Reactions of Co-ordinated Ligands. Part 18.[1] Ring-expansion Reactions of Tricarbonyl(η^4-tetramethylcyclobutadiene)iron; Molecular and Crystal Structures of $[Fe\{\eta^4\text{-}C_6Me_4(CF_3)_2\}(CO)_3]$ and $[Fe\{C_8Me_4(CF_3)_2O_2\}(CO)_3]$

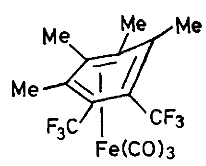
By **Alan Bond, Martin Bottrill, Michael Green,*** and **Alan J. Welch,** Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS

Irradiation (u.v.) of a solution of $[Fe(\eta^4\text{-}C_4Me_4)(CO)_3]$ and hexafluorobut-2-yne affords the arene tricarbonyl iron complex $[Fe\{\eta^4\text{-}C_6Me_4(CF_3)_2\}(CO)_3]$ identified by *X*-ray crystallography. The crystals are monoclinic, space group $P2_1/n$, Z = 4, in a unit cell of dimensions a = 13.377(5), b = 8.959(5), c = 13.544(6) Å, and β 100.54(3)°. A second product in the reaction is a bicyclic diketone $[Fe\{C_8Me_4(CF_3)_2O_2\}(CO)_3]$, which has also been structurally characterized by *X*-ray crystallography. The crystals are monoclinic, space group $P2_1/n$, Z = 4, in a unit cell of dimensions a = 9.031(7), b = 17.865(16), c = 11.519(10) Å, and β 105.49(6)°. A similar irradiation reaction between trifluoroethylene and $[Fe(\eta^4\text{-}C_4Me_4)(CO)_3]$ afforded two isomeric η-cyclobutenyl complexes, one of which arises by a formal fluorine migration reaction and contains the arrangement $FeCH(CF_3)C$. Thermolysis of this latter species results in a ring-enlargement reaction and the formation of $[Fe_2(CO)_4\{\eta^4\text{-}C_5Me_4(CF_3)\}]$. A minor product in this reaction is obtained in higher yield by carbonylation, and is formulated as a ring-expanded η^3-C_5Me_4CO complex. The mechanism of formation of these products is discussed.

IN an elegant series of investigations [2] Pettit and his co-workers synthesised tricarbonyl(η-cyclobutadiene)iron, studied the reactions of the co-ordinated cyclobutadiene, and by oxidative-displacement reactions furthered considerably our understanding of the nature of cyclobutadiene. An interesting side-product found in the study of the acylation of $[Fe(\eta\text{-}C_4H_4)(CO)_3]$ with Ph-COCl–$AlCl_3$ was (η^5-benzoyloxycyclopentadienyl)dicarbonylchloroiron arising by a ring-expansion reaction of the C_4 ring, and possibly involving the intermediacy of a carbyne complex. In continuing our study of the photochemical reactions of fluoro-olefins [3] and hexafluorobut-2-yne with tricarbonyl(η^4-tetramethylcyclobutadiene)iron, unusual ring-expansion reactions have been observed. We report details of our studies together with single-crystal *X*-ray diffraction studies on two of the products.

RESULTS AND DISCUSSION

Irradiation (u.v.) of a hexane solution of $[Fe(\eta^4\text{-}C_4Me_4)(CO)_3]$ and hexafluorobut-2-yne affords two products, which were separated by column chromatography. The first product (1), which was eluted with hexane, was obtained as orange-red crystals and analyzed as a 1 : 1 adduct, showing in the i.r. spectrum terminal carbonyl



(1)

bands corresponding to the presence of an $Fe(CO)_3$ group. The ^1H and ^{19}F n.m.r. data showed resonances due to four inequivalent methyl groups and two inequivalent trifluoromethyl groups, an observation which is consistent with at least three alternative structures. For this reason a single-crystal *X*-ray diffraction study was conducted. Figure 1 shows the projection of a single molecule on to the plane defined by carbon atoms 11, 41, 42, and 43 and demonstrates the atomic-numbering

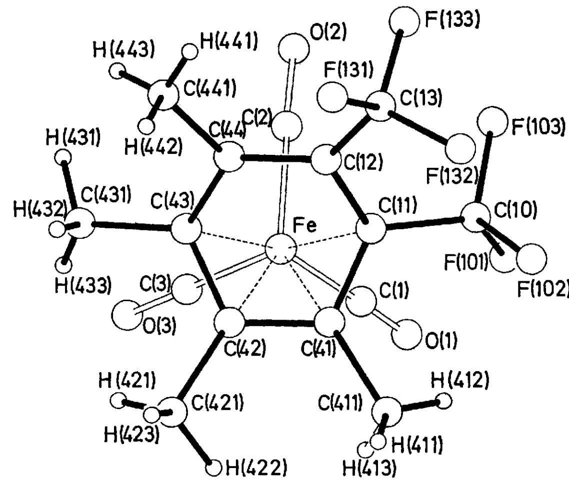


FIGURE 1 Perspective view of the complex $[Fe\{\eta^4\text{-}C_6Me_4(CF_3)_2\}(CO)_3]$ (1)

scheme adopted. Table 1 lists interatomic distances (uncorrected for thermal effects) and Table 2 the important interbond angles. Angular data involving hydrogen atoms are deposited as Appendix A.†

The crystallographic study clearly reveals that the formation of the arene in (1) proceeds *via* the formal addition of an acetylene molecule to the co-ordinated cyclobutadiene derivative. Such a concerted reaction had been proposed as an explanation for the formation of substituted benzenes from acetylenes. However, the isolation of only the arene and not a complex could always be explained in terms of a ($\pi^4s + \pi^2s$) reaction of free cyclobutadiene and, in addition, elegant experi-

† All Appendices may be recovered from Supplementary Publication No. SUP 22140 (41 pp.). For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

[1] Part 17, M. Bottrill and M. Green, *J.C.S. Dalton*, preceding paper.
[2] R. Pettit, *J. Organometallic Chem.*, 1975, **100**, 205.
[3] A. Bond and M. Green, *J.C.S. Dalton*, 1972, 763.

ments by Whitesides and Ehmann [4] had precluded the intermediacy of co-ordinated cyclobutadiene in reactions catalyzed by Cr, Co, and Ni. The actual isolation and detailed geometry of the arene complex (1) were, therefore, of considerable interest.

