Reactions of Co-ordinated Ligands.   Part XIII.[1]   Ring Opening of 2,3-Bis-(hydroxymethyl)methylenecyclopropane   with   Nonacarbonyldi-iron: Molecular and Crystal Structures of Tricarbonyl-η^4-[3-methylene-*endo*-4-vinyldihydrofuran-2(3*H*)-one]iron(o)   and   Tetracarbonyl-η^2-[3-methyl-ene-*exo*-4-vinyldihydrofuran-2(3*H*)-one]iron(o)

By **Barbara M. Chisnall, Michael Green,** * **Russell P. Hughes,** and **Alan J. Welch,** Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS

trans- or *cis*-2,3-Bis(hydroxymethyl)methylenecyclopropanes react with [Fe$_2$(CO)$_9$] to produce tricarbonyl-η^4-[3-methylene-*endo*-4-vinyldihydrofuran-2(3*H*)-one]iron(0) and tetracarbonyl-η^2-[3-methylene-*exo*-4-vinyldihydrofuran-2(3*H*)-one]iron(0). The structural identities of these two complexes have been established by the analysis of single-crystal *X*-ray data recorded on a four-circle diffractometer.

The tricarbonyl complex is triclinic, space group $P\bar{1}$, with $a = 7.745(5)$, $b = 6.787(3)$, $c = 9.873(4)$ Å, $\alpha = 96.46(3)$, $\beta = 86.79(4)$, $\gamma = 94.05(4)°$, and $Z = 2$. Full-matrix least-squares refinement using 1 435 independent observed reflections has converged to $R = 0.029$, R_w 0.031. The metal co-ordination geometry approximates to that of a square pyramid with the alkene fragments in *cis*-equatorial positions.

Four molecules of the tetracarbonyl crystallise in the monoclinic space group $P2_1/a$ with $a = 12.419(4)$, $b = 6.527(1)$, $c = 15.321(4)$ Å, $\beta = 91.21(2)°$. The model has been refined to R 0.041, R_w 0.044 for 1 679 reflections. In this complex the Fe(CO)$_4$ moiety is attached to the opposite side of the organic fragment *via* the rigid alkene function, which occupies one equatorial site of a trigonal bipyramidal co-ordination geometry.

Analogous reactions of *trans*-2,3-bis(dideuteriohydroxymethyl)methylenecyclopropane and *trans*-2,3-dideuterio-2,3-bis(hydroxymethyl)methylenecyclopropane with [Fe$_2$(CO)$_9$] yield analogous deuteriated iron complexes with no deuterium scrambling. ^{1}H and ^{13}C N.m.r. spectra are reported and a plausible mechanism is presented.

THE reactions of methylenecyclopropane and its sub-stituted derivatives with transition-metal systems have provided considerable insight into the mechanisms of
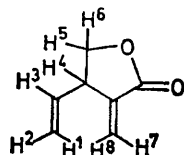
metal-promoted opening reactions of cyclopropane rings.[2]   Both *trans*- and *cis*-2,3-dimethoxycarbonyl-methylenecyclopropane, (1a) and (1b) respectively, have

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[1] Part XII, R. Goddard, M. Green, R. P. Hughes, and P. Woodward, preceding paper.

[2] M. Green and R. P. Hughes, *J.C.S. Chem. Comm.*, 1974, 686, and references cited therein; *J.C.S. Dalton*, 1976, 1880.

been shown to form a variety of stable η^2-bonded olefin complexes with Rh^I, Ir^I, Pt^0, Pt^{II},[2,3] and Fe^0 [4] species, in which the cyclopropane ring remained intact. Such complexes proved to have remarkable thermal stability; the ring-opening process. The factors affecting both the facility and direction of cleavage of methylenecyclopropane bonds by Fe^0 species are, therefore, at best, only tenuously defined.

TABLE 1

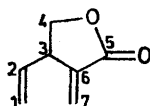^{1}H N.m.r. data for complexes (3) and (4) (CDCl$_3$, 34 °C, 100 MHz)

τ(multiplicity); J(Hz)

Complex	H^1	H^2	H^3	H^4	H^5	H^6	H^7	H^8
(3a)	8.58(d) $J_{1,2}=13$	8.10(d) $J_{2,3}=7$	6.46(m) $J_{1,3}=13$ $J_{2,3}=7$ $J_{3,4}=3$	6.78(m) $J_{4,5}=5$ $J_{4,6}=9$	5.29(dd) $J_{4,5}=5$ $J_{5,6}=10$	5.11(dd) $J_{5,6}=10$ $J_{4,6}=9$	8.12(d) $J_{7,8}=3$	8.78(d) $J_{7,8}=3$
(3b)			6.46(d) $J_{3,4}=3$	6.78(d) $J_{3,4}=3$			8.12(d) $J_{7,8}=3$	8.78(d) $J_{7,8}=3$
(3c)	8.58(s)	8.10(s)			5.29(d) $J_{5,6}=10$	5.11(d) $J_{5,6}=10$	8.12(d) $J_{7,8}=3$	8.12(d) $J_{7,8}=3$
(4a)	4.97(d) $J_{1,2}=17$	4.90(d) $J_{2,3}=10$	4.12(m) $J_{1,3}=17$ $J_{2,3}=10$ $J_{3,4}=8$	7.04(dd) $J_{3,4}=8$ $J_{4,6}=6$	5.69(d) $J_{5,6}=9$	5.33(dd) $J_{5,6}=9$ $J_{4,6}=6$	6.95(d) $J_{7,8}=3$	7.30(d) $J_{7,8}=3$
(4b)			4.12(d) $J_{3,4}=8$	7.04(d) $J_{3,4}=8$			6.95(d) $J_{7,8}=3$	7.30(d) $J_{7,8}=3$
(4c)	4.97(s)	4.90(s)			5.69(d) $J_{5,6}=9$	5.33(d) $J_{5,6}=9$	6.95(d) $J_{7,8}=3$	7.30(d) $J_{7,8}=3$

in particular the iron complexes (2a) and (2b) rearranged only slowly in refluxing toluene to yield substituted [Fe(CO)$_3$(1,3-diene)]] complexes, via cleavage of the 1,2-bond of the cyclopropane ring.[4]

It has been previously demonstrated that complexation of (1a) and (1b) to Pd^{II} is followed rapidly by ring-opening across the 1,2-bond, provided that a nucleophile is available, either as a ligand on the metal, or as an

TABLE 2

^{13}C N.m.r. data for complexes (3) and (4)^a (CDCl$_3$, 34°, 25.15 MHz)

δ(p.p.m. downfield from internal SiMe$_4$)

Complex	C^1	C^2	C^3	C^4	C^5	C^6	C^7	Carbonyl ligands
(3a)	54.12	35.86	44.23	71.04	177.47	22.63	36.83	211.13
(3b)		35.86	44.23		177.47	22.63	36.83	211.13
(3c)	54.12			71.04	177.47	22.63	36.83	211.13
(4a)	115.94	138.03	49.75	69.65	178.61	59.15	32.82	206.59
(4b)		138.03	49.75		178.61	59.15	32.82	206.59
(4c)	115.94			61.65	178.61	59.15	32.82	206.59

^{a} Assignments were confirmed using off-resonance decoupling techniques.

