The Crystal and Molecular Structure of Tetracarbonyl-(2-methyl-3-prop-1-ynylmaleoyl)iron(0)

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The title compound (I) is a new iron complex prepared by the photochemical reaction of $Fe(CO)_5$ and dimethyldiacetylene (DMDA) in THF. (I) crystallizes in space group $P2_1/c$ with $a=6\cdot848$ (2), $b=32\cdot396$ (8), $c=7\cdot361$ (2) Å, $\beta=128\cdot91$ (2)°, $Z=4$. The structure was solved by Patterson and Fourier phasing methods, and refined by block-diagonal least-squares calculations to a weighted R value of $0\cdot059$ and an unweighted R value of $0\cdot042$. The Fe coordination is a distorted octahedron and consists of four carbonyl groups and a bidentate maleoyl group. The axial carbonyl groups are tilted slightly ($\sim 7°$) toward the plane of the ferrole ring. The two C atoms of the ferrole ring not coordinated to the Fe atom have a methyl and a prop-1-ynyl group bonded to them, respectively.

Introduction

There are numerous compounds known to result from the reaction of transition metal carbonyl complexes with acetylenes, and many of these have been characterized by X-ray crystallography (Bowden & Lever, 1968). One type of complex resulting from such reactions that has received only scant attention is the metal maleoyls. The structure of a rhodium maleoyl complex has been briefly noted (Mague, Nutt & Gause, 1973), and maleoyl complexes of iridium have recently been inferred from analytical, spectral, and chemical data (Canziani, Malatesta & Longoni, 1975). A prelimininary report (Pettersen, Cihonski, Young & Levenson, 1975) has presented the preparation and structure of tetracarbonyl-(2-methyl-3-prop-1-ynyl-maleoyl)iron(0) (I). The detailed structure of (I) is presented here as an aid in the understanding of the bonding in metal–maleoyl complexes.

Experimental

(I) was synthesized by the photochemical reaction of dimethyldiacetylene (DMDA) with $Fe(CO)_5$ in THF. Red-orange crystals of $(DMDA)Fe(CO)_6$ were grown from an acetonitrile solution at $-10°C$. The crystals were very well formed hexagonal prisms, and one of a suitable size was obtained for the X-ray analysis by cutting a large one with a razor blade.

Crystal data are given in Table 1. Accurate cell dimensions were obtained by a least-squares refinement of carefully measured 2θ values for 49 independent reflections. The molecular formula was originally thought to contain five CO groups, but several consistent density measurements and the unit-cell constants indicated a sixth CO group to be present. This was subsequently verified by the structure determination. Unit-cell data and subsequent intensity measurements were obtained with a General Electric XRD-7 quarter-circle manual diffractometer using Mo X-rays (Mo $K\alpha=0\cdot71069$ Å). The take-off angle for the cell data was $1\cdot0°$, and for the intensity data $5\cdot0°$. Intensity measurements were made by the stationary-crystal stationary-counter method using balanced Zr and Y filters. 10 s counts were taken with a scintillation counter for each of the filters. 1197 independent reflections were measured ($2\theta_{max}=40\cdot00°$; $(\sin \theta/\lambda)_{max}=0\cdot4813$). The intensities of five reflections were periodically measured during the course of data collection to monitor crystal alignment and/or decomposition. No significant variation was noted from these measurements. The data were corrected for Lorentz and polarization effects by the program *INCON* (Davis, 1965). No absorption corrections were made. A background correction for the scattered Mo $K\alpha$ radiation was determined as a function of 2θ using the Zr filter and added directly onto the Y filter measurements. The criterion for a reflection to be used for the structure analysis was taken as:

$$[I_{Zr}-2\sigma(I_{Zr})]-[I_Y+2\sigma(I_Y)]\geq 100$$ counts where I_{Zr} and I_Y are the measured counts for the Zr and Y filters respectively, and $\sigma(I_{Zr})$ and $\sigma(I_Y)$ are the usual standard deviations from counting statistics. A total of 997 reflections met this criterion. A weight w was assigned to each reflection where $w=1/[\sigma(F_o)]^2$ and

$$\sigma(F_o)=\tfrac{1}{2}\left[(LP)^{-1}\cdot\frac{I_{Zr}+I_Y+(KI_{Zr})^2}{I_{Zr}-I_Y}\right]^{\frac{1}{2}}.$$

Table 1. *Crystal data*

$C_{12}H_6O_6Fe$	F. W. 302·0
Space group $P2_1/c$	Systematic absences
$a=6\cdot848$ (2) Å	$h0l$: $l=2n+1$
$b=32\cdot396$ (8)	$0k0$: $k=2n+1$
$c=7\cdot361$ (2)	$Z=4$
$\beta=128\cdot91$ (2)°	$D_c=1\cdot58$ g cm^{-3}
$V=1270\cdot9$ Å^3	$D_m=1\cdot57$ g cm^{-3} (flotation, aqueous KI)
$\mu=12\cdot3$ cm^{-1}	
(Mo $K\alpha$ radiation)	Crystal size: $0\cdot64\times0\cdot54\times0\cdot27$ mm
	Crystal shape: hexagonal prism

LP is the Lorentz–polarization factor and K, an empirical instrumental factor, was assigned a value of 0·03.