TABLE 1

Interatomic distances (Å) * for complex (1)

Fe–C(1)	1.812(5)	C(41)–C(42)	1.410(5)
C(1)–O(1)	1.134(6)	C(42)–C(43)	1.462(5)
Fe–C(2)	1.808(4)	C(43)–C(44)	1.490(5)
C(2)–O(2)	1.134(5)	C(41)–C(411)	1.513(5)
Fe–C(3)	1.790(4)	C(42)–C(421)	1.509(5)
C(3)–O(3)	1.137(6)	C(43)–C(431)	1.525(5)
Fe–C(11)	2.105(3)	C(44)–C(441)	1.504(5)
Fe–C(41)	2.066(3)		
Fe–C(42)	2.072(3)	C(411)–H(411)	0.91(6)
Fe–C(43)	2.118(3)	C(411)–H(412)	0.97(7)
		C(411)–H(413)	0.91(6)
C(44)–C(12)	1.352(5)	C(421)–H(421)	0.91(6)
C(12)–C(13)	1.500(5)	C(421)–H(422)	0.98(7)
C(12)–C(11)	1.514(5)	C(421)–H(423)	0.92(7)
C(11)–C(10)	1.506(5)	C(431)–H(431)	0.98(5)
C(11)–C(41)	1.453(4)	C(431)–H(432)	0.82(6)
C(13)–F(131)	1.349(5)	C(431)–H(433)	0.98(6)
C(13)–F(132)	1.339(5)	C(441)–H(441)	0.85(6)
C(13)–F(133)	1.330(5)	C(441)–H(442)	0.90(6)
C(10)–F(101)	1.344(6)	C(441)–H(443)	0.92(6)
C(10)–F(102)	1.357(5)		
C(10)–F(103)	1.336(5)		

* Estimated standard deviations, shown in parentheses throughout this paper, are right-adjusted to the least significant digit in the preceding number.

TABLE 2

Interbond angles (°) in complex (1) not involving hydrogen atoms

Fe–C(1)–O(1)	176.3(4)	C(13)–C(12)–C(11)	123.3(3)
Fe–C(2)–O(2)	176.9(4)	C(13)–C(12)–C(44)	121.9(3)
Fe–C(3)–O(3)	179.2(5)	C(11)–C(12)–C(44)	114.3(3)
C(2)–Fe–C(1)	101.17(18)	C(10)–C(11)–C(41)	118.8(3)
C(2)–Fe–C(3)	100.92(20)	C(10)–C(11)–C(12)	117.1(3)
C(2)–Fe–C(42/43) [a]	115.04(16)	C(41)–C(11)–C(12)	115.9(3)
C(2)–Fe–C(11/41) [a]	111.87(17)	C(411)–C(41)–C(42)	122.5(3)
C(1)–Fe–C(3) [b]	85.62(21)	C(411)–C(41)–C(11)	124.6(3)
C(3)–Fe–C(42/43) [b]	93.99(17)	C(42)–C(41)–C(11)	112.9(3)
C(42/43)–Fe–C(11/41) [b]	61.53(14)	C(421)–C(42)–C(43)	122.5(3)
C(11/41)–Fe–C(1) [b]	99.36(16)	C(421)–C(42)–C(41)	122.3(3)
C(12)–C(13)–F(131)	111.5(2)	C(43)–C(42)–C(41)	115.2(3)
C(12)–C(13)–F(132)	113.0(3)	C(431)–C(43)–C(44)	116.8(3)
C(12)–C(13)–F(133)	113.4(3)	C(431)–C(43)–C(42)	118.0(3)
F(131)–C(13)–F(132)	103.3(3)	C(44)–C(43)–C(42)	116.1(3)
F(131)–C(13)–F(133)	107.1(3)	C(441)–C(44)–C(12)	126.6(3)
F(132)–C(13)–F(133)	105.6(3)	C(441)–C(44)–C(43)	118.6(3)
C(11)–C(10)–F(101)	113.8(3)	C(12)–C(44)–C(43)	114.6(3)
C(11)–C(10)–F(102)	114.4(3)		
C(11)–C(10)–F(103)	111.3(3)		
F(101)–C(10)–F(102)	102.8(3)		
F(101)–C(10)–F(103)	106.9(3)		
F(102)–C(10)–F(103)	107.0(3)		

[a] C(42/43) represents the centre of the C(42)–C(43) bond and has fractional co-ordinates 0.0049(2),0.3117(4),0.3235(2). Similarly C(11/41) has co-ordinates 0.0603(2),0.1111(4), 0.2960(2). [b] *cis*-Basal angles only.

Complex (1), in fact, represents the first example of a arene tricarbonyliron complex.* The arene ring is asymmetrically η^4-bonded to iron (*i.e.* as a butadiene derivative) with only one of the metal-bonded ring carbons carrying an electronegative substituent.

The geometry and molecular parameters of the Fe(butadiene)$(CO)_3$ fragment are in accord with previous studies [5] in that: (*i*) the metal co-ordination approximates to square pyramidal (s.p.) with the apical carbonyl function [C(2)O(2)] lying in an approximate fragment mirror plane; (*ii*) the average iron–' inner ' carbon(41,42) separation [2.069(3) Å] is significantly shorter than the average iron–' outer ' carbon(11,43) distance [2.112(3) Å]; and (*iii*) the C(inner)–C(inner) bond [1.410(5) Å] is somewhat shorter (*ca.* 0.056 Å) than the average C(inner)–C(outer) bond, reversing the observation for unco-ordinated butadienes [6] and indicating substantial back donation from iron to the lowest-lying antibonding molecular orbital of the organic ligand.

The degree of back donation in (1) appears to be comparable with that in $[Ru(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)]$ [7] but somewhat less than in $[Rh(\eta\text{-}C_5H_5)\{\eta^4\text{-}C_6(CF_3)_6\}]$ [8] and $[Rh(C_9H_7F_6O_2)\{\eta^4\text{-}C_6(CF_3)_6\}]$.[9] Clearly this division could be interpreted either in terms of the π-acidity of the groups *trans* to the butadiene, or as a consequence of the greater electronegativity of CF_3 over CH_3. It is noteworthy, although not statistically significant, that the greater C(inner)–C(outer) bond lengthening in (1) occurs adjacent to the CF_3 group.

The arene ring is completed by the localized double bond C(44)–C(12) [1.352(5) Å]. With respect to the plane of projection (Figure 1), the atomic sequence C(43)C(44)C(12)C(11) is tipped 43.0° out of the plane, away from the metal atom. This may be compared with the corresponding dihedral angles of 42.8, 42, and 47.9° respectively for the η^4-arene complexes above. Full details of molecular planes and torsion angles [10] around the six-membered ring may be found in Table 3(*b*). In each case, torsion angles have been calculated with respect to the pendent carbon atoms, since the intramolecular contacts listed in Table 3(*a*) reveal that the pendent groups play the major role in ring twisting.

Other molecular parameters require little or no comment. The average Fe–CO, C–O, $C(sp^2)$–$C(sp^2)$, $C(sp^2)$–$C(sp^3)$, C–H, and C–F distances are 1.803(12), 1.135(2), 1.502(17), 1.510(9), 0.92(5), and 1.343(13) Å respectively. Figure 2 presents a view of the crystal packing, seen along the *b* axis, looking towards the origin. There are no short intermolecular contacts.

* The stereochemical rigidity of the complex in solution is illustrated by the temperature invariance of the ^1H and ^{19}F n.m.r. spectra.

[4] G. M. Whitesides and W. J. Ehmann, *J. Amer. Chem. Soc.*, 1969, **91**, 3800.

