphere was cooled to −90° by partial immersion in a liquid nitrogen bath. In one portion, 8 ml of a 5.1% solution of methyllithium[11] in ether (1 equiv) was added to the stirred solution and the reaction mixture was allowed to warm up slowly. At −65°, an exothermic reaction took place with a simultaneous color change from light yellow to dark red. The reaction mixture was stirred for an additional 30 min at −40° and solvent was removed *in vacuo*. The residual liquid was stirred with a few milliliters of ether and chromatographed on 150 g of dry silica gel by eluting successively with 500-ml fractions of pentane, 1:1 pentane–ether, and ether.

The ether fraction, upon concentration, yielded 0.8 g of a crude orange oil which was sublimed [80° (0.1 mm)] to afford 0.7 g (21%) of pure **4** as bright orange-yellow crystals: mp 99–102° dec (uncorr); ir ($CDCl_3$) 2820 (exo C—H of methylene group), 2020, 1945 ($-C \equiv O$), and 1620 cm^{-1} ($>C=O$); nmr, 60 MHz ($CDCl_3$), doublet at δ 7.33 (1 H, β proton of enonyl group), multiplet at 6.37 (1 H, internal olefinic proton), doublet at 5.61 (1 H, α proton of enonyl group), multiplet at 4.6 (1 H, internal olefinic proton), multiplet at 3.71 (1 H, terminal olefinic proton), multiplet at 3.48 (1 H, terminal olefinic proton), multiplet at 2.6 (1 H, *endo*-methylene proton), and multiplet at 2.05 (1 H, *exo*-methylene proton); mass spectrum (50 eV, *m/e*) 244 (molecular ion, $FeC_8H_8(CO)_3^+$) and 56 (base peak).

Anal. Calcd for $C_{11}H_8O_3Fe$: C, 54.15; H, 3.28; Fe, 22.95. Found:[10] C, 54.02; H, 3.31; Fe, 22.83.

X-Ray Diffraction Data. Orange crystals of **4** suitable for X-ray analysis were obtained by crystallization at 0° from a saturated ether–pentane solution. Weissenberg and precession photographs revealed monoclinic diffraction symmetry. The systematic absences, $0k0$ ($k = 2n + 1$) and $h0l$ ($l = 2n + 1$), corresponded to $P2_1/c$, a space group which was subsequently confirmed by the structural analysis.

A crystal, 0.4 × 0.3 × 0.2 mm, was sealed in a 0.5-mm thin-walled capillary tube to protect it from a slow degradative oxidation earlier observed. All data were recorded with Zr-filtered Mo Kα radiation on a Picker FACS-I automatic diffractometer. A least-squares refinement of the setting angles of 29 automatically centered reflections (at $\pm 2\theta$) within the angular range $33° < |2\theta| < 40°$ yielded the lattice constants $a = 10.740 \pm 0.003$, $b = 6.967 \pm 0.002$, $c = 13.154 \pm 0.004$ Å, and $\beta = 97.64 \pm 0.01°$; $V = 1011.2$ Å^3 and the calculated density of 1.603 g/cm^3 corresponds to four molecules per unit cell ($Z = 4$).

The intensity data were recorded using the θ–2θ scanning mode at 1°/min over 1.6° with allowance for dispersion and 40-sec background counts taken at both ends of the scan. Periodic monitoring of three standard reflections showed no evidence of crystal degradation. A total of 2280 independent reflections was investigated within the range $\sin \theta/\lambda \leq 0.6496$. Application of the criterion $|F_o| > 0.675\sigma_F$ retained 1836 reflections as statistically observable; $\sigma_F = (C + k^2B)^{1/2}/(2|F_o|Lp)$, where C is the total count for the 2θ scan, B is the background count, and k is the ratio of the total scanning time to the total background counting time. The data were corrected for Lorentz and polarization effects but no absorption ($\mu = 15.0$ cm^{-1}) or extinction corrections were applied. Cromer–Mann atomic scattering factors[12] were used and appropriate corrections for the anomalous scattering of the iron atom were included.[13]