In contrast, 2,2-diphenylmethylenecyclopropane, and 2-phenylmethylenecyclopropane have been shown to react smoothly with [Fe$_2$(CO)$_9$] to produce substituted [Fe(CO)$_3$(trimethylenemethane)]] complexes, via cleavage of the 2,3-bond of the cyclopropane ring.[5] No η^2-bonded complexes analogous to (2a) and (2b) were observed, though they were presumably intermediates in

external solvent molecule, to attack the co-ordinated olefin and thereby generate a cyclopropylmethyl-metal intermediate.[2] This paper reports an analogous reaction, in which the initial nucleophile is incorporated into the methylenecyclopropane structure itself, and the structural characterisation of the products by spectroscopic

[3] M. Green, J. A. K. Howard, R. P. Hughes, S. C. Kellet, and P. Woodward, J.C.S. Dalton, 1975, 2007.

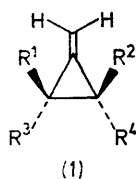[4] T. H. Whitesides and R. W. Slaven, J. Organometallic Chem., 1974, 67, 99.

[5] R. Noyori, T. Nishigama, and H. Takaya, Chem. Comm., 1969, 89.

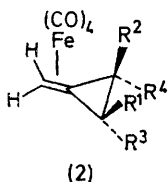and crystallographic methods. A preliminary account of some of this work has appeared.[6]

RESULTS

trans-2,3-Bis(hydroxymethyl)methylenecyclopropane (1c) reacted smoothly (16 h, 20 °C) with an excess of $[Fe_2(CO)_9]$ in diethyl ether under an atmosphere of carbon monoxide, to yield two organo-iron complexes which were easily separated by column chromatography.
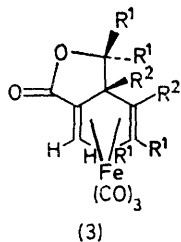
The major product isolated as air-stable orange crystals [48% yield based on (1c)] was shown by microanalysis, mass spectrometry, and i.r. spectroscopy (see Experimental section) to be a tricarbonyliron complex of empirical formula $[Fe(CO)_3(C_7H_8O_2)]$. The i.r. spectrum also exhibited a medium intensity band at 1 760 cm^{-1} (hexane), characteristic of an ester carbonyl function. The ^1H (Table 1) and ^{13}C (Table 2) n.m.r. spectra showed that all the protons and all the carbons of the organic ligand were non-equivalent, indicating an unsymmetrical structure.
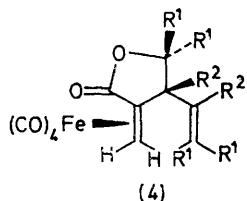
a : $R^1=R^4=CO_2Me$; $R^2=R^3=H$
b : $R^1=R^2=CO_2Me$; $R^3=R^4=H$
c : $R^1=R^4=CH_2OH$; $R^2=R^3=H$
d : $R^1=R^2=CH_2OH$; $R^3=R^4=H$
e : $R^1=R^4=CD_2OH$; $R^2=R^3=H$
f : $R^1=R^4=CH_2OH$; $R^2=R^3=D$

(1)

a : $R^1=R^4=CO_2Me$; $R^2=R^3=H$
b : $R^1=R^2=CO_2Me$; $R^3=R^4=H$
c : $R^1=R^4=CH_2OH$; $R^2=R^3=H$
d : $R^1=R^2=CH_2OH$; $R^3=R^4=H$
e : $R^1=R^4=CD_2OH$; $R^2=R^3=H$
f : $R^1=R^4=CH_2OH$; $R^2=R^3=D$

(2)

a : $R^1=R^2=H$
b : $R^1=D$; $R^2=H$
c : $R^2=D$; $R^1=H$

(3)

a : $R^1=R^2=H$
b : $R^1=D$; $R^2=H$
c : $R^2=D$; $R^1=H$

(4)

The minor product, isolated as pale yellow crystals (30%), was slightly more air-sensitive than the orange material, and was shown by an identical combination of physical methods to be a tetracarbonyliron complex of empirical formula $[Fe(CO)_4(C_7H_8O_2)]$. The presence of a medium intensity i.r. band at 1 756 cm^{-1}, and similarities

[6] M. Green, R. P. Hughes, and A. J. Welch, *J.C.S. Chem. Comm.*, 1975, 487.

between the ^1H and ^{13}C n.m.r. spectra of the two complexes, suggested that both complexes contained an identical ligand $C_7H_8O_2$, though bonded differently to the metal in each complex.

However, no single, unambiguous structure could be assigned to either complex on the basis of the available spectroscopic data. Accordingly, both complexes were subjected to a single crystal X-ray diffraction study.

The X-ray analysis of the orange tricarbonyl complex showed it to be (3a), the overall structure of which is shown in Figure 1.

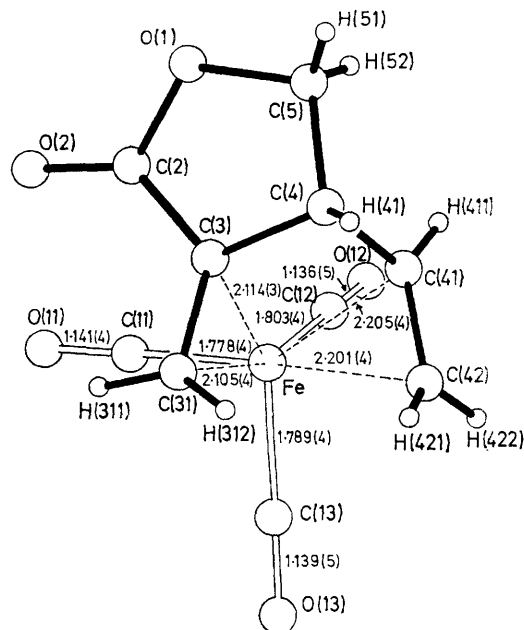FIGURE 1 Perspective view of the η^4-furanone iron tricarbonyl complex

Similarly, the X-ray analysis of the yellow tetracarbonyliron complex showed it to be (4a), the overall structure of which is shown in Figure 2.