[5] See, for example, Table 4 of F. A. Cotton, V. W. Day, B. A. Frenz, K. I. Hardcastle, and J. M. Troup, *J. Amer. Chem. Soc.*, 1973, **95**, 4522.

[6] W. Haugen and M. Traetteberg in ' Selected Topics in Structure Chemistry,' eds. P. Anderson, O. Bastiansen, and S. Furberg, Universitetsfurlaget, Oslo, 1967, pp. 113—123.

[7] G. Huttner, S. Lange, and E. O. Fischer, *Angew. Chem. Internat. Edn.*, 1971, **10**, 556; G. Huttner and S. Lange, *Acta Cryst.*, 1972, **B28**, 2049.

[8] M. R. Churchill and R. Mason, *Proc. Roy. Soc.* (*A*), 1966, **292**, 61; *Adv. Organometallic Chem.*, 1967, **5**, 100.

[9] D. M. Bartex, J. A. Evans, R. D. W. Kemmitt, and D. R. Russell, *Chem. Comm.*, 1971, 331.

[10] W. Klyne and V. Prelog, *Experientia*, 1960, **16**, 521.

An insight into the mode of formation of (1) was obtained by the isolation from the reaction mixture of a second product. Elution with methylene chloride–hexane gave yellow crystals of complex (2), which showed in the i.r. spectrum not only terminal carbonyl bands due to $Fe(CO)_3$ but also two bands at 1 749 and 1 728 cm^{-1}, indicating the presence of ketonic carbonyl groups. This was confirmed by the elemental analysis and a mass spectrum, which indicated that (2) was a 1 : 1 adduct of $[Fe(\eta^4\text{-}C_4Me_4)(CO)_3]$ and $CF_3C_2CF_3$ plus two molecules of carbon monoxide. The ^1H and ^{19}F

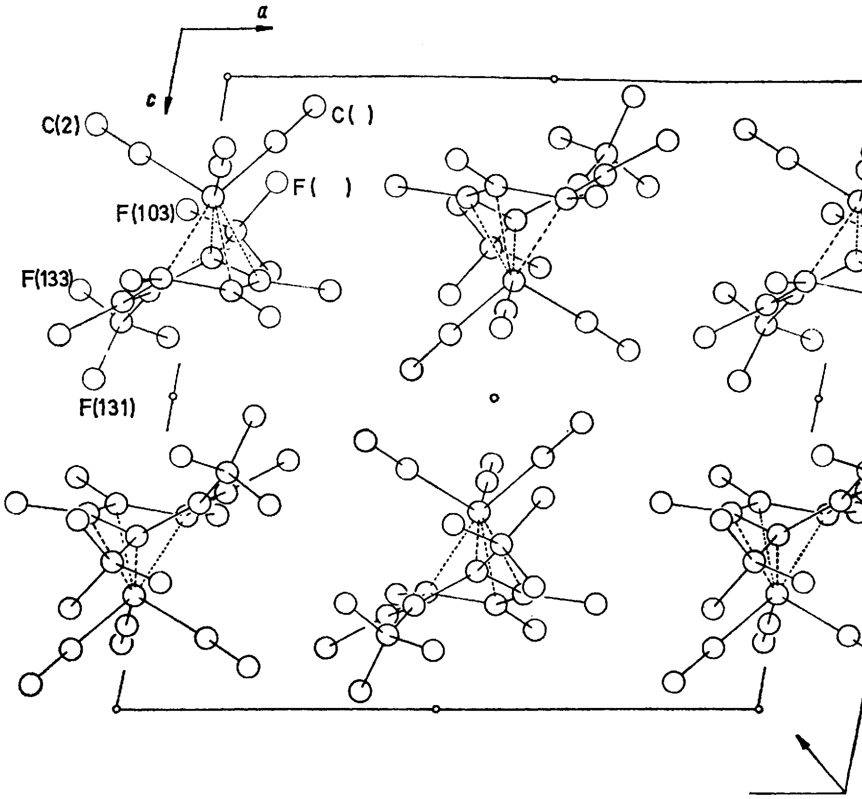


FIGURE 2 Packing diagram for (1), looking along the *b* axis. Hydrogen atoms are omitted for clarity, and only the minimum complement of symmetry elements necessary to describe the array is included

TABLE 3

Intramolecular contacts (Å) and equations of least-squares planes [deviations (Å) from planes in square brackets] for complex (1)

(*a*) Intramolecular short contacts

F(132) · · · F(102)	2.521(5)	H(421) · · · H(433)	2.09(8)
F(102) · · · H(412)	2.69(7)	H(431) · · · H(443)	2.32(9)
F(101) · · · H(412)	2.45(6)	H(441) · · · F(131)	2.40(6)
H(413) · · · H(422)	2.21(9)		

(*b*) Unweighted least-squares planes

Plane (i): C(11), C(41), C(42), C(43)

$$-2.414x - 2.437y + 13.035z = 3.444$$

[C(11) 0.004, C(41) −0.008, C(42) 0.008, C(43) −0.004, Fe −1.640, C(12) 0.958, C(44) 0.906, C(10) −0.256, C(411) −0.005, C(421) 0.032, C(431) −0.229]

Plane (ii): C(11), C(12), C(44), C(43)

$$6.369x + 0.424y + 10.517z = 3.101$$

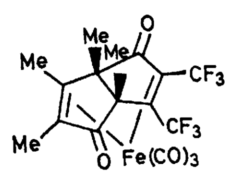
[C(11) −0.011, C(12) 0.021, C(44) −0.021, C(43) 0.011, Fe −1.005, C(10) −0.325, C(13) 0.263, C(441) −0.003, C(431) −0.199]

Dihedral angle: (i)–(ii) 43.0 °

Torsion angles * (°)

C(441)–C(44)–C(12)–C(13)	+7.7
C(13)–C(12)–C(11)–C(10)	−23.2
C(10)–C(11)–C(41)–C(411)	+12.0
C(411)–C(41)–C(42)–C(421)	+0.1
C(421)–C(42)–C(43)–C(431)	−10.2
C(431)–C(43)–C(44)–C(441)	+10.9

* Sign convention as defined in ref. 12.



(2)

spectra again showed resonances corresponding to an asymmetric structure, and it was decided to structurally characterize (2) by means of single-crystal *X*-ray crystallography.

The molecular structure and atomic-numbering scheme are shown in Figure 3. Internuclear distances (uncorrected for libration) and important interbond angles are presented in Tables 4 and 5. Angles involving hydrogen atoms are deposited as Appendix B.