Structure Analysis and Refinement

The position of the iron atom was determined from a three-dimensional Patterson synthesis. Subsequent three-dimensional electron density maps revealed the positions of all of the nonhydrogen atoms. Two cycles of full-matrix least-squares refinement[14] with isotropic temperature factors reduced the agreement factor, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, to 0.16. Hydrogen atom positions were located on a difference Fourier map in conjunction with calculations based upon tetrahedral geometry for the methylene carbon atom and trigonal geometry for the other carbon atoms. Three additional cycles of full-matrix least-squares refinement were completed using anisotropic thermal parameters; hydrogen atom parameters were not refined and they were arbitrarily assigned isotropic thermal parameters 20% larger than those of the carbon atoms to which they were bonded. A final, unweighted residual $R = 0.052$ was obtained; a parallel calculation using a weighting function $w = 1/\sigma^2$, where $\sigma = \Sigma_0^3 a_n|F_o|^n$, yielded a weighted residual $R_w = 0.034$, where $R_w = [\Sigma w(|F_o| - |F_c|)^2]^{1/2}/[\Sigma w|F_o|^2]^{1/2}$. In the weighting scheme, the expansion coefficients a_n were derived from a least-squares fitting of the curve $||F_o| - |F_c|| = \Sigma_0^3 a_n|F_o|^n$. A final difference Fourier map was featureless and showed no peak larger than 0.56 e/Å^3.

Results[15]

Final atomic positional parameters are presented in Table I. The anisotropic thermal parameters (B_{ij})

---

[6] A. J. Speziale and K. W. Ratts, *J. Amer. Chem. Soc.*, **84**, 854 (1962).

[7] D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J. H. Treiber, and S. R. Dowd, *ibid.*, **87**, 4259 (1965).

[8] This reagent was freshly prepared from iron pentacarbonyl according to the procedure of King.[9] When commercial triiron dodecarbonyl (Alfa Inorganics) was used, an undesirable mixture of products was obtained.

[9] R. B. King, *Organometal. Syn.*, **1**, 95 (1965).

[10] Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

[11] Commercially obtained from Foote Chemical Co.

[12] D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

[13] D. T. Cromer, *ibid.*, **18**, 17 (1965).

[14] W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

[15] A list of the calculated and observed structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

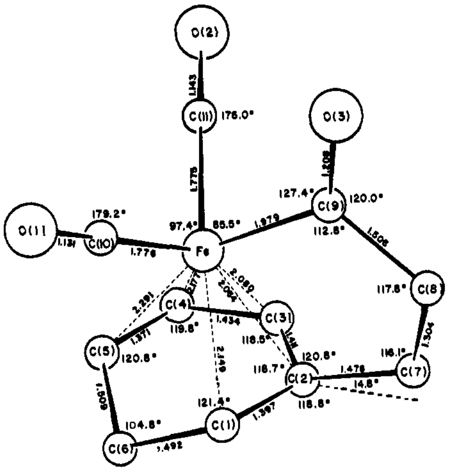


Figure 1. A perspective drawing of the $C_8H_8COFe(CO)_2$ molecule **4** showing the values of the molecular parameters. The iron atom is positioned 1.659 Å above the pentadienyl plane formed by atoms C(1), C(2), C(3), C(4), and C(5).

including the equivalent values of the corresponding isotropic thermal parameters (*B*) are listed in Table II. Intramolecular bond lengths and bond angles are presented in Table III.[16] Figure 1 provides a labeled perspective view of the molecular on which pertinent molecular dimensions are indicated.

Discussion of the Structure

A stereospecific representation of the molecular geometry of the complex is presented in Figure 2; the atoms are shown as 50% probability ellipsoids[17] based upon the anisotropic thermal parameters.

