Table VI. Equations of Weighted Least-Squares Planes[a] and Deviations of the Atoms from the Planes for $Pd_2(C_{17}H_{14}O)_3 \cdot CH_2Cl_2$

Atom	Distance, Å	Atom	Distance, Å
Plane through Pentadienone Group C(1)-C(5) $12.06X - 4.16Y + 1.74Z = 4.55$			
C(1)	−0.02 (2)	C(4)	−0.01 (2)
C(2)	0.02 (2)	C(5)	0.00 (2)
C(3)	0.01 (1)	O(1)	−0.00 (1)
Pd(1)	2.15[b]	Pd(2)	2.11[b]
Plane through Pentadienone Group C(6)-C(10) $7.91X + 7.97Y - 9.63Z = 1.60$			
C(6)	0.02 (3)	C(9)	0.01 (2)
C(7)	−0.02 (2)	C(10)	−0.01 (3)
C(8)	−0.00 (2)	O(2)	0.00 (1)
Pd(1)	2.15[b]	Pd(2)	2.12[b]
Plane through Pentadienone Group C(11)-C(15) $4.18X - 11.62Y + 10.63Z = -3.32$			
C(11)	−0.01 (2)	C(14)	−0.03 (2)
C(12)	0.00 (1)	C(15)	0.02 (1)
C(13)	−0.02 (2)	O(3)	0.01 (1)
Pd(1)	2.13[b]	Pd(2)	2.16[b]

[a] Least-squares planes calculated according to W. C. Hamilton, *Acta Crystallogr.*, 14, 185 (1961). Equations given in triclinic coordinates. [b] Not included in the calculation of the plane.

conformational geometries of the ligands as observed two olefin groups are directed roughly normal to the trigonal plane while the other four are much closer to the plane (Table V). A structural feature normally associated with olefin coordination to nucleophilic metals is the direction of substituents back from the olefin plane, away from the olefin-metal bond.[16,17] This is generally viewed to reflect a decrease in the C-C bond order and has been found to occur for ethylene as well as for olefins with electron-withdrawing substituents.[18] The coordinated dibenzylideneacetone ligands in both $Pd_2(DBA)_3$ and $Pd(DBA)_3$, however, show only minor deviations from planarity reflecting weak palladium-olefin bonding (Table VI). The Pd-C distances in $Pd_2(DBA)_3$ are relatively long, averaging to 2.26 (1) Å but varying significantly over values from 2.124 (12) to 2.421 (11) Å. This average value agrees well with the average Pd-C distance of 2.25 (1) Å in $Pd(DBA)_3$. These features are consistent with the observed lability of the DBA ligands in these complexes.

Acknowledgments. We wish to thank the Research Corp. and the West Virginia University Computing Center for support of this work.

Registry No. $Pd_2(DBA)_3 \cdot CH_2Cl_2$, 51364-52-4.

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 $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1891.

(18) C. D. Cook and K. Y. Wan, *J. Amer. Chem. Soc.*, 92, 2595 (1970).

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Molecular Structure of η^2-(*cis*-2,3-Dicarbomethoxymethylenecyclopropane)iron Tetracarbonyl (*cis*-Feist's Ester Iron Tetracarbonyl). An Olefin-Iron Complex Stabilized by Relief of Strain

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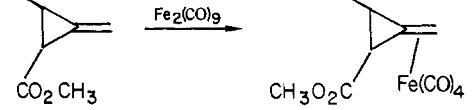
Received January 16, 1974 AIC400332

The structure of η^2-*cis*-2,3-dicarbomethoxymethylenecyclopropane)iron tetracarbonyl ($C_{12}H_{10}FeO_8$) has been determined by X-ray crystallographic techniques. The compound crystallizes in the orthorhombic space group *Pcmn*, with lattice constants $a = 7.047$ (1) Å, $b = 13.690$ (3) Å, and $c = 14.510$ (2) Å; $V = 1399.9$ (4) Å^3, $Z = 4$. Full-matrix anisotropic least-squares refinement on the diffractometer-collected intensities of 882 independent reflections resulted in a final conventional R value of 4.3%. The refined structure shows several interesting features. The iron atom is located on the same side of the three-membered ring as the ester groups, and intramolecular distances suggest substantial steric congestion between the ester carbonyl groups and the $Fe(CO)_4$ unit. Considerable rehybridization has occurred at the olefinic linkage in the three-membered ring, and the geometry around the iron atom is interpreted as being intermediate between trigonal bipyramidal and octahedral. The bonding in the complex, and its remarkable stability, are discussed in terms of relief of angle strain accompanying the rehybridization, and the mechanistic implications of the observed stereochemistry are considered.