Complex (2) is thus formulated as a tricarbonyl(diene)iron complex in which the unsaturated hydrocarbon functions reside in a bicyclic diketone. Examination of the angles subtended at the metal suggest a distorted trigonal-bipyramidal (t.b.p.) geometry with C(2) and the C(113)–C(114) alkene as apices. All three Fe–CO distances are significantly different with Fe–CO(axial) the shortest. In the t.b.p. parent molecule,

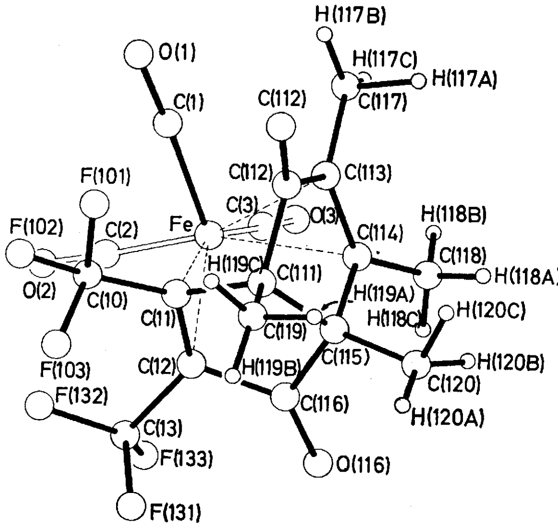


FIGURE 3 Perspective view of the complex $[Fe\{C_8Me_4(CF_3)_2O_2\}(CO)_3]$ (2)

TABLE 4

Interatomic distances (Å) in complex (2)

Fe–C(1)	1.822(3)	C(11)–C(12)	1.455(4)
C(1)–O(1)	1.140(4)	C(12)–C(116)	1.485(4)
Fe–C(2)	1.800(3)	C(116)–C(115)	1.530(4)
C(2)–O(2)	1.140(4)	C(115)–C(111)	1.557(4)
Fe–C(3)	1.843(3)	C(115)–C(114)	1.540(4)
C(3)–O(3)	1.137(4)	C(114)–C(113)	1.393(4)
Fe–C(11)	2.055(3)	C(113)–C(112)	1.511(4)
Fe–C(12)	2.109(3)	C(112)–C(111)	1.545(4)
Fe–C(113)	2.306(3)	C(111)–C(11)	1.562(4)
Fe–C(114)	2.371(3)		
		C(115)–C(120)	1.530(4)
C(11)–C(10)	1.512(4)	C(120)–H(120A)	0.97(5)
C(10)–F(101)	1.346(4)	C(120)–H(120B)	0.94(6)
C(10)–F(102)	1.345(4)	C(120)–H(120C)	0.99(5)
C(10)–F(103)	1.351(4)	C(114)–C(118)	1.505(4)
C(12)–C(13)	1.510(4)	C(118)–H(118A)	0.91(5)
C(13)–F(131)	1.358(3)	C(118)–H(118B)	0.95(4)
C(13)–F(132)	1.344(4)	C(118)–H(118C)	0.93(5)
C(13)–F(133)	1.353(4)	C(113)–C(117)	1.510(5)
		C(117)–H(117A)	0.91(5)
C(116)–O(116)	1.219(3)	C(117)–H(117B)	1.01(4)
C(112)–O(112)	1.209(4)	C(117)–H(117C)	0.96(4)
		C(111)–C(119)	1.529(4)
		C(119)–H(119A)	1.05(4)
		C(119)–H(119B)	0.97(5)
		C(119)–H(119C)	0.96(4)

$[Fe(CO)_5]$, the relative lengths of Fe–C(axial) and Fe–C(equatorial) are still a subject of some debate.[11] Only three monosubstituted $[Fe(alkene)(CO)_4]$ complexes, invariably t.b.p. with the alkene fragment equatorially positioned, have been accurately studied [12-14] and again the available evidence is contradictory.

* The positive sign indicates rehybridization towards iron.

[11] B. Beagley in 'Molecular Structure by Diffraction Methods,' eds. G. Sim and L. E. Sutton, The Chemical Society, London, 1973, vol. 1, pp. 146—148.

In (butadiene)iron tricarbonyls [*e.g.* complex (1)] the geometry is exclusively s.p., but non-conjugated diene complexes may adopt either limiting geometry, although intermediacy is often observed. When, however, such $[Fe(diene)(CO)_3]$ molecules are referred to a t.b.p. framework with one alkene equatorial, the other axial, the more electronegatively substituted alkene is invariably equatorially sited. Complex (2), $[Fe(C_7H_8O_2)(CO)_3]$,[14] and $[Fe(C_{15}H_8F_{12})(CO)_2\{P[(OCH_2)_3CMe]\}]$ [15] are

TABLE 5

Interbond angles (°) in complex (2) not involving hydrogen atoms

Fe–C(1)–O(1)	176.3(3)	C(11)–C(10)–F(101)	110.6(3)
Fe–C(2)–O(2)	175.7(3)	C(11)–C(10)–F(102)	112.2(2)
Fe–C(3)–O(3)	178.2(2)	C(11)–C(10)–F(103)	114.2(2)
C(2)–Fe–C(113/114) *	174.8(4)	F(101)–C(10)–F(102)	107.2(3)
C(2)–Fe–C(1)	87.70(14)	F(101)–C(10)–F(103)	105.8(2)
C(2)–Fe–C(3)	86.19(15)	F(102)–C(10)–F(103)	106.3(3)
C(2)–Fe–C(11/12) *	93.64(13)	C(12)–C(13)–F(131)	110.2(2)
C(113/114)–Fe–C(1)	95.27(12)	C(12)–C(13)–F(132)	115.0(2)
C(113/114)–Fe–C(3)	89.02(14)	C(12)–C(13)–F(133)	112.0(3)
C(113/114)–Fe–C(11/12)	88.60(11)	F(131)–C(13)–F(132)	105.9(3)
C(1)–Fe–C(3)	103.19(13)	F(131)–C(13)–F(133)	106.5(2)
C(3)–Fe–C(11/12)	137.17(12)	F(132)–C13)–F(133)	106.8(2)
C(11/12)–Fe–C(1)	119.59(13)	C(115)–C(114)–C(113)	111.7(2)
C(111)–C(11)–C(12)	109.1(2)	C(115)–C(114)–C(118)	119.0(2)
C(111)–C(11)–C(10)	116.8(2)	C(113)–C(114)–C(118)	126.3(3)
C(12)–C(11)–C(10)	125.0(3)	C(114)–C(113)–C(112)	107.4(2)
C(11)–C(12)–C(116)	109.5(2)	C(114)–C(113)–C(117)	125.4(3)
C(11)–C(12)–C(13)	127.7(2)	C(112)–C(113)–C(117)	121.6(2)
C(116)–C(12)–C(13)	114.1(2)	C(113)–C(112)–C(111)	105.6(2)
C(12)–C(116)–C(115)	105.6(2)	C(113)–C(112)–O(112)	126.0(3)
C(12)–C(116)–O(116)	128.2(3)	C(111)–C(112)–O(112)	128.3(3)
C(115)–C(116)–O(116)	126.1(3)	C(119)–C(111)–C(11)	115.4(3)
C(120)–C(115)–C(111)	117.3(2)	C(119)–C(111)–C(115)	116.0(2)
C(120)–C(115)–C(116)	113.7(2)	C(119)–C(111)–C(112)	114.8(2)
C(120)–C(115)–C(114)	113.1(3)	C(11)–C(111)–C(115)	101.7(2)
C(111)–C(115)–C(116)	105.9(2)	C(11)–C(111)–C(112)	104.8(2)
C(111)–C(115)–C(114)	102.6(2)	C(115)–C(111)–C(112)	102.4(2)
C(116)–C(115)–C(114)	102.7(2)		

* C(113/114) represents the centre of the C(113)–C(114) linkage having fractional co-ordinates 0.4632(3),0.1326(2),0.1244(2). C(11/12) is defined similarly as 0.2672-(3),0.1136(1),0.2879(2).

recent examples of this type. As anticipated, Fe ⟶ π*(C=C) back donation occurs to a greater degree in the equatorial plane and results in a relatively weak iron–alkene(axial) link, best demonstrated by the co-ordinated C=C length and degree of rehybridization ($sp^2 \longrightarrow sp^3$) at C. For complex (2), C(113)–C(114) is *ca.* 0.06 Å shorter than C(11)–C(12), and C(11) and C(12) reside *ca.* +0.39 Å* out of the plane defined by C(10), C(13), C(111), and C(116), whilst for C(113) and C(114) the equivalent rehybridization is only *ca.* +0.27 Å.