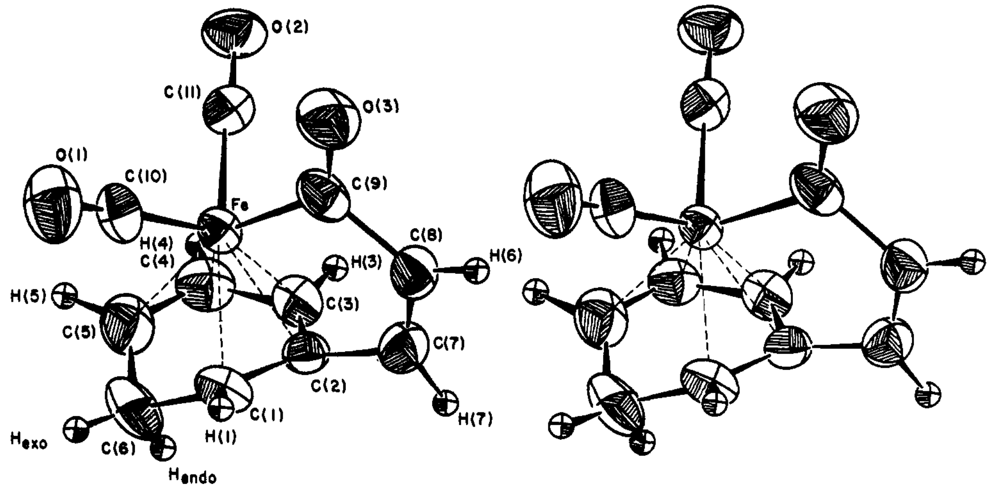


Figure 2. A stereoview of dicarbonyl-3-[π-(2-cyclohexadienyl)]-σ-propenoyliron with the nonhydrogen atoms drawn as 50% probability ellipsoids of thermal motion.

Table I. Final Atomic Fraction Coordinates[a]

Atom[b]	10^4x	10^4y	10^4z
Fe	2300 (1)	646 (1)	720 (1)
O(1)	330 (4)	3453 (7)	881 (4)
O(2)	1822 (4)	119 (7)	−1439 (3)
O(3)	3259 (4)	3925 (6)	−231 (3)
C(1)	2878 (5)	719 (7)	2304 (3)
C(2)	3799 (4)	−20 (7)	1784 (3)
C(3)	3507 (5)	−1623 (7)	1158 (4)
C(4)	2261 (5)	−2399 (8)	1074 (4)
C(5)	1402 (5)	−1626 (9)	1626 (5)
C(6)	1827 (6)	−499 (9)	2564 (4)
C(7)	4906 (5)	1179 (9)	1676 (4)
C(8)	4740 (5)	2531 (8)	1004 (4)
C(9)	3468 (5)	2673 (7)	388 (3)
C(10)	1090 (4)	2355 (7)	814 (4)
C(11)	1990 (4)	264 (7)	−589 (4)
H(1)	2900	2100	2550
H(3)	3900	−2300	700
H(4)	2000	−3400	550
H(5)	450	−2000	1400
H(7)	5600	800	2150
H(8)	5400	3800	1000
H(exo)	1200	100	2900
H(endo)	2300	−1000	2900

[a] The estimated standard deviations[16] in parentheses apply to the last significant digit. [b] The numbering of each hydrogen atom corresponds to the number of the carbon atom to which it is bonded. H(exo) and H(endo) refer to the methylene hydrogen atoms.

Cyclohexadienyl Ring. In spite of the fact that the three atoms C(1), C(2), and C(5) involve bonds that project out of the idealized sp^2 hybridization plane, the five atoms constituting the pentadienyl group in the cyclohexadienyl ring are coplanar to within 0.01 Å (see Table IV). Moreover, the interior bond angles within the pentadienyl group closely approximate the ideal value of 120°. The bond lengths in the ring are in close agreement with the values reported for the simpler complex,[3] $C_6H_7Mn(CO)_3$, in which a mirror plane bisects the cyclohexadienyl ring. In fact, given the overall structural dissimilarity between the two complexes, the virtual equivalence of the ring geometries is striking. The most significant difference involves a somewhat smaller dihedral angle in the iron complex between the C(1)-C(6)-C(5) plane and the pentadienyl plane; this corresponds to a perpendicular distance of 0.543 Å from C(6) to the pentadienyl mean plane as compared 0.635 Å for the Mn complex. The minor variations in bond lengths which appear across the

---

(16) Estimated standard deviations in each table were calculated using W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," ORNL-TM-306 Oak Ridge National Laboratory, Oak Ridge, Tenn. Standard deviations of the lattice constants were included in the calculations.