Introduction

In a recent paper concerning the reaction of iron carbonyls with the cis and trans isomers of Feist's ester (2,3-dicarbomethoxymethylenecyclopropane, **1**), we[1] reported the isolation of two complexes to which we ascribed the structure **2**, *i.e.*, the tetracarbonyl iron complex of the corresponding olefin. Because Krull[2] had reported obtaining compounds with very similar physical properties from similar reactions, to which however he assigned a different structure, and because the structure of these small-ring species is inherently interesting, we undertook an investigation of one of our



1 2

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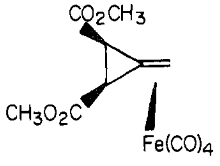
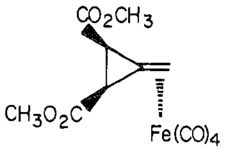
(1) T. H. Whitesides and R. W. Slaven, *J. Organometal. Chem.*, 67, 99 (1974).

(2) (a) I. S. Krull, paper presented at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1973; (b) *J. Organometal. Chem.*, 57, 363 (1973). We thank Professor Krull for a preprint of his article.

compounds by X-ray crystallographic methods. We chose the complex derived from the cis olefin, because, while equivalent bonding information could be obtained from either the cis or trans complex, we were uncertain as to the stereochemistry of the iron atom in the cis compound relative to the esters, *i.e.*, whether the species isolated was **2**-*cis,cis* or **2**-*cis,trans*. The structure we here report confirms



2-*cis,cis*



2-*cis,trans*

our original structure assignment of **2** as an (olefin)iron tetracarbonyl complex. The stereochemical assignment previously made was based on the steric requirement of the bulky $Fe(CO)_4$ moiety and certain speculative aspects of the chemistry of **2**. This stereochemistry is apparently incorrect, and the structure of the compound is unambiguously written as **2**-*cis,cis*. This structure determination, which constitutes, to our knowledge, the third (olefin)tetracarbonyliron complex X-ray structure performed, is apparently of substantially higher precision than the preceding studies[3,4] and contains the novel structural feature of an iron complexed to a species containing a strained ring.

Experimental Section

Clear crystals of **2**-*cis* were obtained by slow evaporation under nitrogen of a solution in pentane. A flat parallelepiped, centrosymmetrically bounded by the (110), (001), and (010) faces (dimensions 0.43 × 0.10 × 0.23 mm, respectively), was mounted in a Lindemann glass capillary under argon and placed on a Syntex $P\bar{1}$ autodiffractometer equipped with a graphite-monochromated Mo Kα radiation source. The preliminary Syntex routines[5] indicated a primitive orthorhombic cell with dimensions $a = 7.047$ (1), $b = 13.690$ (3), and $c = 14.510$ (2) Å; $V = 1399.9$ (4) Å^3. The *mmm* Laue symmetry and the associated lattice constants are verified in the Syntex procedure by partial rotation photographic projections along each of the three unit cell axes. The calculated density for $Z = 4$ of 1.60 g/cm^3 agrees within experimental error with the observed value of 1.59 (1) g/cm^3 (determined by flotation in carbon tetrachloride–trichloroethylene mixtures).

Data were collected at $2° \leq 2\theta \leq 45°$ in the variable-scan speed mode and reduced[6] in the usual fashion to yield 882 independent reflections for which $I > 2\sigma(I)$. Two standard peaks were monitored after every 50 reflections and indicated no evidence of crystal damage or electronic instability. The deviation of intensities of these standard reflections was about ±3% and appeared to be random. Later the data were corrected for effects of crystal absorption; a range of transmission factors from 0.79 to 0.89 (linear absorption coefficient $\mu = 11.45$ cm^{-1}) was calculated. The observed systematic absences of $0kl$ ($l = 2n + 1$) and $hk0$ ($h + k = 2n + 1$) are consistent with the centric space group *Pcmn* (nonstandard setting of *Pnma*, No. 62, $D_{2h}{}^{16}$ [7]) or its acentric equivalent $Pc2_1n$. The centric space group, chosen because of the suspected molecular symmetry, was later confirmed by the successful refinement of the structure.