Both complexes crystallise as discrete, neutral, monomer molecules (with neither effective nor space-group required
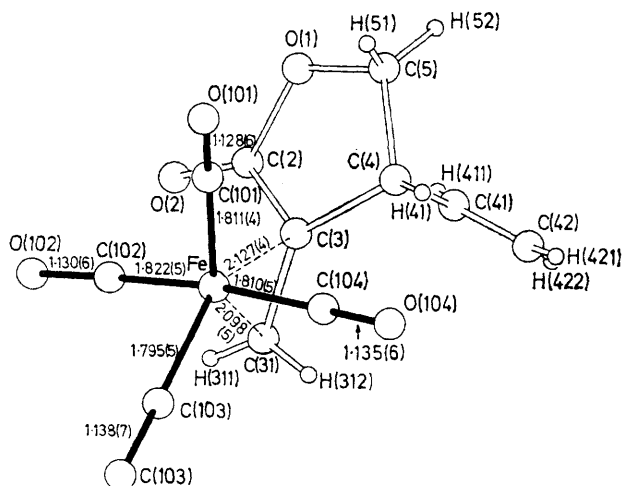

FIGURE 2 Perspective view of the η^2-furanone iron tetracarbonyl complex

symmetry). Note that we have employed separate carbonyl group numbering schemes to avoid any implication of an inter-relationship.

Fe–C and FeC–O distances (Å, uncorrected for thermal effects) appear on the Figures. Fe–C–O and the metal co-ordination angles [utilising, where necessary, Z(3) and Z(4), the mid-points of the C(3)–C(31) and C(41)–C(42) alkene fragments] appear in Table 3. Distances and angles

TABLE 3

Fe–C–O and metal co-ordination angles (°) *

(A) Tricarbonyl complex (3a)

Angle	Theoretical, TBP [a]	Complex, (3a)	Theoretical, SP [b]
C(13)–Fe–C(12)	120.0	105.1(2)	>90.0
C(13)–Fe–Z(3) [c]	120.0	111.0(2)	>90.0
Z(3)–Fe–C(12)	120.0	143.9(2)	<180.0
C(11)–Fe–C(12)	90.0	87.2(2)	<90.0
C(11)–Fe–C(13)	90.0	96.1(2)	>90.0
C(11)–Fe–Z(3)	90.0	91.2(2)	<90.0
Z(4) [d]–Fe–C(12)	90.0	90.8(2)	<90.0
Z(4)–Fe–C(13)	90.0	100.3(2)	>90.0
Z(4)–Fe–Z(3)	90.0	80.9(2)	<90.0
Z(4)–Fe–C(11)	180.0	163.5(2)	<180.0

Also Fe–C(11)–O(11)		177.3(3)
Fe–C(12)–O(12)		176.7(4)
Fe–C(13)–O(13)		178.2(3)

(B) Tetracarbonyl complex (4a)

Atoms	Angle	Atoms	Angle
Fe–C(101)–O(101)	178.2(4)	C(102)–Fe–C(104)	176.5(2)
Fe–C(102)–O(102)	175.0(4)	C(102)–Fe–C(101)	90.1(2)
Fe–C(103)–O(103)	179.2(5)	C(102)–Fe–C(103)	88.0(3)
Fe–C(104)–O(104)	178.2(4)	C(102)–Fe–Z(3)	91.7(3)
Z(3) [e]–Fe–C(101)	126.6(3)	C(104)–Fe–C(101)	91.2(2)
C(101)–Fe–C(103)	109.1(2)	C(104)–Fe–C(103)	88.5(3)
C(103)–Fe–Z(3)	123.8(3)	C(104)–Fe–Z(3)	90.2(3)

[a] Trigonal bipyramidal geometry, C(11) and Z(4) axial. [b] Square pyramidal geometry, C(13) axial. [c,d] Z(3) and Z(4), the mid point of C(3)–C(31) and C(41)–C(42), have fractional co-ordinates 0.1185(4), 0.4395(6), 0.3399(3), and 0.1174(6), 0.0643(6), 0.2565(4) respectively. [e] For the tetracarbonyl, Z(3) has fractional co-ordinates 0.1135(4), 0.1067(9), and 0.2948(3).

* Estimated standard deviations are given in parentheses throughout this paper.

within the organic ligands may be found on the schematic Figures 3 and 4.

The Metal Co-ordination.—The tricarbonyl complex (3a) is unique in that it represents the first example of an η^4-1,4-diene of iron(0) in which the alkene units are not incorporated into a ring system.

The co-ordination geometry of the metal atom, although strictly intermediate between square pyramidal [SP, C(13) axial] and trigonal bipyramidal [TBP, C(11) and Z(4) axial], is somewhat closer to the former (Table 3). Both alkene fragments bond to the metal atom symmetrically within experimental error, and the 6-atom alkene planes are nearly perpendicular (81.3 and 85.3° respectively) to the lines Fe–Z(3) and Fe–Z(4).

Fe–C(41,42) separations are, averaged, *ca.* 0.09 Å longer than Fe–C(3,31); C(3)–C(31) is *ca.* 0.03 Å longer than C(41)–C(42); and atoms C(3) and C(31) are found to be dis-

[7] M. Bottrill, R. Goddard, M. Green, R. P. Hughes, M. K. Lloyd, B. Lewis, and P. Woodward, *J.C.S. Chem. Comm.*, 1975, 253; R. Goddard, personal communication.

[8] A. R. Luxmore and M. R. Truter, *Acta Cryst.*, 1962, **15**, 1117; D. Bright and O. S. Mills, *Chem. Comm.*, 1966, 211; *J. Chem. Soc. (A)*, 1971, 759.

placed *ca.* 0.19 and 0.21 Å respectively out of the plane defined by C(2), C(4), H(311), and H(312) in a direction towards Fe (*i.e.* towards sp^3 hybridisation), whereas only C(42) deviates from the pendant alkene function and then merely by *ca.* 0.13 Å. All these observations are mutually compatible and suggest iron–alkene linkages of measurably different strengths.

In general Fe–alkene and Fe–CO bond distances in the present complex are similar to those found for the complex [Fe(C$_7$H$_8$)(C$_4$F$_6$)$_2$(CO)$_2${P(OCH$_3$)$_3$CMe}] [7] in which the alkene units (1,4 with respect to each other) are contained within separate 5-atom rings of an 11-carbon quadricyclic ligand.

The η^2-furanone iron tetracarbonyl complex (4a) features the Fe(CO)$_4$ unit bonded on the *opposite* side of the organic ligand to the vinyl olefin *via* the co-ordinated double bond C(3)–C(31). Our determination of the structure of this [Fe(CO)$_4$(alkene)] complex represents only the third such analysis to have been carried out ' accurately ', *i.e.* bond lengths accurate to within less than 0.01 Å. In common
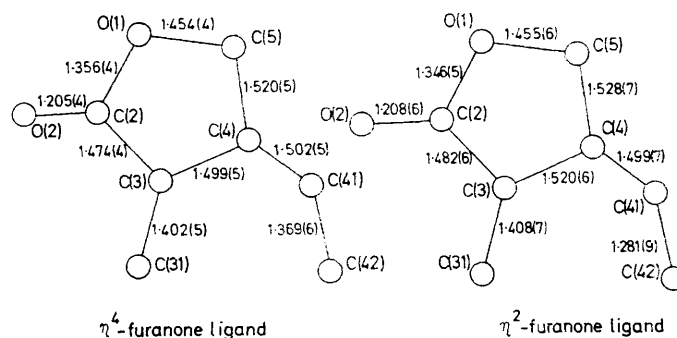