(17) The program used for the stereopair illustrations and calculation of intermolecular distances was C. K. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program," Oak Ridge National Laboratory, Oak Ridge, Tenn.

Table II. Thermal Parameters (Å^2)[a,b]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B^c
Fe	3.41 (2)	2.70 (2)	3.27 (2)	−0.37 (2)	0.68 (2)	0.04 (2)	3.07
O(1)	5.0 (2)	5.7 (2)	8.5 (3)	1.3 (2)	2.1 (2)	0.3 (2)	5.9
O(2)	7.1 (2)	6.3 (2)	3.9 (2)	−0.7 (2)	0.2 (2)	−0.6 (2)	5.6
O(3)	6.4 (2)	5.0 (2)	5.4 (2)	−2.0 (2)	0.9 (2)	1.6 (2)	5.1
C(1)	5.5 (2)	4.0 (2)	3.2 (2)	0.0 (2)	1.3 (2)	0.1 (2)	4.1
C(2)	4.0 (2)	4.1 (2)	3.0 (2)	0.3 (2)	0.2 (1)	0.4 (2)	3.7
C(3)	4.7 (2)	3.2 (2)	4.3 (2)	0.5 (2)	0.9 (2)	0.1 (2)	4.0
C(4)	5.9 (3)	3.4 (2)	4.6 (2)	−0.7 (2)	0.5 (2)	0.4 (2)	4.5
C(5)	5.1 (3)	4.6 (3)	6.4 (3)	−0.7 (2)	1.5 (2)	2.1 (2)	4.8
C(6)	6.4 (3)	5.0 (3)	5.7 (3)	−0.1 (2)	3.0 (2)	1.2 (2)	5.1
C(7)	3.9 (2)	5.6 (3)	4.0 (2)	−0.4 (2)	0.2 (2)	−0.8 (2)	4.4
C(8)	4.2 (2)	5.2 (3)	4.2 (2)	−1.8 (2)	0.8 (2)	−1.0 (2)	4.2
C(9)	4.5 (2)	3.2 (2)	3.7 (2)	−1.1 (2)	1.3 (2)	−0.2 (1)	3.5
C(10)	3.7 (2)	3.8 (2)	4.7 (2)	−0.4 (2)	1.3 (2)	−0.1 (2)	3.9
C(11)	4.2 (2)	3.0 (2)	4.3 (2)	−0.3 (2)	0.4 (2)	0.0 (2)	3.8

[a] The estimated standard deviations[16] in parentheses apply to the last significant digit. [b] The anisotropic B_{ij} values (Å^2) are related to the dimensionless β_{ij} employed during the least-squares refinement, by $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$, where β_{ij} is given by the expression $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [c] The isotropic thermal parameters were calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

Table III. Interatomic Distances (Å) and Bond Angles (Deg)[a]

Atoms	Distance	Atoms	Angle
Fe–C(1)	2.149 (5)	C(1)–Fe–C(2)	38.4 (2)
Fe–C(2)	2.064 (5)	C(2)–Fe–C(3)	29.8 (2)
Fe–C(3)	2.080 (5)	C(3)–Fe–C(4)	39.3 (2)
Fe–C(4)	2.177 (5)	C(4)–Fe–C(5)	35.6 (2)
Fe–C(5)	2.291 (5)	C(9)–Fe–C(10)	91.7 (2)
Fe–C(9)	1.979 (5)	C(9)–Fe–C(11)	85.5 (2)
Fe–C(10)	1.779 (5)	C(10)–Fe–C(11)	97.4 (2)
Fe–C(11)	1.775 (5)	C(2)–C(1)–C(6)	121.4 (5)
O(1)–C(10)	1.131 (6)	C(1)–C(2)–C(3)	118.7 (5)
O(2)–C(11)	1.143 (6)	C(1)–C(2)–C(7)	118.5 (5)
O(3)–C(9)	1.208 (6)	C(3)–C(2)–C(7)	120.5 (4)
C(1)–C(2)	1.387 (7)	C(2)–C(3)–C(4)	118.5 (5)
C(1)–C(6)	1.492 (7)	C(3)–C(4)–C(5)	119.8 (5)
C(2)–C(3)	1.411 (7)	C(4)–C(5)–C(6)	120.8 (5)
C(2)–C(7)	1.476 (7)	C(1)–C(6)–C(5)	104.6 (4)
C(3)–C(4)	1.434 (7)	C(2)–C(7)–C(8)	116.1 (5)
C(4)–C(5)	1.371 (8)	C(7)–C(8)–C(9)	117.6 (4)
C(5)–C(6)	1.509 (9)	C(8)–C(9)–O(3)	120.0 (4)
C(7)–C(8)	1.304 (8)	Fe-C(9)–C(8)	112.6 (3)
C(8)–C(9)	1.506 (7)	Fe–C(9)–O(3)	127.4 (4)
C(1)–H(1)	1.02	Fe–C(10)–O(1)	179.2 (40)
C(3)–H(3)	0.92	Fe-C(11)–O(2)	176.0 (9)
C(4)–H(4)	1.01		
C(5)–H(5)	1.06		
C(7)–H(7)	0.95		
C(8)–H(8)	1.13		
C(6)–H(*exo*)	0.96		
C(6)–H(*endo*)	0.73		