Solution and Refinement of Structure

The structure was determined by classical heavy-atom methods. From the coordinates of the iron atom determined from a Patterson synthesis[8] an electron density map was calculated ($R_1 = 32.8\%$),[9] which allowed the approximate location of all nonhydrogen atoms. Several cycles of full-matrix isotropic least-squares[10] refinement resulted in $R_1 = 10.2\%$ and $R_2 = 12.5\%$. At this point, a difference map yielded peaks corresponding to the expected positions of the hydrogen atoms. Large thermal anisotropy at the iron atom was also observed.

After correction of the data for absorption, four cycles of full-matrix least-squares refinement on all coordinates, anisotropic temperature factors for all nonhydrogen atoms, and isotropic temperature factors for hydrogen atoms resulted in final $R_1 = 4.3\%$ and $R_2 = 4.9\%$. In the last cycle, the maximum shift in any nonhydrogen atom parameter was 0.15σ. The standard deviation in an observation of unit weight was 1.17. Comparison of the observed and calculated structure factor amplitudes is made in Table I.[11] The final positional and thermal parameters, with errors estimated from the full variance-covariance matrix, are given in Table II. Selected bond lengths and angles are shown in Tables III and IV.

Description of the Structure

The molecule is crystallographically constrained to C_s symmetry with the mirror plane passing through the iron, the two carbon atoms of the C=C double bond, and two of the metal carbonyl groups. The four discrete molecules in the unit cell are separated by normal van der Waals contacts (Table V). The molecular structure, in agreement with our original proposal, is seen to be that of an iron tetracarbonyl-olefin complex of *cis*-Feist's ester, in which the three-membered ring remains intact. In addition, the structure (Figure 1) shows the iron atom and the ester functions are all cis to one another, in contrast to our original assignment.

The $Fe(CO)_4$ unit is similar to those found for acrylonitrileiron tetracarbonyl[4] and (fumaric acid)iron tetracarbonyl.[3] The C–O bond lengths of the carbonyl groups are very close to 1.13 Å (average 1.130 (7) Å), which is the same within experimental error as those found in carbon monoxide (1.13 Å), $Fe(CO)_5$ (1.14 (4) Å),[12] (fumaric acid)$Fe(CO)_4$ (1.12 (6) Å), and (acrylonitrile)$Fe(CO)_4$ (1.13 (2) Å). There is a slight distortion of the C(13)–Fe–C(13)′ angle (175.1°) from linearity; the distortion is *toward* the olefin. The angle between the carbonyl groups in the mirror plane (*i.e.*, C(9)–Fe–C(11)) is 107.4 (3)°, and the angles C(3)–Fe–C(9) and C(2)–Fe–C(11) are 108.1 (2) and 104.7 (3)°, respectively. A more meaningful picture of the coordination geometry at iron is afforded by use of the midpoint (M) of the double bond as a reference. The angles C(9)–Fe–M and C(11)–Fe–M are 128.3 and 124.4°, respectively (Figure 2). The geometry at iron is intermediate between trigonal bipyramidal (TBP) and octahedral. Thus, the angle C(9)–Fe–C(11) is 12.6° smaller than 120° (expected for accurate TBP geome-

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[3] (a) C. Pedone and A. Sirigu, *Inorg. Chem.*, 7, 2614 (1968); (b) C. Pedone and A. Sirigu, *Acta Crystallogr.*, 23, 759 (1967).

[4] A. R. Luxmoore and M. R. Truter, *Acta Crystallogr.*, 15, 1117 (1962).

[5] R. A. Sparks, *et al.*, "Operations Manual. Syntex $P\bar{1}$ Diffractometer," Syntex Analytical Instruments, Cupertino, Calif., 1970.