Structure determination

Coordinates for the single Fe atom were readily deduced from a sharpened Patterson map. The remaining structure was determined by Fourier phasing methods and subsequently refined by block-diagonal least-squares calculations. The function minimized in the refinement is $\sum w(|F_o| - |F_c|)^2$ where w is the weight, and $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes respectively. Scattering factors for neutral atoms and the dispersion corrections for Fe were taken from *International Tables for X-ray Crystallography* (1974). Positions for the six H atoms were determined in the latter stages of refinement by means of a difference Fourier synthesis. The final least-squares refinement included coordinates of all 25 atoms and anisotropic temperature factors for the 19 non-hydrogen atoms. Isotropic B's of 7·5 were held fixed for the six H atoms. The final agreement indices are $R = 0·042$ and $R_w = 0·059$ where $R = \sum |F_o| - |F_c|| / \sum F_o$ and $R_w = [\sum w|F_o - |F_c||^2 / \sum w F_o]^{1/2}$. The error in an observation of unit weight, defined as $[\sum w|F_o - |F_c||^2 / (M - S)]^{1/2}$ is 2·81. M is the number of observations (997) and S is the number of refined parameters (190). The parameter shifts on the final cycle of least-squares refinement were all less than one standard deviation and nearly all were of the order of 0·1σ or less. A final difference map showed no peaks over

0·3 e Å^{-3}. Table 2 lists the atomic coordinates and thermal parameters along with the estimated standard errors.*

Discussion

Fig. 1 is a perspective view of the refined structure (Johnson, 1965). Bond lengths and angles are listed in Table 3. The average of the six C–H bond distances is 0·96 Å with a standard deviation of 0·09 Å. The average H–C–H valency angle is $104 \pm 11°$ and the average C–C–H valency angle is $114 \pm 4°$.
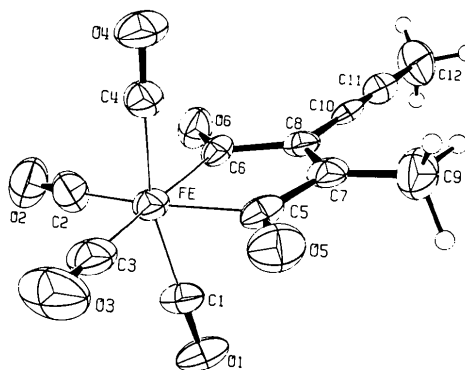

Fig. 1. A perspective view of tetracarbonyl-(2-methyl-3-prop-1-ynylmaleoyl)iron(0).

Table 2. *Fractional coordinates and thermal parameters with estimated standard deviations in parentheses*