FIGURE 3 Bond lengths, Å, within the two organic ligands

with all such previously reported structures [8-12] the metallo-bonded alkene fragment occupies one equatorial position of a distorted trigonal bipyramidal (TBP) metal geometry. The orientation of this unit relative to the equatorial plane
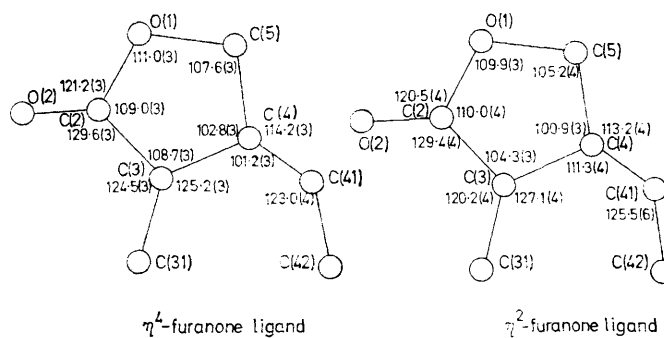
FIGURE 4 Bond angles, degrees, within the two organic ligands

of the metal is similar to that observed in the tricarbonyl and, further, C(3) and C(31) show deviations from planarity of the same order of magnitude.

The line C(102)–Fe–C(104) kinks slightly (3.5°) at the

[9] C. Pedone and A. Sirigu, *Acta Cryst.*, 1967, **23**, 759; *Inorg. Chem.*, 1968, **7**, 2614.

[10] M. I. Davis and C. S. Speed, *J. Organometallic Chem.*, 1970, **21**, 407.

[11] T. H. Whitesides, R. W. Slaven, and J. C. Calabrese, *Inorg. Chem.*, 1974, **13**, 1895.

[12] F. A. Cotton and P. Lahuerta, *Inorg. Chem.*, 1975, **14**, 116.

metal atom with the axial carbonyl groups bending towards C(103)–O(103); we believe this to be principally the result of efficient intramolecular interligand packing (Table 4).

$$\Delta = [\text{Fe–CO(axial)}] - [\text{Fe–CO(equatorial)}] = +0.013 \text{ Å}$$

The Furanone Ligands.—Bond lengths and angles within these new organic ligands are compared in Figures 3 and 4. Apart from the co-ordinated double bonds, interatomic separations are in good correspondence with each other and with values calculated from covalent radii,[13] notable exceptions being O(1)–C(1), presumably a reasonably polarised bond, and the free double bond (tetracarbonyl) C(41)–C(42), at 1.281(9) Å some 0.05 Å shorter than expected.

Major differences between the organic ligands of the two complexes reside (i) in the C(41)–C(42) bond lengths; (ii) the C(3)–C(4)–C(41) angles and the orientation of the C(41)–C(42) alkene fragment relative to the parent furanone, both of which imply a relatively strained η^4-ligand; and (iii) the buckling of the 5-atom rings—skew in the η^4-ligand with C(2) unique, but envelope with C(4) apical in the η^2-ligand.

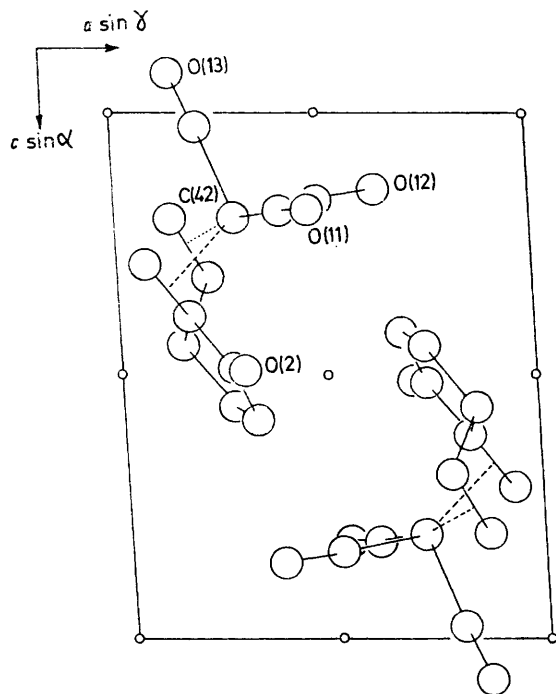Figures 5 and 6 demonstrate the crystal packings (hydro-

FIGURE 5   Packing of the η^4-furanone iron tricarbonyl complex in ($h0l$) projection

gen atoms omitted for clarity). Although there are no severe intermolecular contacts for either complex, a number of intramolecular interactions exist, the most important of which appear in Table 4.

To gain some insight into the possible mechanisms of this remarkable iron-promoted transformation of (1c) into the 3-methylene-4-vinyldihydrofuran-2(3H)-one ligand, the reaction of cis-2,3-bis(hydroxymethyl)methylenecyclopropane (1d) with $[\text{Fe}_2(\text{CO})_9]$ was carried out under identical

[13] L. Pauling, ' The Nature of the Chemical Bond,' Cornell University Press, 1960.
[14] M. Green and R. P. Hughes, *J.C.S. Dalton*, following paper.

conditions. The identical complexes (3a) and (4a) were obtained, indicating that the stereochemistry of at least one carbon centre must be lost during the reaction.
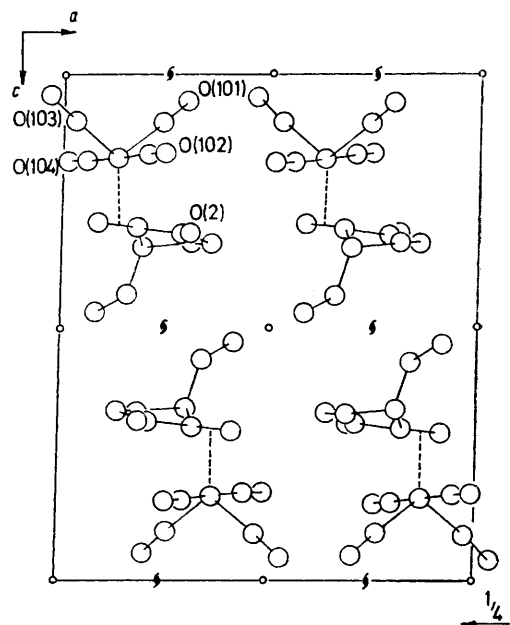
FIGURE 6   ($h0l$) Projection of the crystal structure of the η^2-furanone iron tetracarbonyl complex

Similarly, the tetradeuteriated methylenecyclopropane (1e) reacted with $[\text{Fe}_2(\text{CO})_9]$ to yield the analogous complexes (3b) and (4b), and the dideuteriated methylenecyclopropane (1f) similarly afforded (3c) and (4c). The positions of deuterium incorporation into the 3-methylene-4-vinyldihydrofuran-2(3H)-one ligand were readily deduced from the ^{1}H n.m.r. spectra (Table 1) of the products and, once established, were used to assign unambiguously resonances in the ^{13}C n.m.r. spectra. No evidence for deuterium scrambling between sites was evident within the limit of ^{1}H n.m.r. integration.