[6] The integrated intensity (I) was calculated according to the expression $I = [S - (B_1 + B_2)/B_R]T_R$ where S is the scan counts, B_1 and B_2 are the background counts, B_R is the ratio of background time to scan time ($B_R = 0.67$ for this data set) and T_R is the 2θ scan rate in degrees per minute. The standard deviation of I was calculated as $\sigma(I) = T_R[S + (B_1 + B_2)/B_R{}^2 + q(I)^2]^{1/2}$ where q in this case was set equal to 0.003.

[7] "International Tables for X-Ray Crystallography," Vol. I, 2nd ed, Kynoch Press, Birmingham, England, 1965, p 151. The coordinates of equivalent positions for our setting of *Pcmn* were taken as $\pm[x, y, z; {}^1/_2 - x, y, {}^1/_2 + z; {}^1/_2 + x, {}^1/_2 + y, {}^1/_2 - z; -x, {}^1/_2 + y, -z]$.

[8] All crystallographic programs used in structural determination and least-squares refinement were written by J. C. C. The absorption correction program DEAR (J. F. Blount) uses the gaussian integration method of Busing and Levy. Plots were made using ORTEP (C. K. Johnson).

[9] $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100\%$ and $R_2 = [\Sigma w_i||F_o| - |F_c||^2/\Sigma w_i|F_o|^2]^{1/2} \times 100\%$.

[10] All least-squares refinements were based on the minimization of $\Sigma w_i||F_o| - |F_c||^2$ with the individual weights $w_i = 1/\sigma(F_o)^2$. Atomic scattering factors used for all nonhydrogen atoms are from H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964); those for the hydrogen atoms are from R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965). Included in the least-squares refinement was a correction for the anomalous dispersion at iron ($\Delta f' = 0.4$, $\Delta f'' = 1.0$) taken from "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 215.

[11] See paragraph at end of paper regarding supplementary material.

[12] A. W. Hanson, *Acta Crystallogr.*, 15, 930 (1962).

Table II

Positional Parameters ($\times 10^4$) for All Atoms and Isotropic Temperature Factors for Hydrogen Atoms ($\times 10^4$)[a]

Atom	*x*	*y*	*z*	*B*, Å^2
Fe	383.4 (13)	2500.0 (–)	1051.4 (6)	
C(2)	−1649 (10)	2500 (–)	0 (5)	
C(3)	211 (8)	2500 (–)	−341 (4)	
C(4)	1163 (6)	1936 (3)	−1080 (3)	
C(5)	2938 (6)	1364 (3)	−944 (3)	
O(6)	3907 (5)	1365 (3)	−275 (2)	
O(7)	3271 (5)	808 (2)	−1671 (2)	
C(8)	4862 (14)	155 (7)	−1584 (5)	
C(9)	2889 (9)	2500 (–)	1370 (4)	
O(10)	4413 (7)	2500 (–)	1580 (3)	
C(11)	−975 (10)	2500 (–)	2104 (5)	
O(12)	−1867 (8)	2500 (–)	2755 (4)	
C(13)	397 (8)	1184 (4)	999 (3)	
O(14)	427 (6)	356 (3)	967 (3)	
HC(2)	−2235 (65)	1899 (28)	−7 (31)	3.6 (11)
HC(4)	421 (52)	1685 (28)	−1495 (27)	1.9 (8)
HC(8A)	4513 (88)	−198 (51)	−1001 (47)	8.7 (19)
HC(8B)	6042 (86)	544 (45)	−1409 (41)	6.7 (19)
HC(8C)	4986 (83)	−99 (46)	−2074 (43)	6.7 (17)