Alkene and carbonyl ligands in complexes of this type compete for metal ⟶ ligand back bonding, and in the $[Fe(diene)(CO)_3]$ molecules discussed above the iron–alkene(equatorial) link is sufficiently strong to render a substantial lengthening of Fe–CO(equatorial) over Fe–CO(axial). Additionally, a large discrepancy in OC(equatorial)-Fe-alkene(equatorial) angles may result in different Fe–CO(equatorial) distances. In complex (2), for example, Fe–C(3) (more *trans* to alkene) is *ca.* 0.02 Å longer than Fe–C(1). Finally, since metal ⟶ CO back donation is antibonding with respect to the C≡O bond, long Fe–CO should result in short C–O;

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

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

[14] B. M. Chisnall, M. Green, R. P. Hughes, and A. J. Welch, *J.C.S. Dalton*, 1976, 1899.

[15] R. J. Goddard, Ph. D. Thesis, University of Bristol, 1976, pp. 133—157.

although in complex (2) C(3)–O(3) *is* slightly less (0.004 Å) than C(1)–O(1) and C(2)–O(2), the difference here is clearly not a significant one.

The bicycle dienone in (2) is folded by *ca.* 97.9° along C(111)–C(115), and the three-dimensional nature of this ligand may explain the comparatively little intramolecular crowding. Table 6 lists the three short contacts

TABLE 6

Intramolecular contacts (Å) and equations of least-squares planes [deviations (Å) from planes in square brackets] for complex (2)

(*a*) Intramolecular short contacts

F(101) · · · H(119C)	2.46(4)	F(103) · · · F(132)	2.624(3)
H(120A) · · · H(119A)	2.37(5)		

(*b*) Molecular planes

Plane (*i*): O(1), C(1), Fe, O(3), C(3)

$$-7.693x + 7.830y + 5.805z = 0.404$$

[O(1) 0.017, C(2) −0.028, Fe 0.011, O(3) 0.002, C(3) −0.003, C(11) −0.142, C(12) 0.346]

Plane (*ii*): C(111), C(10), C(116), C(13)

$$0.416x + 12.817y - 7.858z = -1.087$$

[C(111) −0.025, C(10) 0.019, C(116) 0.026, C(13) −0.020, C(11) 0.395, C(12) 0.388]

Plane (*iii*): C(112), C(117), C(115), C(118)

$$-7.297x + 10.290y + 3.866z = -1.801$$

[C(112) −0.024, C(117) 0.018, C(115) 0.024, C(118) −0.018, C(113) 0.284, C(114) 0.249]

Plane (*iv*): C(111), C(11), C(12), C(116)

$$-2.793x + 11.412y - 8.772z = -0.483$$

[C(111) −0.006, C(11) 0.009, C(12) −0.010, C(116) 0.006, C(115) 0.444]

Plane (*v*): C(112), C(113), C(114), C(115)

$$7.992x - 7.538y - 4.912z = 2.091$$

[C(112) 0.014, C(113) −0.024, C(114) 0.024, C(115) −0.014, C(111) −0.503]

Planes (*vi*) and (*vii*) are the three-atom sequences C(111),C(115), C(116) and C(112),C(111),C(115), and make dihedral angles of 28.5 and 31.2° with (*iv*) and (*v*) respectively.

Torsion angles(°)*	
C(13)–C(12)–C(11)–C(10)	−1.14
C(10)–C(11)–C(111)–C(119)	+40.52
C(119)–C(111)–C(112)–O(112)	−18.12
O(112)–C(112)–C(113)–C(117)	−1.18
C(117)–C(113)–C(114)–C(118)	−1.96
C(118)–C(114)–C(115)–C(120)	+50.08
C(120)–C(115)–C(111)–C(119)	−29.61
C(120)–C(115)–C(116)–O(116)	−25.39
O(116)–C(116)–C(12)–C(13)	+16.78

* Sign convention defined in ref. 12.

observed, together with molecular planes and a full complement of torsion angles, again defined with respect to the pendent CH_3, CF_3, and O groups. Individually, the two five-membered rings are not planar, with the carbon atom opposite the alkene function acting as apex of an envelope conformation. Both atoms are folded towards the metal, C(115) by *ca.* 28.5° and C(111) by *ca.* 31.2°. Figure 4 shows the disposition of molecules within one unit cell. There are no close intermolecular contacts.

It is suggested * that both (1) and (2) are formed from a common intermediate (A) (Scheme 1). Structurally related species have been isolated from the reaction (u.v. irradiation) of fluoro-olefins with both [Fe(η-C_4H_4)(CO)$_3$] and [Fe(η^4-C_4Me_4)(CO)$_3$].[3] Moreover, the irradiation of a solution of, for example, (buta-1,3-diene)tricarbonyliron and hexafluorobut-2-yne has been shown [16] to lead to an oxidative reaction in which the acetylene links the iron and C_4 framework exactly as depicted in (A). However, our understanding of these