[a] The estimated standard deviations[16] in parentheses apply to the last digit.

Table IV. Equations for Best Least-Squares Planes and Distances of Atoms from Planes (Å)

Atom	Distance	Atom	Distance
A. Plane through Atoms C(1), C(2), C(3), C(4), and C(5) $-0.2033x + 0.6149y - 0.7619z = -2.593$			
C(1)	−0.006	C(5)	−0.011
C(2)	−0.001	C(6)	−0.543
C(3)	−0.009	C(7)	+0.377
C(4)	+0.015	Fe	+1.659
B. Plane through Atoms C(2), C(7), C(8), C(9), and O(3) $0.3714x - 0.6362y - 0.6762z = -0.2017$			
C(2)	0.009	O(3)	0.013
C(7)	−0.006	C(10)	1.199
C(8)	0.006	C(11)	−1.450
C(9)	−0.022	Fe	−0.133
Dihedral angle between planes A and B 87.2° (4)[a]			

[a] The estimated standard deviation in parentheses applies to last digit given.

pseudomirror plane through C(3) and C(6) are undoubtedly due to the propenoyl side chain and its effect on the π-cyclohexadienyl–iron interaction. The structural integrity of the pentadienyl group in these two structures strongly suggests that the symmetric geometry is a characteristic feature of metal–π-cyclohexadienyl complexes.

Propenoyl Side Chain. A conspicuous feature of the molecule involves the propenoyl side chain as an intramolecular linkage between the iron dicarbonyl moiety and the cyclohexadienyl ring.

As indicated in Table IV, the five atoms C(2), C(7), C(8), C(9), and O(3) constitute a second plane (within 0.02 Å) which is nearly orthogonal (87.2 ± 0.4°) to the pentadienyl plane. The C(2)–C(7) bond length is well within the range of the average[18] C(sp^2)–C(sp^2) single-bond distance of 1.466 ± 0.01 Å. The C(9)–O(3) bond distance of 1.208 ± 0.006 Å is also normal.[19] The C(9)–C(8) bond length is considerably longer than would be expected[19] in a fully conjugated enonyl group (1.506 ± 0.007 *vs.* 1.44 ± 0.01 Å) and, correspondingly, the C(7)–C(8) bond distance is shorter (1.304 ± 0.008 *vs.* 1.36 ± 0.01 Å); this implies some loss of conjugation in the enonyl group. Equally significant is the systematic deviation of all of the internal bond angles from the ideal sp^2 value; all three angles are smaller than 120° and the distortion at C(9) amounts to 7.4°. In addition, an unusually large inclination angle (14.8°) of the C(2)–C(7) bond to the pentadienyl plane is also observed. This pattern of bonding parameters provides clear evidence of an accumulation and distribution of a considerable degree of molecular strain in the propenoyl side chain. It is certain that an equivalent amount of strain must reside in the iron–cyclohexadienyl π-bonding system, but it is considerably more difficult to characterize this strain energy in terms of meaningful structural criteria.