Anisotropic Temperature Factors for Nonhydrogen Atoms ($\times 10^4$)[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	135.6 (18)	52.7 (6)	29.1 (4)	0 (–)	1.0 (9)	0 (–)
C(2)	153 (17)	79 (6)	39 (4)	0 (–)	−21 (6)	0 (–)
C(3)	110 (12)	52 (4)	27 (3)	0 (–)	−6 (5)	0 (–)
C(4)	165 (9)	40 (2)	31 (2)	−11 (4)	−20 (4)	−4 (2)
C(5)	174 (10)	41 (2)	32 (2)	4 (4)	5 (4)	0 (2)
O(6)	278 (10)	91 (3)	54 (2)	74 (4)	−44 (4)	−24 (2)
O(7)	316 (10)	63 (2)	36 (2)	56 (4)	−2 (3)	−9 (2)
C(8)	478 (29)	97 (6)	56 (4)	126 (11)	16 (9)	−8 (4)
C(9)	175 (17)	44 (3)	32 (3)	0 (–)	−6 (6)	0 (–)
O(10)	159 (11)	95 (4)	47 (2)	0 (–)	−28 (5)	0 (–)
C(11)	159 (16)	89 (6)	46 (4)	0 (–)	8 (7)	0 (–)
O(12)	255 (15)	163 (6)	46 (3)	0 (–)	48 (5)	0 (–)
C(13)	241 (11)	66 (3)	38 (2)	−34 (5)	0 (5)	3 (3)
O(14)	525 (14)	58 (2)	76 (3)	−51 (5)	1 (5)	5 (2)

[a] Standard deviations in least significant digits in parentheses.

Table III. Bond Lengths (Å)[a]

Fe–C(2)	2.092 (7)	C(5)–O(7)	1.322 (5)
Fe–C(3)	2.024 (5)	C(8)–O(7)	1.439 (7)
Fe–C(9)	1.825 (7)	C(9)–O(10)	1.117 (7)
Fe–C(11)	1.803 (7)	C(11)–O(12)	1.135 (8)
Fe–C(13)	1.804 (5)	C(13)–O(14)	1.134 (6)
C(2)–C(3)	1.401 (9)	C(2)–HC(2)	0.920 (38)
C(3)–C(4)	1.481 (6)	C(4)–HC(4)	0.868 (39)
C(4)–C(4)′	1.543 (8)	C(8)–HC(8A)	1.005 (68)
C(4)–C(5)	1.490 (6)	C(8)–HC(8B)	1.020 (59)
C(5)–O(6)	1.187 (5)	C(8)–HC(8C)	0.796 (62)

[a] Standard deviations in least significant digits in parentheses.

Table IV. Bond Angles (deg)[a]

Fe–C(2)–C(3)	67.5 (4)	C(5)–C(4)–HC(4)	112.9 (25)
Fe–C(3)–C(2)	72.7 (4)	C(3)–C(4)–HC(4)	115.8 (25)
Fe–C(3)–C(4)	134.0 (3)	O(7)–C(8)–HC(8A)	100.5 (39)
C(2)–C(3)–C(4)	132.8 (4)	O(7)–C(8)–HC(8B)	109.4 (35)
C(4)–C(3)–C(4)′	62.8 (4)	O(7)–C(8)–HC(8C)	106.1 (45)
C(3)–C(4)–C(4)′	58.6 (2)	HC(8A)–C(8)–HC(8B)	103.9 (51)
C(3)–C(4)–C(5)	124.0 (4)	HC(8A)–C(8)–HC(8C)	124.6 (62)
C(4)′–C(4)–C(5)	121.8 (2)	HC(8B)–C(8)–HC(8C)	111.2 (59)
C(4)–C(5)–O(6)	126.2 (4)	C(2)–Fe–C(3)	39.8 (3)
C(4)–C(5)–O(7)	110.3 (4)	C(2)–Fe–C(9)	147.9 (3)
O(6)–C(5)–O(7)	123.5 (4)	C(2)–Fe–C(11)	104.7 (3)
C(5)–O(7)–C(8)	115.2 (4)	C(2)–Fe–C(13)	88.4 (2)
Fe–C(9)–O(10)	178.8 (5)	C(3)–Fe–C(9)	108.1 (2)
Fe–C(11)–O(12)	178.5 (6)	C(3)–Fe–C(11)	144.5 (3)
Fe–C(13)–O(14)	179.3 (5)	C(3)–Fe–C(13)	87.6 (1)
Fe–C(2)–HC(2)	108.4 (29)	C(9)–Fe–C(11)	107.4 (3)
HC(2)–C(2)–HC(2)′	126.7 (58)	C(9)–Fe–C(13)	90.3 (2)
C(3)–C(2)–HC(2)	114.6 (29)	C(11)–Fe–C(13)	92.2 (2)
C(4)′–C(4)–HC(4)	113.3 (25)	C(13)–Fe–C(13)′	175.1 (3)

[a] Standard deviations in least significant digits in paraentheses.

try) and 17.4° larger than 90° (expected for accurate octahedral geometry). The other distortions in the equatorial plane likewise are in a direction consistent with this interpretation. The previously determined structures have been discussed in terms of TBP geometry, but they both show distortions similar to those determined here. Perhaps the best view of all three compounds is an intermediate structure (*vide infra*).