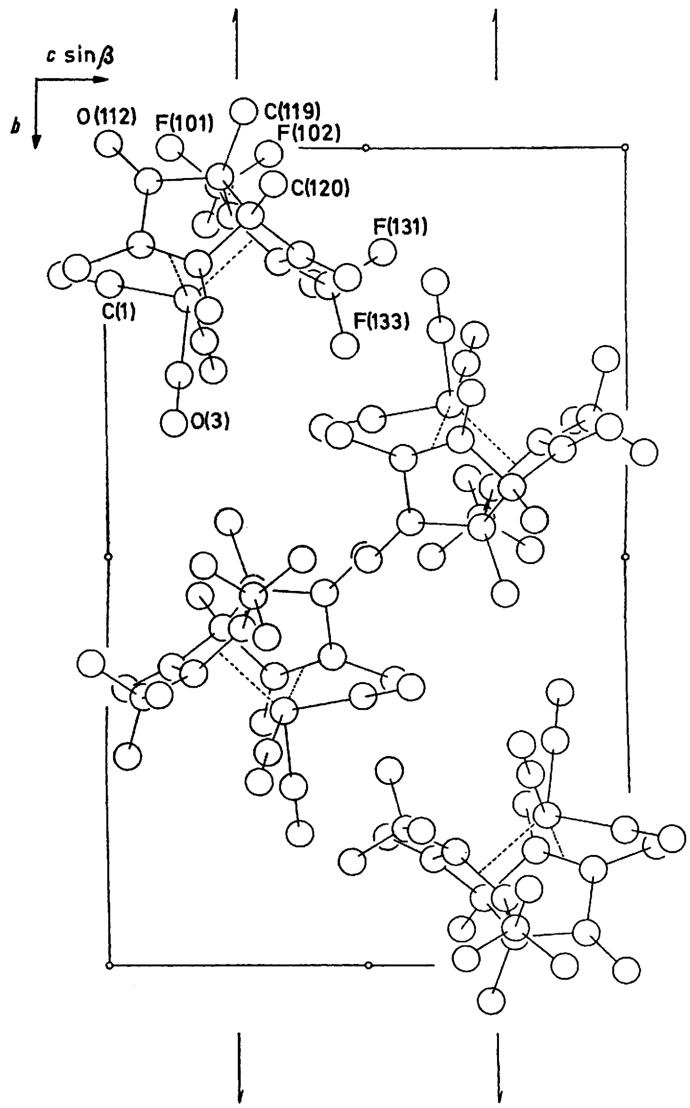


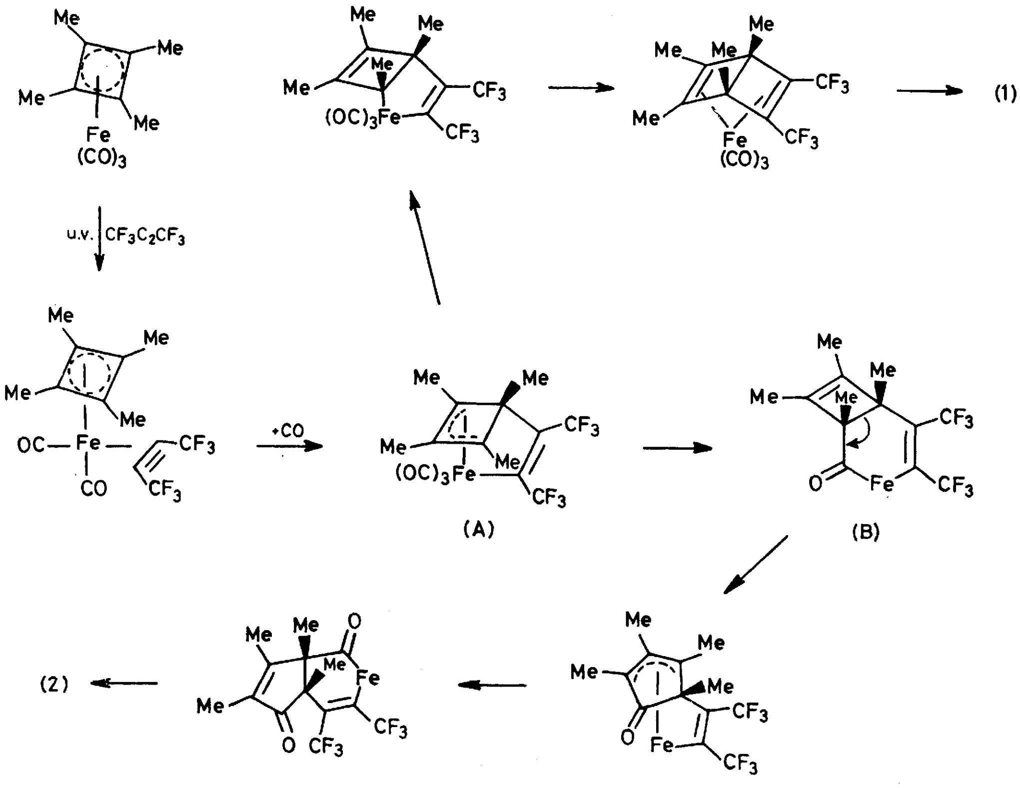
FIGURE 4 Crystal structure of complex (2), as seen along the *a* axis, looking towards the origin. Hydrogen atoms and the diagonal glide symmetry element are omitted for sake of clarity

* An alternative route to (1) involves the conversion of [Fe(η^4-C_4Me_4)(CO)$_3$] into the ferracyclopentadiene [Fe{C(Me)=C(Me)C(Me)=C(Me)}(CO)$_3$] followed by insertion of a hexafluorobut-2-yne molecule to give a ferracycloheptatriene, which could then be converted into an arene complex. However, such species could not serve as precursors for the diketone (2), and it is more persuasive to argue that (1) and (2) are formed from a common reaction path.

[16] M. Bottrill, R. Davies, R. Goddard, M. Green, R. P. Hughes, B. Lewis, and P. Woodward, *J.C.S. Dalton*, 1977, 1252

initial steps is not complete since the exact mode of formation of (A) remains to be elucidated. One possibility is shown in Scheme 1, and is supported by various observations. Irradiation of [$Fe(\eta$-$C_4H_4)(CO)_3$] in tetrahydrofuran (thf) has been shown [17] to lead to loss of CO and the formation of a monotetrahydrofuran adduct; dimethyl maleate [2] and hexafluoroacetone [3] form similar η^2-bonded dicarbonyl species, the latter on treatment with phosphite or phosphines giving a hexafluoroacetone-linked product isostructural with (A). Nevertheless, a difficulty here is that products (1) and (2) are tricarbonyl species, whereas the initial step requires loss of carbon monoxide. A way out of this difficulty is to postulate that the displaced carbon monoxide does not move beyond the solvent cage, and that recombination initiates carbon–carbon bond formation. Clearly a simple alternative is to postulate that irradiation can lead to a finite concentration of an η^2-bonded C_4Me_4 species. Unfortunately, in order to make a firm decision, it is not only necessary to know how easily these two alternative species can be generated but also their relative reactivities towards a reactant like hexafluorobut-2-yne.

As illustrated, intermediate (A) is a potential precursor of both (1) and (2),* reductive ($Fe^{II} \longrightarrow Fe^0$) carbon–carbon bond formation giving directly a tricarbonyl-(Dewar benzene)iron complex, which might be expected to readily rearrange to the isolated arene complex (1). There is precedent for the initial step in this sequence in that the 1 : 1 adduct of [$Fe(C_4H_6)(CO)_3$] and hexafluorobut-2-yne undergoes a ring-closure reaction on heating to form a tricarbonyl(cyclohexadiene)iron complex,[16,18] and a similar reaction with (A) can be readily envisaged.† If (A) is written as a σ,η-allyl system then it can be seen that a 'carbonyl-insertion' reaction would lead to the formation of the acyl species (B). Ring enlargement with concomitant movement of the $Fe(CO)_3$ group to stabilize the resulting η^3-allyl species would lead to (C), which could then, *via* a further 'carbonyl-insertion' step, give an immediate precursor of (2).