TABLE 4

Selected intramolecular contacts [a] (Å)

η^4-Furanone tricarbonyl complex

H(312)···H(421)	2.30(5)	C(13)···H(421)	2.75(4)
H(411)···H(52)	2.17(5)	C(13)···H(312)	2.75(3)
H(411)···C(12)	2.54(4)	C(11)···H(311)	2.63(3)

η^2-Furanone tetracarbonyl complex

H(41)···C(104)	2.51(4)	H(312)···C(104)	2.65(5)
C(3)···C(102)	2.874(6)	H(311)···C(102)	2.62(5)
C(3)···C(104)	2.784(6)	O(2)···C(102)	2.759(6)
C(2)···C(102)	2.890(6)		

[a] Van der Waals radii taken as C 1.85 Å, O 1.4 Å, H 1.2 Å.

Complexes (3) and (4) were not thermally interconvertible, although both rearranged under very mild conditions to yield different products.[14]   It would appear, therefore, that neither of the complexes is a precursor of the other.

DISCUSSION

Both complexes (3) and (4), incorporating the 3-methylene-4-vinyldihydrofuran-2(3H)-one ligand, represent the first examples of η^4- and η^2-bonded 1,4-diene complexes of iron(0) in which the olefinic functions are

not incorporated into a ring system. Any mechanistic proposals must account for the structures of the two products, the eventual positions of deuterium labels in the products, and the observation that identical products

must be formation of an η^2-bonded olefin complex (2e), analogous to the complex (2a)[4] obtained from the reaction of (1a) with $[Fe_2(CO)_9]$. Molecular models of (2e) indicate that the *endo*-CH_2OH group is ideally situated
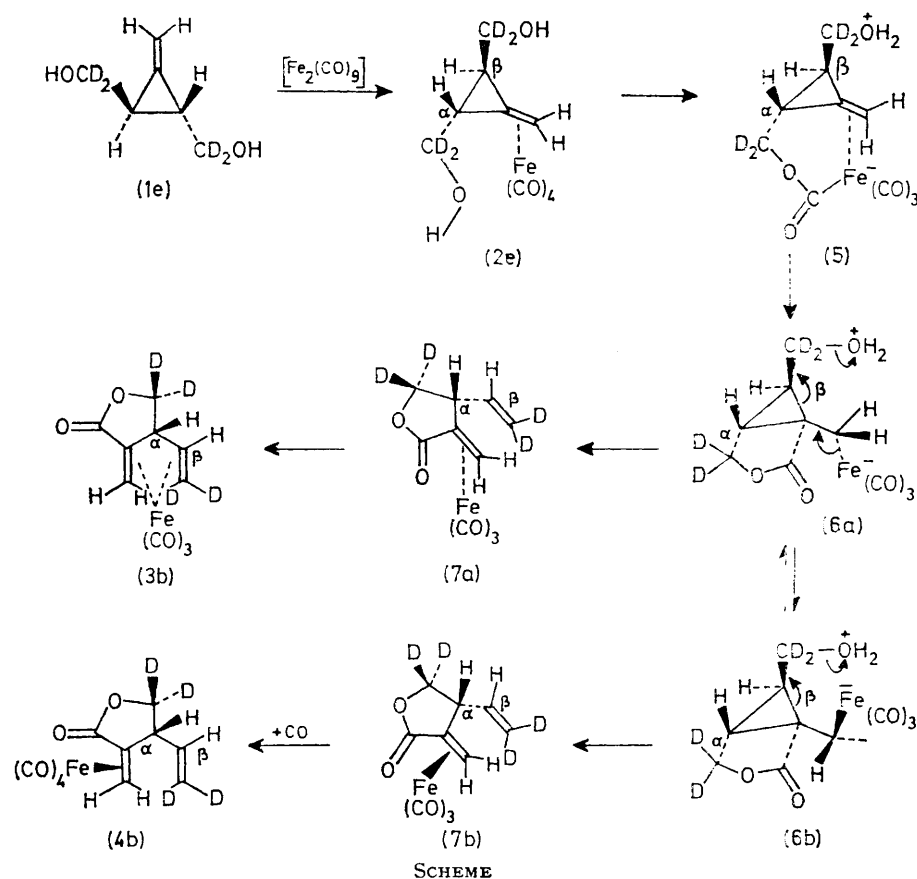

SCHEME

are obtained using either the *trans*- or *cis*-bis(hydroxy-methyl)methylenecyclopropanes (1c) or (1d).

The proposed mechanism is shown in the Scheme, using as an example the formation of complexes (3b) and (4b) from the tetradeuteriomethylenecyclopropane (1c) and $[Fe_2(CO)_9]$. Identical mechanisms can be drawn for the corresponding reactions of (1c) and (1f) with $[Fe_2(CO)_9]$.

The most probable first step in the reaction sequence

* An alternative pathway may involve equilibrium formation of small concentrations of a ferracyclobutanone (I) and capture of this species by nucleophilic attack at the now ketonic carbon. Similar equilibria involving co-ordinated olefin and carbene ligands (II) have recently been proposed as key mechanistic features of the transition-metal promoted dismutation of olefins.[17]
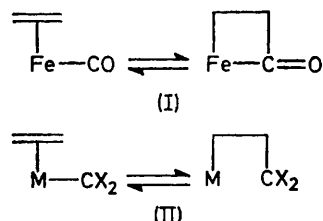
for an intramolecular nucleophilic attack on a co-ordinated CO ligand. Nucleophilic attack by alkoxide ions on CO ligands co-ordinated to cationic metal centres is well established.[15] It is conceivable that, once complex (2e) is formed, the lack of a positive entropy term for intramolecular attack, due to the forced proximity of the two reaction centres, lowers the activation energy sufficiently for the reaction to proceed under the mild, non-basic conditions of this system. Ferrolactone species similar to intermediate (5) have been isolated from the reactions of mono-epoxy-1,3-dienes with $Fe(CO)_5$.[16,*]

cis-Insertion of the co-ordinated olefinic function in (5) into the acyl–iron bond leads to (6a), generating both the lactone ring system and a substituted cyclopropyl-methyl-iron tricarbonyl species. By analogy with the palladium(II) systems previously studied,[2] such a co-ordinatively unsaturated cyclopropylmethyl-iron species

[15] M. Green, in ' MTP International Rev. of Science,' Butterworths, London, Part 2, p. 186.

[16] R. Aumann, H. Averbeck, K. Frohlich, and H. Ring, International Symposium on Metals in Organic Chemistry, Venice, 1974, A6.