As in previously determined structures, the carbon–carbon bond of the olefin is substantially lengthened on coordination. The geometry of *trans*-Feist's acid has been determined[13] and is shown in Figure 3. The C=C bond length in this compound (1.32 Å) should be very close to that in uncomplexed **2**-*cis*. Thus, the bond length has increased by 0.08 Å to 1.401 (9) Å, compared to 0.06 and 0.07 Å in the acrylonitrile and fumaric acid complexes, respectively. The other striking geometric change which has taken place is tilting of C(2) out of the plane of the three-membered ring. The angle between the plane determined by C(3), C(4), and C(4)′ and the line determined by C(2)–C(3) is 37.6° (Figure 2). For pure sp^3 hybridization, this angle would be 54.8°, and for sp^2, 0°. Thus, considerable rehybridization has occurred on complexation. While direct comparison is difficult, similar distortions are seen in the case of the fumaric acid and acrylonitrile complexes.

The remainder of the cyclopropane ring shows no changes within experimental precision from the uncomplexed geometry with bond lengths of 1.481 Å (C(3)–C(4)) and 1.543 Å

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[13] (a) D. Lloyd, T. C. Downie, and J. C. Speakman, *Chem. Ind. (London)*, 222 (1954); (b) D. R. Petersen, *ibid.*, 904 (1956).

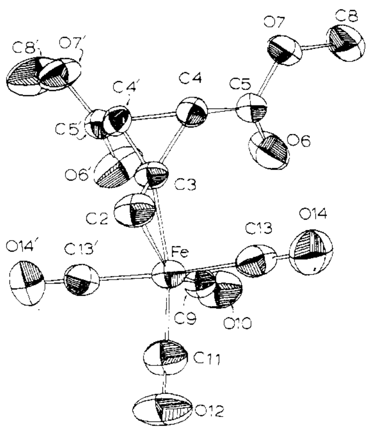


Figure 1. View of the molecular structure of **2**-*cis,cis*, showing 50% probability thermal ellipsoids. Hydrogen atoms omitted for clarity.

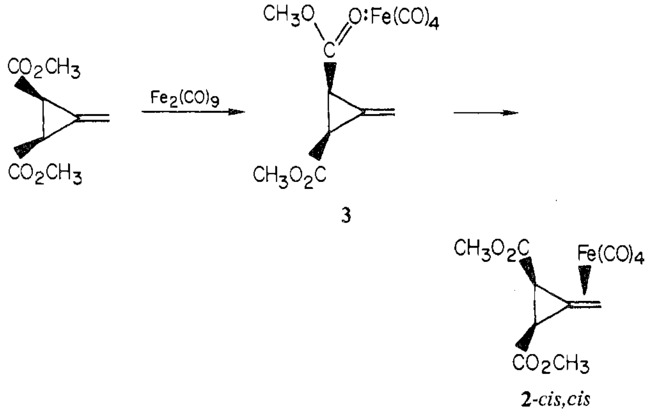
(C(4)-C(4)') and bond angles of 62.8 and 58.6°. Likewise, the ester functions show normal geometry.

There are several important intramolecular interactions (Table VI), notably between the metal carbonyl groups and the ester carbonyl oxygens O(6) and O(6)'. The smallest distances are O(6)-C(9) (2.937 Å), O(6)-O(10) (3.130 Å), and O(6)-C(13) (3.168 Å). These distances are comparable to or smaller than the sum of the van der Waals radii for carbon (1.85 Å)[14] and oxygen (1.4 Å).[14] The resulting repulsions are probably principally responsible for the somewhat greater magnitude of the M-Fe-C(9) angle relative to M-Fe-C(11).