The anisotropic thermal parameters U_{ij} are the mean-square amplitudes of vibration in Å. They are introduced into the structure factor expression as $T = \exp[-2\pi^2(U_{11}h^2a^{2*} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. The U_{ij} have been multiplied by 10^4.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	0·1854 (1)	0·4187 (1)	0·3610 (1)	380 (4)	350 (5)	595 (5)	−9 (7)	370 (9)	22 (8)
C(1)	0·4509 (10)	0·4400 (1)	0·3885 (9)	432 (35)	435 (39)	555 (41)	−27 (55)	337 (68)	93 (57)
C(2)	0·3156 (11)	0·4323 (1)	0·6633 (11)	593 (43)	447 (39)	769 (49)	−41 (63)	491 (82)	−105 (64)
C(3)	−0·0075 (10)	0·4649 (1)	0·2168 (11)	492 (39)	523 (42)	875 (50)	−55 (64)	506 (80)	23 (70)
C(4)	−0·0723 (10)	0·3881 (1)	0·2962 (10)	418 (35)	404 (36)	603 (41)	−15 (57)	368 (68)	−4 (61)
C(5)	0·0828 (9)	0·3952 (1)	0·0557 (9)	338 (32)	514 (39)	455 (36)	−74 (55)	293 (59)	25 (58)
C(6)	0·3740 (9)	0·3650 (1)	0·4840 (9)	310 (32)	404 (35)	445 (35)	0 (53)	293 (61)	6 (54)
C(7)	0·1920 (9)	0·3536 (1)	0·0818 (9)	331 (31)	400 (36)	516 (36)	−84 (53)	311 (60)	−17 (55)
C(8)	0·3409 (9)	0·3383 (1)	0·2993 (9)	321 (31)	315 (32)	490 (35)	−8 (53)	297 (57)	65 (54)
C(9)	0·1327 (11)	0·3333 (2)	−0·1286 (10)	590 (43)	754 (49)	531 (42)	−90 (73)	362 (74)	−112 (70)
C(10)	0·4686 (9)	0·3001 (1)	0·3653 (9)	451 (35)	442 (37)	585 (39)	−120 (56)	456 (66)	−64 (58)
C(11)	0·5883 (11)	0·2689 (1)	0·4346 (10)	626 (40)	423 (37)	662 (42)	−46 (65)	507 (74)	−37 (64)
C(12)	0·7399 (12)	0·2315 (2)	0·5230 (12)	806 (50)	440 (42)	822 (50)	188 (71)	550 (89)	0 (71)
O(1)	0·6050 (7)	0·4532 (1)	0·3948 (7)	484 (25)	822 (33)	711 (29)	−161 (47)	425 (49)	103 (50)
O(2)	0·4025 (9)	0·4384 (1)	0·8500 (8)	897 (36)	899 (38)	853 (36)	−78 (58)	680 (64)	−215 (56)
O(3)	−0·1321 (9)	0·4931 (1)	0·1163 (10)	809 (36)	563 (34)	1700 (53)	243 (53)	803 (75)	381 (66)
O(4)	−0·2297 (7)	0·3682 (1)	0·2559 (8)	556 (28)	666 (30)	957 (36)	−156 (46)	562 (57)	−32 (50)
O(5)	−0·0515 (8)	0·4127 (1)	−0·1300 (7)	629 (29)	681 (31)	549 (28)	0 (45)	344 (49)	140 (44)
O(6)	0·5013 (7)	0·3536 (1)	0·6834 (6)	664 (28)	522 (27)	517 (25)	117 (41)	421 (47)	73 (40)
H(1)	−0·033 (10)	0·330 (2)	−0·245 (9)	7·5 (0)					
H(2)	0·214 (10)	0·306 (2)	−0·091 (10)	7·5 (0)					
H(3)	0·229 (11)	0·349 (1)	−0·173 (10)	7·5 (0)					
H(4)	0·689 (11)	0·212 (1)	0·425 (10)	7·5 (0)					
H(5)	0·750 (11)	0·216 (2)	0·631 (10)	7·5 (0)					
H(6)	0·940 (11)	0·238 (2)	0·644 (10)	7·5 (0)					

Table 3. *Bond lengths* (Å) *and valency angles* (°)
with estimated standard errors in parentheses

Fe——C(1)	1·833 (8)	C(5)—O(5)	1·206 (7)
Fe——C(2)	1·857 (8)	C(6)—O(6)	1·201 (7)
Fe——C(3)	1·829 (6)	C(5)—C(7)	1·494 (9)
Fe——C(4)	1·808 (7)	C(6)—C(8)	1·502 (10)
Fe——C(5)	2·035 (7)	C(7)—C(8)	1·340 (8)
Fe——C(6)	2·012 (5)	C(7)—C(9)	1·485 (11)
C(1)-O(1)	1·112 (10)	C(8)—C(10)	1·414 (8)
C(2)-O(2)	1·120 (10)	C(10)-C(11)	1·195 (8)
C(3)-O(3)	1·148 (8)	C(11)-C(12)	1·457 (9)
C(4)-O(4)	1·124 (9)		

C(1)-Fe——C(2)	94·7 (3)	Fe——C(3)—O(3)	176·7 (8)
C(1)-Fe——C(3)	93·5 (3)	Fe——C(4)—O(4)	178·2 (6)
C(1)-Fe——C(4)	166·3 (3)	Fe——C(5)—O(5)	124·4 (5)
C(1)-Fe——C(5)	83·9 (3)	Fe——C(6)—O(6)	125·7 (5)
C(1)-Fe——C(6)	87·9 (3)	Fe——C(5)—C(7)	113·4 (4)
C(2)-Fe——C(3)	97·5 (3)	Fe——C(6)—C(8)	113·6 (4)
C(2)-Fe——C(4)	95·8 (4)	O(5)—C(5)—C(7)	122·2 (7)
C(2)-Fe——C(5)	170·1 (3)	O(6)—C(6)—C(8)	120·7 (5)
C(2)-Fe——C(6)	88·7 (3)	C(5)—C(7)—C(8)	115·5 (6)
C(3)-Fe——C(4)	93·8 (3)	C(5)—C(7)—C(9)	118·6 (5)
C(3)-Fe——C(5)	92·4 (3)	C(8)—C(7)—C(9)	125·9 (6)
C(3)-Fe——C(6)	173·6 (3)	C(6)—C(8)—C(7)	116·0 (5)
C(4)-Fe——C(5)	84·3 (3)	C(6)—C(8)—C(10)	118·9 (5)
C(4)-Fe——C(6)	83·6 (3)	C(7)—C(8)—C(10)	125·2 (6)
C(5)-Fe——C(6)	81·5 (2)	C(8)—C(10)—C(11)	175·8 (5)
Fe——C(1)-O(1)	176·9 (5)	C(10)-C(11)-C(12)	178·6 (6)
Fe——C(2)-O(2)	175·8 (6)		