[17] T. J. Katz and J. McGinnis, *J. Amer. Chem. Soc.*, 1975, **97**, 1592.

should undergo a ready, concerted, ring-opening as shown, elimination of a molecule of water finally generating the product ligand in (7a). Species (7a), when produced from (6a) as drawn, must contain a tricarbonyliron moiety co-ordinated to the methylene olefin on the same side of the lactone ring as the newly formed vinyl olefin; this pendant vinyl function is thus ideally placed to fill immediately the vacant co-ordination site in (7a) to yield the tricarbonyl complex (3b).

If, however, rotation occurs about the cyclopropyl-methylene σ-bond in (6a) to yield the rotamer (6b), an analogous ring-opening mechanism produces a species (7b), containing a tricarbonyliron moiety co-ordinated to the methylene olefin on the opposite face of the lactone ring to the newly formed vinyl olefin; co-ordination of this olefin to the metal to fill the vacant co-ordination site is thus precluded. Species (7b) must, therefore, take up a molecule of carbon monoxide from the reaction medium to yield the co-ordinatively saturated tetra-carbonyl complex (4b).

An entirely analogous mechanism can be drawn for the reaction of cis-2,3-bis(hydroxymethyl)methylenecyclo-propane (1d) with [Fe$_2$(CO)$_9$]; the only prerequisite is that initial co-ordination of the methylenecyclopropane to the metal must occur to yield an intermediate (2d), in which both CH$_2$OH groups are endo with respect to the metal, thus facilitating intramolecular nucleophilic attack on a co-ordinated CO. This mode of co-ordination seems highly likely in view of the crystallographic-ally determined structure of the stable complex (2b), formed from cis-2,3-dimethoxycarbonylmethylenecyclo-propane (1b) and [Fe$_2$(CO)$_9$], in which both CO$_2$Me groups are indeed endo with respect to the metal.[11] The mechanism for the formation of (2b) is thought to involve initial formation of an Fe · · · O interaction, with subsequent stereochemical direction of the metal onto the face of the olefin cis to the CO$_2$Me groups;[11] an identical sequence must also be possible for the formation of (2d).

Notably, the reaction mechanism as drawn involves loss of any initial stereochemistry at the ring carbon labelled β (Scheme), which becomes sp^2-hybridised in the product-ligand. Retention of configuration is observed at the carbon centre labelled α.[14] The same products, (3a) and (4a), are therefore formed irrespective of whether the two CH$_2$OH groups in the organic starting material are mutually trans or cis.

EXPERIMENTAL

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen.

^{1}H N.m.r. spectra were recorded on a Varian Associates HA100 spectrometer at 100 MHz. ^{13}C N.m.r. spectra were recorded on a Jeol NM-PFT-100 spectrometer, operating in the Fourier-transform mode, at 25.15 MHz. I.r. spectra were recorded on a Perkin-Elmer 257 instrument, in 1-mm path-length cells with CaF$_2$ optics.

trans-2,3-Bis(hydroxymethyl)methylenecyclopropane (1c) was prepared by LiAlH$_4$ reduction of trans-2,3-dimethoxy-

^{18} J. J. Gajewski, J. Amer. Chem. Soc., 1971, 93, 4450.

carbonylmethylenecyclopropane, according to literature methods.[18] Similarly, cis-2,3-bis(hydroxymethyl)methyl-enecyclopropane (1d) was prepared by LiAlH$_4$ reduction of cis-2,3-dimethoxycarbonylmethylenecyclopropane.[18]

trans-2,3-Bis(dideuteriohydroxymethyl)methylenecyclo-propane (1e) was prepared by LiAlD$_4$ reduction of trans-2,3-dimethoxycarbonylmethylenecyclopropane; ^{1}H n.m.r. data (CDCl$_3$): τ 4.70 (CH$_2$), 5.70 (OH), and 8.36 (CH).

trans-2,3-Dideuterio-2,3-bis(hydroxymethyl)methylene-cyclopropane (1f) was prepared by LiAlH$_4$ reduction of trans-2,3-dimethoxycarbonyl-2,3-dideuteriomethylene-cyclopropane which was prepared by literature methods [^{1}H n.m.r. data (CDCl$_3$): τ 4.70 (CH$_2$), 5.70 (OH), 6.20, 6.93 (CH$_2$, J_{AB} = 12 Hz)].

Reaction of [Fe$_2$(CO)$_9$] with trans-2,3-Bis(hydroxymethyl)-methylenecyclopropane.—(N.B. It proved vital in this preparation to maintain the temperature during the reaction and work-up procedure at <20 °C, to avoid rearrangement reactions.[14]) A slurry of trans-2,3-bis(hydroxymethyl)methyl-enecyclopropane (1.0 g, 8.8 mmol) and [Fe$_2$(CO)$_9$] (5.0 g, 13.7 mmol) in diethyl ether (200 cm^3) was stirred (16 h, 20 °C), and then filtered through a Kieselguhr plug to afford a clear orange solution. Evaporation of the solvent under reduced pressure yielded an orange-brown residue (2.0 g) which was chromatographed on a Florisil column (4 × 50 cm). Elution with hexane–diethyl ether (1 : 1) afforded a pale yellow eluate. Evaporation of this solution, and recrystallisation of the residue from diethyl ether–hexane (− 30 °C), yielded tetracarbonyl-η^2-[3-methylene-exo-4-vinyldihydrofuran-2(3H)-one]iron, complex (4a), as pale yellow plates (0.08 g, 31%), m.p. 76—77 °C; v_{CO}(hexane) 2 103, 2 039, 2 015, 1 997, and 1 756 cm^{-1}; m/e 292 (P), 264 (P − CO), 236 (P − 2CO), 208 (P − 3CO), and 180 (P − 4CO) (Found: C, 45.3; H, 2.9. C$_{11}$H$_8$FeO$_6$ requires C, 45.2; H, 2.8%). Further elution with dichloromethane–ether (1 : 1) yielded an orange-yellow eluate. Evaporation, and recrystallisation of the residue from dichloromethane–hexane (− 30 °C), yielded tricarbonyl-η^4-[3-methylene-endo-4-vinyldihydrofuran-2(3H)-one]iron, complex (3a), as orange needles (1.11 g, 48%), m.p. 104—105 °C, v_{CO}(hexane) 2 056, 2 006, 1 976, and 1 760 cm^{-1}; m/e 264 (P), 236 (P − CO), 208 (P − 2CO), and 180 (P − 3CO) (Found: C, 45.3; H, 3.0. C$_{10}$H$_8$FeO$_5$ requires C, 45.4; H, 3.0%).

A similar reaction between cis-2,3-bis(hydroxymethyl)-methylenecyclopropane (1.0 g, 8.8 mmol) and [Fe$_2$(CO)$_9$] (5.0 g, 13.7 mmol) in diethyl ether (200 cm^3) under an atmosphere of carbon monoxide afforded tetracarbonyl-η^2-[3-methylene-exo-4-vinyldihydrofuran-2-(3H)-one]iron, complex (4a) (0.48 g, 19%), and tricarbonyl-η^4-[3-methyl-ene-endo-4-vinyldihydrofuran-2(3H)-one]iron, complex (3a) (0.75 g, 32%).