SCHEME 1 Ligands have been omitted for clarity

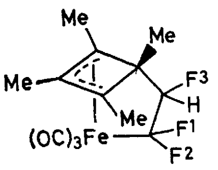
A study [19] of the reactions of trifluoroethylene provided further examples of four- to five-membered ring-expansion reactions. Irradiation of a solution of [$Fe(\eta^4$-$C_4Me_4)(CO)_3$] and trifluoroethylene in hexane afforded two products (3) and (4). Examination of the spectroscopic data, together with elemental analysis and

* A photoinitiated disrotatory ring-opening process to give a ferracycloheptatriene seems, on the basis of lack of precedent, a less likely alternative.

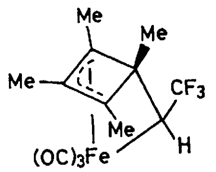
† In a preliminary communication concerned with the mechanism of the oxidative decomposition of tricarbonyl(η-cyclobutadiene)iron complexes (R. H. Grubbs and T. A. Pancoast, *J. Amer. Chem. Soc.*, 1977, **99**, 2382) a related reaction path is postulated.

[17] I. Fischler, K. Hildenbrand, and E. Koerner von Gustorf, *Angew. Chem. Internat. Edn.*, 1975, **14**, 54.
[18] R. Davis, M. Green, and R. P. Hughes, *J.C.S. Chem. Comm.*, 1975, 405.
[19] A. Bond, M. Green, and S. H. Taylor, *J.C.S. Chem. Comm.*, 1973, 112.

mass spectroscopy, suggested that (3) is an analogue of the previously described[3] tetrafluoroethylene adducts, in which the trifluoroethylene bridges the iron and the



(3)

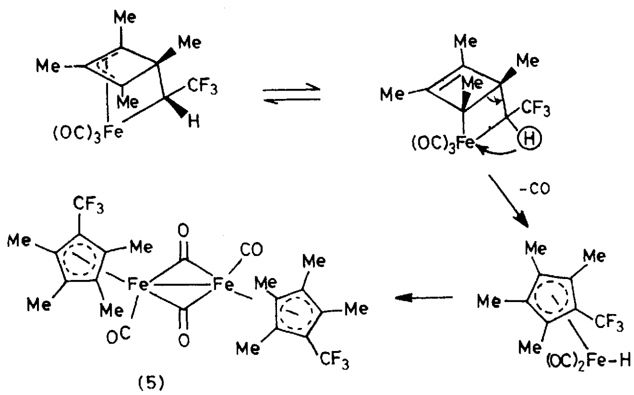


(4)

η^3-cyclobutenyl system. The appearance in the ^{19}F n.m.r. spectrum of resonances and coupling constants consistent with the presence of the arrangement ACF_2·CFHC, and the occurrence of two geminal fluorine resonances at low field, suggest the illustrated structure for the adduct. Recently, a related sequence of reactions between dimethyl maleate and $[Fe(\eta\text{-}C_4H_4)(CO)_3]$ has been reported.[2]

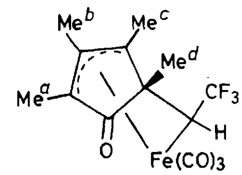
Of greater interest was the second product (4) of the reaction, which was shown by elemental analysis and mass spectroscopy to be isomeric with (3). Although the ^1H spectrum showed four methyl resonances with shifts similar to those observed for the other η^3-cyclobutenyl systems, the low-field $FeCF_2CF\mathit{H}$ resonance was absent and an additional quartet [J(HF) 12.0 Hz] was observed at high field (τ 10.2), suggesting that a fluorine migration reaction had occurred and that the high-field hydrogen was attached to a carbon α to the iron atom. In agreement, the ^{19}F spectrum showed only one resonance, a doublet [J(HF) 12.0 Hz], confirming the presence of the arrangement $FeCH(CF_3)$ as shown in the proposed structure. Related rearrangements of trifluoroethylene [$CFH{=}CF_2 \longrightarrow PtCH(CF_3)Pt$], hexafluoropropene [$CF_3CF{=}CF_2 \longrightarrow PtC(CF_3)_2Pt$],[20] and tetrafluoroethylene [$CoCF_2CF_2Co \longrightarrow CoCF(CF_3)Co$][21] have been observed; however, more detailed work is required before the mechanisms of these rearrangements can be properly understood. It is interesting that separate experiments showed that (3) is not the precursor of the rearranged complex (4), suggesting that competing reaction paths are involved.

When the melting point of (4) was recorded an interesting colour change from yellow to deep red was observed. With this in mind the thermolysis of (4) was examined. In refluxing hexane a black-red crystalline product (5) was obtained. Elemental analysis and mass spectroscopy indicated that (5) is a binuclear species, and this was supported by the appearance in the i.r. spectrum of both terminal (1 960s) and bridging carbonyl bands (1 770s cm^{-1}). These observations, together with the appearance in the ^{19}F n.m.r. spectrum of a sharp singlet resonance due to a trifluoromethyl group, suggested that a ring expansion had occurred, and in support of this the ^1H spectrum showed only two methyl environments. It is, therefore, proposed that (5) is a substituted dicarbonyl(η-cyclopentadienyl)iron dimer arising *via* an elimination reaction. The 1,2-hydrogen shift[22-24] is probably assisted in this case by the release of ring strain in a concerted ring enlargement, *i.e.* four-membered $\longrightarrow$ five-membered ring (Scheme 2). Formation of the Fe–Fe bond and loss of hydrogen would be expected to occur readily in refluxing hexane.[25]



Scheme 2

Careful examination of the thermolysis reaction mixture indicated the presence in low yield of a second product, whose mass spectrum suggested a molecular formula corresponding to the addition of one carbon monoxide molecule to (4). When (4) was heated under a pressure of carbon monoxide a high yield of this material was obtained, and was isolated after chromatography and recrystallization as the yellow crystalline



(5)

complex (6). Analysis and mass spectroscopy confirmed this suggestion, and the i.r. spectrum showed a ketonic carbonyl band at 1 731s cm^{-1} together with bands due to an $Fe(CO)_3$ system. Both the ^1H and ^{19}F spectra showed that (6) still contained the structural feature $FeCH(CF_3)$, and in addition four different methyl environments were present in the ^1H spectrum. These observations are consistent with the illustrated structure * for (6), where a four- to five-membered ring expansion has occurred with formal incorporation of carbon monoxide, the

* A preliminary X-ray study is in agreement with this structure.

[20] M. Green, A. Laguna, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 1011.

[21] B. L. Booth, R. N. Haszeldine, P. R. Mitchell, and J. J. Cox, *J. Chem. Soc. (A)*, 1969, 691.

[22] A. Sanders, L. Cohen, W. P. Giering, D. Kenedy, and C. V. Magatti, *J. Amer. Chem. Soc.*, 1973, **95**, 5430.