Iron–Ligand Geometry. In the unstrained Mn complex, the metal atom lies in the mirror plane bisecting the cyclohexadienyl ring.[3] In the present case, this symmetry is destroyed by the unsymmetrical substitution of the propenoyl side chain on the ring, but

---

(18) M. G. Brown, *Trans. Faraday Soc.*, 55, 694 (1959).

(19) "Tables of Interatomic Distances and Configuration in Molecules and Ions; Supplement 1956–1959," Special Publication No. 18, The Chemical Society, London, 1965.

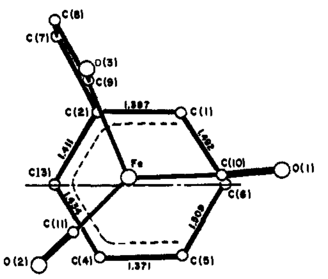


Figure 3. A projection of the $C_8H_8COFe(CO)_2$ molecule **4** on the pentadienyl plane (hydrogen atoms excluded).

a *pseudomirror* reference plane can be considered to pass through C(3) and C(6). A trace of this plane is indicated in Figure 3, which is a projection of the nonhydrogen atoms on the pentadienyl plane.

An interesting consequence of the presence of the constrained side chain is the displacement of the iron atom from this *pseudomirror* plane toward C(2) by 0.117 Å. This shift results in unequal iron distances to the five carbon atoms in the pentadienyl plane, with the shortest distance (2.064 ± 0.005 Å) to C(2). In the symmetrical Mn complex the distances were also unequal, but the shortest distance was, of course, to atom C(3).

The perpendicular distance of the iron atom to the pentadienyl plane is 1.659 Å. The question arises as to what this distance might be in an iron-cyclohexadienyl complex without a constraining side chain; in the present case, the cumulative strain in the propenoyl group surely results in some extension of the equilibrium iron-pentadienyl plane distance. In the case of the manganese π complex[20] (π-C_5H_5)$Mn(CO)_3$, the metal-cyclopentadienyl distance is 1.80 Å; in the $C_6H_7Mn(CO)_3$ complex, the metal atom drops to within 1.686 Å of the pentadienyl plane. Unfortunately, no analogous iron complexes are available, but in the iron-dicarbonyl complex (π-C_5H_5)$Fe(CO)_2C_5H_5$, the metal-cyclopentadienyl plane distance is 1.70 Å. On a proportionate basis, the iron-pentadienyl plane distance in an unstrained cyclohexadienyl system would be about 1.60 Å.

A further analogy can be drawn from the side-chain complex[4] $(C_6H_5C_2CO_2CH_3)_3COFe(CO)_2$, in which the corresponding iron distance is 1.71 Å. This provides a somewhat better comparison in the sense that the iron atom is bonded to two π-carbonyls and an sp^2 carbon atom, although the complete substitution on the cyclopentadienyl ring may affect the π-cyclopentadienyl bonding system. The side chain in this complex exhibits very little evidence of strain. The bond angles and distances are all normal except for an inclination angle of 8.5° of the carbon-oxygen bond with respect to the cyclopentadienyl ring. This moderate strain could effect at most only a slight elongation of the unperturbed equilibrium distance and, once again, it appears that a normal unstrained iron-cyclopentadienyl distance of 1.70 Å is appropriate. Thus both comparisons suggest that there is a strain elongation of about 0.06 Å in the iron-pentadienyl distance in the present case.

Although the perpendicular metal-plane distance provides a convenient measure of the π-bonding interaction, it is also noteworthy that the distances between the iron atom and carbon atoms in π-bonding systems (2.10 ± 0.1 Å) are essentially independent of the ring system and of the molecular geometry. In fact, even the minor detailed variations of these distances around the point of attachment of the side chain in the present structure are almost identical with that found in the "head-to-tail" cyclopentadienyl complex.[4]

The carbon-oxygen bond lengths observed for the two π-carbonyl ligands, C(10)-O(1) and C(11)-O(2), are 1.131 ± 0.006 and 1.143 ± 0.006 Å, respectively; these values are only slightly lower than the mean value (1.16 ± 0.02 Å) found in iron carbonyls.