The Fe coordination is a distorted octahedron. The two axial carbonyl groups are oriented toward the ferrole ring, each making an angle of about 7° with the normal to the ring plane. The ferrole ring is highly planar and the deviations from the best least-squares plane containing atoms Fe, C (5), C (6), C (7) and C (8) are listed in Table 4. The five torsional angles of the ferrole ring are calculated to be 0·0°.

Table 4. *Deviations from the best least-squares plane*
containing the atoms of the ferrole ring [Fe, C(5),
C(6), C(7) *and* C(8)]

Fe	0·001 Å	C(7)	0·003 Å	O(1)	−2·921 Å
C(1)	−1·821	C(8)	−0·002	O(2)	−0·060
C(2)	−0·033	C(9)	−0·010	O(3)	0·111
C(3)	0·069	C(10)	−0·031	O(4)	2·900
C(4)	1·791	C(11)	−0·100	O(5)	−0·017
C(5)	−0·002	C(12)	−0·215	O(6)	0·014
C(6)	0·000				

The ferrole ring can be viewed as a bidentate maleoyl group complexed to the Fe. The bond corresponding to the C–C double bond of maleic acid retains its double-bond character [C(7)–C (8) = 1·340 (8) Å] in the

complex, a fact also noted in the X-ray structures of various maleate salts (Gupta, Prasad & Gupta, 1975; Gupta, Prasad & Yadav, 1972). The presence of the propynyl group attached to C(8) has no unusual effects and the various bond lengths are in very good agreement with those in the summary tables of *Molecular Structures and Dimensions* (Kennard, Watson, Allen, Isaacs, Motherwell, Pettersen & Town, 1972). The molecule is similar to the tetracarbonylperfluoro-butadieneiron(0) complex, $C_4F_6Fe(CO)_4$ (Hitchcock & Mason, 1967). The Fe atom of this complex was reported to be closely octahedral and the ferrole ring to be planar (± 0.02 Å). A rhodium–maleoyl complex has been reported, although details of the structure analysis have not yet been published. The complete structural formula of this compound is

$$(AsPh_3)_2ClRhCOC(CF_3){=}C(CF_3)\overline{CO}.2C_6H_6 \quad (\text{Mague},$$

Nutt & Gause, 1973).

The molecules are held together in the crystal lattice by van der Waals forces and most of the shorter intermolecular distances result from unit-cell translations along either **a** or **c** or both.

References

BOWDEN, F. L. & LEVER, A. B. P. (1968). *Organomet. Chem. Rev.* **3**, 227–279.

CANZIANI, F., MALATESTA, M. C. & LONGONI, G. (1975). *Chem. Commun.* pp. 267–268.

DAVIS, R. E. (1965). *INCON* 2, *a Fortran* IV *Program for I to F Conversion.* Unpublished.

GUPTA, M. P., PRASAD, S. M. & GUPTA, T. N. P. (1975). *Acta Cryst.* **B31**, 37–40.

GUPTA, M. P., PRASAD, S. M. & YADAV, B. (1972). *Cryst. Struct. Commun.* **1**, 211–213.

HITCHCOCK, P. B. & MASON, R. (1967). *Chem. Commun.* pp. 242–243.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP.* Oak Ridge National Laboratory Report ORNL-3794.

KENNARD, O., WATSON, D. G., ALLEN, F. H., ISAACS, N. W., MOTHERWELL, W. D. S., PETTERSEN, R. C. & TOWN, W. G. (1972). *Molecular Structures and Dimensions. Organic and Organometallic Crystal Structures*, Vol. A1, p. S2. Utrecht: Oosthoek.

MAGUE, J. T., NUTT, M. O. & GAUSE, E. H. (1973). *J. Chem. Soc. Dalton*, pp. 2578–2587.

PETTERSEN. R. C., CIHONSKI, J. L., YOUNG, F. R. III & LEVENSON, R. A. (1975). *Chem. Commun.* pp. 370–371.