A similar reaction between trans-2,3-bis(dideuteriohydr-oxymethyl)methylenecyclopropane (0.9 g, 7.6 mmol) and [Fe$_2$(CO)$_9$] (5.0 g, 13.7 mmol) in diethyl ether (200 cm^3) under an atmosphere of carbon monoxide afforded tetra-carbonyl-η^2-[3-dideuteriomethylene-exo-4-(2,2-dideuterio-vinyl)dihydrofuran-2(3H)-one]iron, complex (4b) (0.30 g, 13%); m/e 296 (P), 268 (P − CO), 240 (P − 2CO), 218 (P − 3CO), and 184 (P − 4CO) (Found: C, 44.7; H, 2.8. C$_{11}$H$_4$D$_4$FeO$_6$ requires C, 44.6; H, 2.7%), and tricarbonyl-η^4-[3-dideuteriomethylene-endo-4-(2,2-dideuteriovinyl)-dihydrofuran-2(3H)-one]iron, complex (3b) (1.0 g, 50%), m/e 268 (P), 240 (P − CO), 218 (P − 2CO), and 184 (P − 3CO) (Found: C, 44.8; H, 3.1. C$_{10}$H$_4$D$_4$FeO$_5$ requires C, 44.8; H, 3.0%).

A similar reaction between *trans*-2,3-dideuterio-2,3-bis(hydroxymethyl)methylenecyclopropane (1.0 g, 8.6 mmol) and [Fe₂(CO)₉] (5.0 g, 13.7 mmol) in diethyl ether (200 cm³) under an atmosphere of carbon monoxide afforded tetracarbonyl-η²-[*endo*-4-deuterio-3-methylene-*exo*-4-(1-deuteriovinyl)dihydrofuran-2(3*H*)-one]iron, complex (4c) (0.40 g, 16%), *m/e* 294 (*P*), 266 (*P* − CO), 238 (*P* − 2CO), 210 (*P* − 3CO), and 182 (*P* − 4CO) (Found: C, 45.0; H, 2.7. C₁₁H₆D₂FeO₆ requires C, 44.9; H, 2.7%), and tricarbonyl-η⁴-[*exo*-4-deuterio-3-methylene-*endo*-4-(1-deuteriovinyl)dihydrofuran-2(3*H*)-one]iron, complex (3c) (0.95 g, 42%), *m/e* 266 (*P*), 238 (*P* − CO), 210 (*P* − 2CO), and 182 (*P* − 3CO) (Found: C, 45.2; H, 3.0. C₁₀H₆D₂FeO₅ requires C, 45.1; H, 3.0%).

TABLE 5

η⁴-Furanone tricarbonyl complex: final positional parameters (Fe × 10⁵; O, C × 10⁴) of the non-hydrogen atoms

Atom	x	y	z
Fe	28 737(6)	33 304(7)	19 546(4)
O(1)	3 227(3)	4 426(3)	5 852(2)
C(2)	2 690(4)	5 459(5)	4 873(3)
O(2)	2 972(3)	7 233(4)	4 920(2)
C(3)	1 679(4)	4 093(5)	3 903(3)
C(31)	691(4)	4 697(6)	2 894(3)
C(4)	1 518(4)	2 076(5)	4 396(3)
C(41)	2 200(5)	816(5)	3 160(4)
C(42)	1 348(6)	471(6)	1 969(4)
C(5)	2 704(5)	2 324(5)	5 587(4)
C(11)	3 985(4)	5 711(5)	1 931(3)
O(11)	4 702(3)	7 227(4)	1 861(3)
C(12)	4 961(5)	2 296(3)	1 660(4)
O(12)	6 301(4)	1 720(5)	1 438(3)
C(13)	2 019(5)	3 235(6)	300(4)
O(13)	1 443(4)	3 207(5)	−738(3)

Crystal Structure Determinations of Complexes (3a) *and* (4a).—The tricarbonyl complex (3a) crystallised from a dichloromethane–hexane solution (−30 °C) as well-formed orange needles, whereas the tetracarbonyl (4a) was deposited

TABLE 6

η⁴-Furanone tricarbonyl complex: the anisotropic thermal parameters [a] of the non-hydrogen atoms [Å²: Fe × 10⁴; O, C × 10³]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	309(5)	375(3)	325(3)	87(2)	−10(2)	31(2)
O(1)	39(1)	44(1)	36(1)	6(1)	−5(1)	6(1)
C(2)	27(2)	39(2)	33(2)	9(1)	7(1)	4(1)
O(2)	45(2)	36(2)	50(1)	5(1)	2(1)	2(1)
C(3)	27(2)	37(2)	30(2)	8(1)	6(1)	7(1)
C(31)	29(2)	46(2)	37(2)	10(2)	1(1)	7(1)
C(4)	29(2)	39(2)	41(2)	3(1)	1(1)	10(1)
C(41)	51(2)	30(2)	50(2)	6(2)	−2(2)	7(1)
C(42)	60(3)	42(2)	57(3)	−2(2)	−7(2)	−1(2)
C(5)	44(2)	45(2)	43(2)	8(2)	−3(2)	12(2)
C(11)	34(2)	45(2)	32(2)	13(2)	5(1)	6(1)
O(11)	56(2)	44(2)	65(2)	2(1)	13(1)	13(1)
C(12)	45(2)	48(2)	49(2)	12(2)	1(2)	−1(2)
O(12)	43(2)	77(2)	106(3)	29(2)	9(2)	1(2)
C(13)	41(2)	58(2)	42(2)	10(2)	1(2)	4(2)
O(13)	74(2)	113(3)	41(2)	10(2)	−21(1)	8(2)

[a] The anisotropic thermal parameter is defined as
$$\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)].$$

as rather irregular pale yellow plates. The data collection and the solution and refinement of both structures followed similar lines and will be described for the tricarbonyl complex (3a) only. Data in parentheses represent differences in respect of the tetracarbonyl complex (4a).