Discussion

In view of the rather short nonbonded distances found in this molecule it is particularly surprising that the molecule has the cis,cis stereochemistry and that it displays such pronounced thermal stability. One possible explanation for the observed stereochemistry is that the initial interaction of the ligand with the metal involves one of the ester carbonyl groups (structure **3**) and that the formation of the thermodynamically more stable olefin complex occurs *via* an intramolecular transfer (Scheme I). Stereochemical direction of an iron moiety has also been observed in these laboratories in the formation of the iron-diene complex **4**.[15]

Scheme I



The other unusual feature of these iron tetracarbonyl complexes is their unusually high thermal stability. Cardaci and Narciso[16] have shown that (olefin)Fe$(CO)_4$ complexes decompose *via* a dissociative mechanism in the range 30-70° with half-lives on the order of a few hours. We have observed qualitatively that disubstituted alkylolefin complexes are considerably less stable than monosubstituted olefin complexes.[17] In contrast, complex **2** can be recovered in good yield after refluxing in hexane for 72 hr. This surprising stability is probably due to a combination of circumstances. In general, complexes with electron-withdrawing substitutents

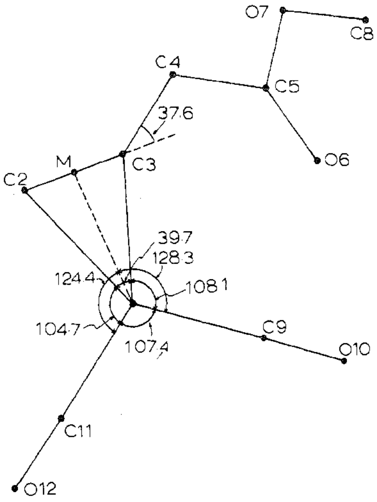


Figure 2. Schematic view of **2**-*cis,cis* projected in the crystallographic mirror plane. The axial carbonyl groups, as well as the hydrogen atoms, have been omitted.

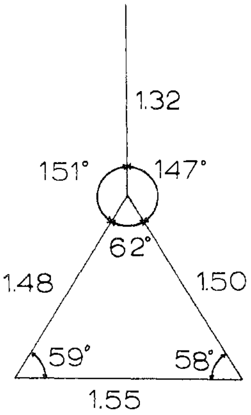


Figure 3. Relevant features of the structure of *trans*-Feist's acid taken from ref 13b.

Table V. Intermolecular Distances (Å)[a]

C(4)···O(14) (B)	3.336 (5)	O(10)···C(11) (C)	3.337 (8)
C(5)···O(14) (B)	3.341 (6)	O(10)···O(12) (C)	3.127 (8)
O(7)···O(14) (B)	3.221 (6)	O(14)···O(14) (B)	3.031 (8)

[a] Symmetry operation codes: (B) 0, −*x*, −*y*, −*z*; (C) 0, 1 + *x*, *y*, *z*.

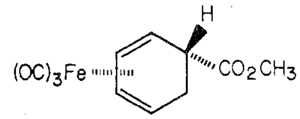


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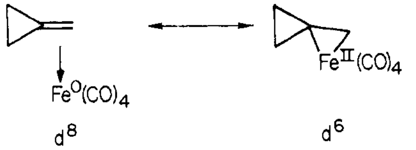
Table VI. Selected Nonbonded Intramolecular Distances (Å)

C(4)-C(9)	3.835	O(6)-C(9)	2.937
C(4)-C(13)	3.406	O(6)-C(13)	3.168
C(4)-O(10)	4.555	O(6)-O(10)	3.130
C(4)-O(14)	3.712	O(6)-O(14)	3.342
C(4)-Fe	3.235	O(6)-Fe	3.505