The associated iron-carbon bond lengths, however, are significantly longer than those observed in two related iron-dicarbonyl complexes. Dahl and coworkers[4] reported values of 1.72 ± 0.03 and 1.68 ± 0.04 Å for their intramolecular head-to-tail complex and Bennett, *et al.*,[21] found a mean distance of 1.70 ± 0.02 Å in the iron-dicarbonyl complex (π-C_5H_5)$Fe(CO)_2C_5H_5$. Since both of these complexes can be formally considered as Fe(I) derivatives, it was suggested[21] that the unexpectedly short iron-carbon distances might reflect the normal decrease in the metal atom radius with increasing oxidation state. In the present case, which formally corresponds to an Fe(l) derivative, the corresponding bond lengths are 1.779 ± 0.005 and 1.775 ± 0.005 Å for Fe-C(10) and Fe-C(11), respectively. Since these values more nearly agree with those found for Fe(0) derivatives such as $(C_6H_5)_2PFe(CO)_4$ (1.79 Å)[22] and $C_8H_8Fe(CO)_3$ (1.80 Å),[23] it is clear that the explanation of these somewhat anomalous values must lie in a more subtle interpretation of the interaction of the iron atom and the π-bonding systems.

The remaining σ iron-carbon bond length is 1.979 ± 0.005 Å. This is in excellent agreement with the corresponding value of 1.99 ± 0.02 Å obtained for the other head-to-tail complex[4] and it falls well within the range of 1.94-2.10 Å listed[4] for analogous iron-carbon σ bonds.

As can be seen in Figures 1 and 3, the approximate threefold symmetry around the iron atom is significantly distorted by the side chain. The atoms C(9), C(10), and C(11) subtend bond angles at the iron atom which range from 85.5 to 97.4° (Table III). The upward normal of the C(9)-C(10)-C(11) plane is tilted 8.6° toward C(1) from the normal to the pentadienyl plane; this tilt is, of course, coupled with the shift of the iron atom toward C(2) and results in an asymmetric disposition of the carbonyl groups with respect to the pentadienyl ligand.

The bond angles[24] Fe-C(10)-O(1) and Fe-C(11)-O(2) are 179.2 ± 4.0 and 176.0 ± 0.9°; such minor discrepancies from the ideal linear configuration have been explained on the basis of symmetry arguments in terms of variations in the population of the π^*-acceptor levels of the π-carbonyl groups.[26]

---

(20) A. F. Berndt and R. E. Marsh, *Acta Crystallogr.*, **16**, 118 (1963).

(21) M. J. Bennett, Jr., F. A. Cotton, A. Davison, J. W. Falter, S. J. Lippard, and S. M. Morehouse, *J. Amer. Chem. Soc.*, **88**, 4371 (1966).

(22) B. T. Kilbourn, U. A. Raeburn, and D. T. Thompson, *J. Chem. Soc. A*, 1906 (1969).

(23) B. Dickens and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **83**, 4862 (1961).

(24) The phenomenon of different carbon-metal-carbon bond angles in metal carbonyls has been discussed in some detail for $M(CO)_n$ (n = 1, 2, 3, and 4) groups.[25] Sufficient X-ray data were available to make structural correlations for $M(CO)_3$ groups, but not for $M(CO)_2$.

(25) S. F. A. Kettle, *J. Chem. Soc. A*, 420 (1966).