A single crystal, 0.040 × 0.038 × 0.023 {0.061 × 0.028 × 0.011} cm was centred optically on a Syntex *P*2₁ four-circle diffractometer, and the unit cell and intensity data recorded

TABLE 7

η²-Furanone tetracarbonyl complex: positional (Fe × 10⁵; O, C × 10⁴) parameters of the non-hydrogen atoms

Atom	x	y	z
Fe	13 271(5)	8 332(9)	16 518(4)
O(1)	3 621(2)	104(5)	3 349(2)
C(2)	2 861(4)	1 508(7)	3 152(3)
O(2)	3 079(2)	3 311(5)	3 148(2)
C(3)	1 811(3)	484(6)	2 983(2)
C(31)	859(4)	1 649(9)	2 913(3)
C(4)	1 944(3)	−1 619(7)	3 396(3)
C(41)	1 582(4)	−1 620(9)	4 323(3)
C(42)	834(5)	−2 740(10)	4 629(4)
C(5)	3 156(4)	−1 941(7)	3 314(4)
C(101)	2 338(4)	−403(6)	999(3)
O(101)	2 952(3)	−1 159(6)	573(2)
C(102)	2 026(4)	3 272(7)	1 545(3)
O(102)	2 425(4)	4 796(6)	1 420(3)
C(103)	278(4)	1 844(8)	951(4)
O(103)	−386(4)	2 465(8)	502(3)
C(104)	568(3)	−1 527(8)	1 716(3)
O(104)	80(3)	−2 998(6)	1 735(3)

in a way already detailed; [19] 15 reflections, 27° > 2θ > 15° {24° > 2θ > 12°} were taken from a 25 {30} min rotation photograph and automatically centred in θ, ω, and χ; the unit cell was defined by inspection of the real-space vectors

TABLE 8

η²-Furanone tetracarbonyl complex: thermal parameters [a] [Å²: Fe × 10⁴; O, C × 10³] of non-hydrogen atoms

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	457(3)	422(3)	486(3)	−6(3)	1(2)	−8(3)
O(1)	50(2)	50(2)	80(2)	−1(2)	−9(1)	−1(2)
C(2)	59(3)	43(3)	51(2)	−12(2)	−4(2)	−5(2)
O(2)	74(2)	46(2)	87(2)	−13(2)	−13(2)	−4(2)
C(3)	49(2)	41(2)	40(2)	−1(2)	4(2)	−3(2)
C(31)	57(3)	49(3)	53(3)	6(2)	10(2)	−9(2)
C(4)	52(2)	42(2)	48(2)	−10(2)	−2(2)	1(2)
C(41)	71(3)	78(4)	54(3)	−7(3)	−4(2)	12(3)
C(42)	83(4)	121(6)	72(4)	−15(4)	4(3)	32(4)
C(5)	62(3)	43(3)	78(3)	0(2)	−1(3)	3(3)
C(101)	56(2)	41(2)	48(2)	−8(2)	4(2)	−1(2)
O(101)	78(2)	65(2)	76(2)	0(2)	27(2)	−7(2)
C(102)	72(3)	47(3)	55(3)	−4(2)	2(2)	1(2)
O(102)	130(3)	47(2)	85(3)	−26(2)	2(2)	11(2)
C(103)	67(3)	61(3)	75(3)	9(3)	−7(3)	3(3)
O(103)	94(3)	99(3)	118(3)	27(3)	−45(3)	11(3)
C(104)	46(2)	66(3)	54(2)	−4(2)	−4(2)	−3(2)
O(104)	73(2)	79(3)	93(3)	−36(2)	−1(2)	−3(2)

[a] See footnote, Table 6.

and intervector cosines produced by the auto-indexing program; data collection employed graphite-monochromated Mo-K_α radiation ($\lambda_{\alpha 1} = 0.709\ 26$, $\lambda_{\alpha 2} = 0.713\ 54$ Å) and a θ − 2θ scan in 96 steps; 2.9° ⩽ 2θ ⩽ 50.0°; variable scan rates from 0.0652 {0.0488}° s⁻¹ for preliminary 2 s peak counts ⩽150, to 0.4883° s⁻¹ for counts ⩾1 500; 3 check reflections were monitored once every 23 {28} counts but subsequent analysis [20] of their net intensities as a function of time implied no significant crystal decomposition or machine variance had occurred over the *ca.* 27 {60} h X-ray exposure; of the 1 543 {2 526} independent reflections measured, 1 435 {1 679} were above the significance

[19] A. G. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.
[20] A. G. Modinos, ' DRSYN,' a Fortran programme for data analysis.

threshold of 2.5σ (I) and were used to solve and refine the structure.

Crystal Data.—$C_{10}H_8FeO_5$, $M = 264.02$, Triclinic, space group $P\bar{1}$, $a = 7.745(5)$, $b = 6.787(3)$, $c = 9.873(4)$ Å, $\alpha = 96.46(3)$, $\beta = 86.79(4)$, $\gamma = 94.05(4)°$, $U = 513.8(4)$ Å^3, $D_m = 1.70$ (flotation), $Z = 2$, $D_c = 1.706$, $F(000) = 268$, Mo-K_α X-radiation ($\bar{\lambda} = 0.710\ 69$ Å), μ(Mo-K_α) $= 15.1$ cm^{-1}.

$C_{11}H_8FeO_6$, $M = 292.03$, Monoclinic, space group $P2_1/a$, $a = 12.419(4), b = 6.527(1), c = 15.321(4)$ Å, $\beta = 91.21(2)°$, $U = 1\ 241.8(5)$ Å^3, $D_m = 1.55$ (flotation), $Z = 4$, $D_c = 1.561$, $F(000) = 592$, Mo-K_α X-radiation, μ(Mo-K_α) $= 12.6$ cm^{-1}.

Data were corrected for Lorentz and polarisation effects, but not for X-ray absorption. The iron atom was easily located *via* a three-dimensional Patterson map and used to calculate the first set of phases. Oxygen and carbon positions were readily taken from an electron-density difference synthesis after three cycles of refinement of the iron parameters. Inclusion of these atoms reduced R to *ca.* 0.06 {0.08} and examination of their internuclear separations allowed probable distinction to be made between O(1) and C(5). The identities of these atoms were unambiguously established when the molecules' eight hydrogen atoms were then located.

* For details see Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index, issue.

21 D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.
22 D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

Reflections were weighted according to $w = (xy)^{-1}$ with $x = b/\sin\theta$ if $\sin\theta < b$, $x = 1$ if $\sin\theta \geqslant b$, and $y = F_o/a$ if $F_o > a$, $y = 1$ if $F_o \leqslant a$, in which a and b were 20.0 {40.0} and 0.25 respectively. Full-matrix least-squares refinement (Fe, O, C atoms anisotropic, H isotropic) converged to R 0.029 {0.041}, R_w 0.031 {0.044} at a data : variable ratio of 8.06 {8.15} : 1. In the final cycle the mean shift-to-error was less than 0.002 {0.001}, and the largest maximum on a final ΔF synthesis *ca.* 0.40 {0.45} eÅ^{-3} near Fe.

Atomic scattering factors for neutral atoms were taken from ref. 21 for iron, ref. 22 for oxygen and carbon, and ref. 23 for hydrogen. Those of iron were adjusted for both the real and imaginary components of anomalous dispersion.[24]

Tables 5—8 list the derived parameters for Fe, O, and C. Those involving hydrogen atoms, details of molecular planes, and a comparison of the observed and calculated structure factor amplitudes are listed in Supplementary Publication No. SUP 21796 (22 pp., 1 microfiche).*

All calculations were performed on the University of London CDC 7600 computer with the ' X-ray 1972 ' crystallographic computing system,[25] except where otherwise stated.

23 R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
24 ' International Tables for X-ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. III.
25 Technical Report TR 192 of the Computer Science Centre, University of Maryland, June 1972.