are more stable than those without.[16-18] Complex **2** contains two ester functions separated from the double bond by a cyclopropane ring, which might be expected to transmit electronic effects to the olefinic linkage reasonably effectively. The increased stability of electron-deficient olefin complexes is presumably due to the increased importance of the π-acceptor capabilities of the olefin ligand. In the case of **2**, another influence which increases the π-acceptor ability of the olefinic linkage is the strain associated with the incorporation of an sp^2 center in the three-membered ring. In valence-bond terms, increasing the π-acceptor component of the bond is equivalent to increasing the contribution of resonance structure **5b**. Associated with the contribution of this structure should be a distortion of the geometry of the ligand toward sp^3 hybridization at C(3) and a distortion of the coordination geometry at iron toward that characteristic of a d^6 complex (*i.e.*, octahedral). The considerable tilting of the three-membered ring away from the metal can be interpreted in terms of just such a distortion, magnified in this case by intramolecular repulsions between the ester groups and metal carbonyls. The enhanced importance of structure **5b** means that the methylenecyclopropane double bond is effectively a better π acceptor than a normal double bond. Because of the associated charge withdrawal from the metal the π-donor component of the C=C metal bond may be increased also, in order to maintain approximate charge neutrality in the system as a whole. Thus the total metal-C=C interaction is synergistically enhanced, and the complex substantially stabilized.



5a **5b**

Acknowledgment. Support by the National Science Foundation through Grant GP-16358 and a departmental instrument grant, which allowed the purchase of the automated diffractometer, is gratefully acknowledged, as is a grant for computing to R. W. S. by the Research Committee of the Graduate School of the University of Wisconsin.

Registry No. η^2-(*cis*-2,3-Dicarbomethoxymethylenecyclopropane)-iron tetracarbonyl, 51464-41-6.

Supplementary Material Available. Table I, a comparison of observed and calculated 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 $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1895.

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Molecules with an M_4X_4 Core. III.[1,2] Comparison of the X-Ray Crystallographically Determined Molecular Structures of Tetrameric Triethylphosphinecopper(I) Iodide and Triethylarsinecopper(I) Iodide

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Received January 17, 1974 AIC40038Z

The crystal and molecular structure of tetrameric triethylphosphinecopper(I) iodide, $[PEt_3CuI]_4$, has been determined and that for tetrameric triethylarsinecopper(I) iodide, $[AsEt_3CuI]_4$ (originally studied by Wells in 1936) has been accurately redetermined. The species $[PEt_3CuI]_4$ crystallizes in the noncentrosymmetric cubic space group $I\bar{4}3m$ (T_d^3; No. 217) with $a = 13.024$ (1) Å and $Z = 2$; $[AsEt_3CuI]_4$ is both isomorphous and isostructural, with $a = 13.148$ (1) Å. For each species, X-ray diffraction data complete to $2\theta = 55°$ (Mo Kα radiation) were collected with a Picker FACS-1 diffractometer and the structure was solved by conventional methods. Resulting discrepancy indices are $R_F = 3.48\%$ and $R_{wF} = 3.57\%$ for $[PEt_3CuI]_4$ (284 independent reflections) and $R_F = 4.07\%$ and $R_{wF} = 3.96\%$ for $[AsEt_3CuI]_4$ (295 independent reflections). Each of the tetrameric molecules lies on a site of T_d ($\bar{4}3m$) symmetry. The four copper and four iodine atoms, taken alternately, define the eight corners of a highly distorted "cubane" framework in which the Cu–I distance is 2.684 (1) Å for $[PEt_3CuI]_4$ and 2.677 (2) Å for $[AsEt_3CuI]_4$. The intramolecular Cu· · ·Cu distances are 2.927 (2) Å for $[PEt_3CuI]_4$ and 2.783 (2) Å (*in contrast* to the value of 2.60 Å reported by Wells) for $[AsEt_3CuI]_4$. While the Cu· · ·Cu distances in the two molecular species differ substantially, the intramolecular I· · ·I contacts are closely similar (I· · ·I = 4.380 (1) Å in $[PEt_3CuI]_4$ and 4.424 (2) Å in $[AsEt_3CuI]_4$).

Introduction

The crystal structure of tetrameric triethylarsinecopper(I) iodide, $[AsEt_3CuI]_4$, was originally reported by Wells in 1936;[3,4] the molecule was found to lie on a site of T_d ($\bar{4}3m$) symmetry and the (apparently nonbonding) copper· · ·copper distance was reported as 2.60 Å.[3,4]

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