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

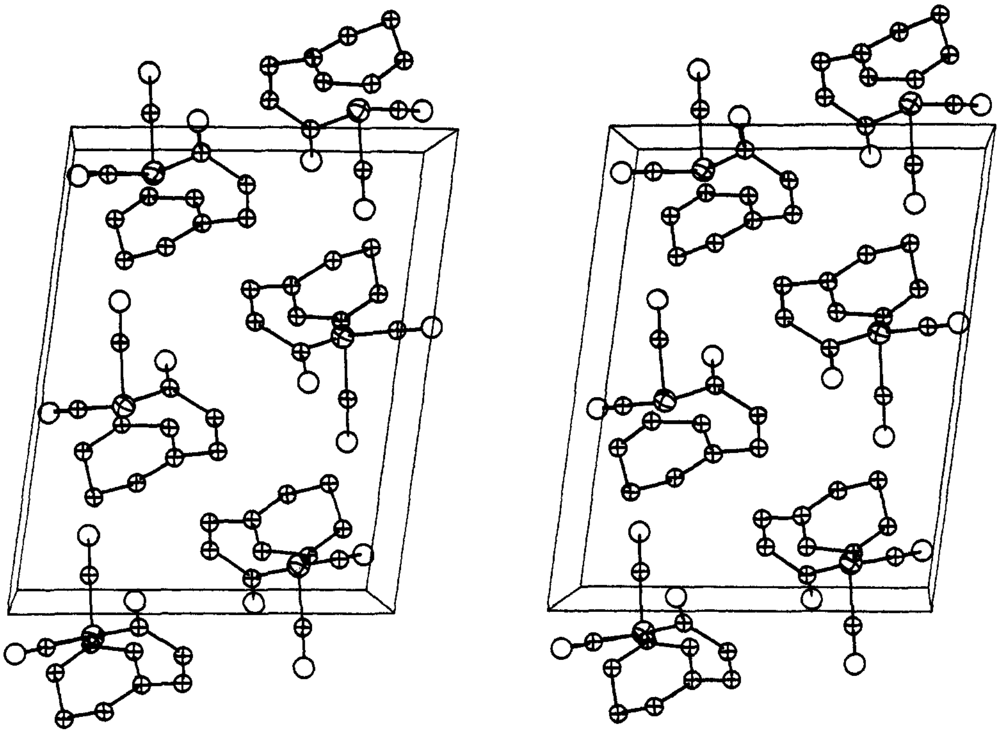


Figure 4. A stereoview of the molecular packing diagram of $C_8H_8COFe(CO)_2$ viewed down the crystallographic y axis. The origin of the unit cell was arbitrarily chosen at 0, $-{}^1/_4$, 0.

A detailed calculation[17] of all intermolecular distances revealed no unusually short contacts. Indeed, at the point of closest approach, the intermolecular distance of 2.46 Å is within 3% of the sum of the relevant van der Waals radii.[27] Stereographic representation[17] of the molecular packing is shown in Figure 4.

Infrared Spectrum. Churchill and Scholer[3] speculated that the anomalously low C–H(exo) stretching frequencies (2730–2830 cm^{-1}) observed in the infrared spectra of π-cyclohexadienyl complexes are caused by some specific ligand–transition metal atom interaction. In the present complex, the absorption band appears at 2820 cm^{-1}, which is at essentially the same frequency observed[3] for $C_6H_7Mn(CO)_3$ (2830 cm^{-1}). The only significant difference between the π-cyclohexadienyl ligands in these two complexes (*vide supra*) is a decrease in the dihedral angle between the pentadienyl and C(1)–C(6)–C(5) planes from 42° 19′ in the manganese complex[3] to 36° 16′ in the iron complex. It is difficult to meaningfully correlate this modest conformational change with the equally modest frequency change (10 cm^{-1}) in that an equally plausible interpretation could be based upon the observed differences[28] in the metal–ligand interactions. Perhaps a clue to the origin of the shift in the stretching frequency lies in the fact that the anomalous absorption band disappears entirely in the ionic iron complex[29] $[(\pi\text{-}C_6H_7)Fe(CO)_3]^+$. In any case, the results presented herein do not lend strong support to either a conformational or a metal–ligand coupling effect.

Acknowledgment. Generous financial support was received from the National Institutes of Health (Grant No. GM-148322-03) and the National Science Foundation (Grant No. GP-13085). Additional support was received through the Advanced Research Projects Agency through the use of the Central Facilities of the Materials Science Center, Cornell University.

---

(27) A. I. Kitaigorodskii, "Organic Chemical Crystallography," Consultants Bureau, New York, N. Y., 1961, p 7.

(28) We have found that in the related complex $C_8H_{10}COFe(CO)_3$, in which the side chain has been hydrogenated, the anomalous C–H(exo) stretching frequency appears at 2810 cm^{-1} (CCl_4) in its infrared spectrum. In this case, the relatively strain-free side chain would not be expected to cause any significant iron atom shift. Once again, there appears to be only a small change in frequency (10 cm^{-1}) associated with this change in metal–ligand interaction

(29) D. Jones, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4458 (1962).