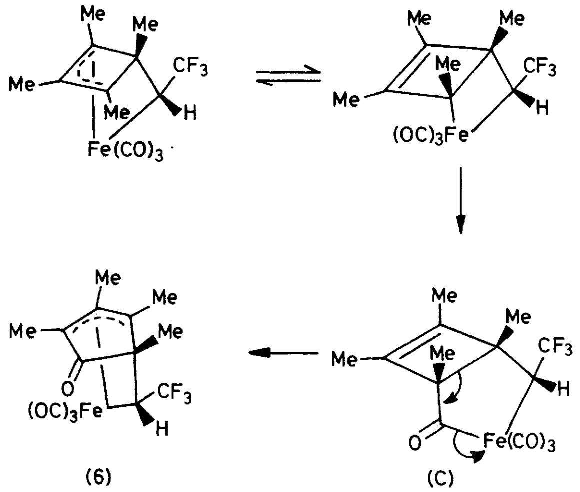
[23] N. J. Cooper and M. L. H. Green, *J.C.S. Chem. Comm.*, 1974, 761.

[24] R. R. Schrock, *J. Amer. Chem. Soc.*, 1974, **96**, 6796.

[25] P. L. Pauson, *Proc. Chem. Soc.*, 1960, 297; R. K. Kochhar and R. Pettit, *J. Organometallic Chem.*, 1966, **6**, 272.

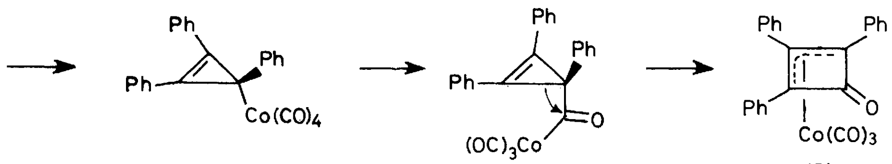
$Fe(CO)_3$ group becoming bonded to the resulting η^3-allyl system.

This reaction is clearly related to the second stage in the formation of (2). Conversion of the η^3-allyl into a σ,η-system (Scheme 3) followed by a ' carbonyl-insertion ' reaction leads to the intermediate (C), which then ring expands to (6).



SCHEME 3

It is interesting that the reaction of $Na[Co(CO)_4]$ with the triphenylcyclopropenium cation has been shown[26] by *X*-ray crystallography to give the four-membered η^3-allylic species (7). It is suggested that a similar ring



expansion (three to four) to those reported in this paper is involved, indicating the possible generality of this type of reaction.

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were recorded on a Varian Associates HA100 spectrometer at 100 MHz with $SiMe_4$ (τ 10.00) as internal reference. Fluorine-19 spectra were obtained on a JEOL PFT-100 spectrometer at 94.1 MHz; chemical shifts are relative to $CFCl_3$ as external reference. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer using Nujol mulls. The mass spectra were obtained on an A.E.I. MS 902 spectrometer operating at 70 eV.* Reactions, except those in sealed tubes, were conducted in a dry oxygen-free nitrogen atmosphere.

Reaction of Hexafluorobut-2-yne with Tricarbonyl(η^4-tetramethylcyclobutadiene)iron.—Hexafluorobut-2-yne (1.92 g, 12 mmol) was condensed (−196 °C) into a Carius tube (100 cm^3) containing tricarbonyl(η^4-tetramethylcyclobutadiene)iron (1.1 g, 4.4 mmol) dissolved in hexane (20 cm^3). The tube and contents were irradiated (250-W Hanovia u.v. lamp) for 4 d. The reaction was repeated four times, and the total reaction products were combined. The reaction mixture was filtered and the solvent removed *in vacuo*. Column chromatography (Florisil-packed column, 1 × 200 cm) of the residue and elution with hexane gave first unchanged $[Fe(\eta^4\text{-}C_4Me_4)(CO)_3]$, followed by an orange band. Removal of the solvent followed by recrystallization (−78 °C) from hexane afforded orange-red *crystals* of (1) (1.03 g, 14.0%), m.p. 62 °C (Found: C, 43.2; H, 3.1; F, 28.1. $C_{15}H_{12}F_6FeO_3$ requires C, 43.9; H, 2.9; F, 27.8%), ν(CO) at 2 069s, 2 013s, and 1 991m cm^{-1}. N.m.r. spectra in $CDCl_3$: ^1H, τ 7.40(br m, 3 H), 7.58(s, 3 H), 8.28[q, 3 H, *J*(HF) 3.0 Hz], and 8.44(s, 3 H); ^{19}F, 52.2[q, 3 F, *J*(FF) 18.0] and 55.4 p.p.m. [qq, 3 F, *J*(HF) 3.0, *J*(FF) 18.0 Hz]. The mass spectrum (base peak *m/e* 251) showed peaks at *m/e* 382 (*P* − CO, 25%), 354 (*P* − 2CO, 35%), 355 (*P* − 2CO − F, 4%), 270 (*P* − Fe − 3CO, 100%), and 251 (*P* − Fe − 3CO − F, 100%).

Further elution with hexane–methylene chloride (1 : 1) gave a yellow band, which was collected and the solvent removed. Recrystallization (−30 °C) from hexane–methylene chloride gave dark yellow *crystals* of (2) (0.2 g, 2.4%) (Found: C, 43.8; H, 2.7. $C_{17}H_{12}F_6FeO_5$ requires C, 43.8; H, 2.6%), ν(CO) (hexane) at 2 083s, 2 035s, 2 013s, 1 749m, and 1 728m cm^{-1}. N.m.r. spectra in $CDCl_3$: ^1H, τ 8.0(s, 3 H), 8.1(s, 3 H), and 8.9(s, 6 H). ^{19}F, 51.2 [q, 3 F, *J*(FF) 10.0] and 53.9 p.p.m. [q, 3 F, *J*(FF) 10.0 Hz]. The mass spectrum (base peak *m/e* 288) showed peaks at *m/e* 466 (*P*, 1%), 438 (*P* − CO, 8%), 410 (*P* − 2CO, 28%), 382 (*P* − 3CO, 31%), 326 (*P* − 3CO − Fe, 10%), and 288 (*P* − Fe − 3CO − 2F, 100%).

Reaction of Trifluoroethylene with Tricarbonyl(η^4-tetramethylcyclobutadiene)iron.—Similarly, u.v. irradiation (24 h) of a solution of $[Fe(\eta^4\text{-}C_4Me_4)(CO)_3]$ (0.30 g, 1.2 mmol) and trifluoroethylene (0.20 g, 2.4 mmol) in hexane (25 cm^3) gave, after chromatography [eluted with hexane–methylene chloride (1 : 1)] and recrystallization (−78 °C) from hexane–methylene chloride, yellow *crystals* of (3) (0.24 g, 60%), m.p. 120 °C (Found: C, 47.1; H, 3.9; F, 17.0. $C_{13}H_{13}F_3FeO_3$ requires C, 47.4; H, 4.0; F, 17.3%), ν(CO) (hexane) at 2 071m, 2 015s, and 1 993s cm^{-1}. N.m.r. spectra in $CDCl_3$: ^1H, τ 5.87[m, 1 H, CHF, *J*(HF^3) 54.0, *J*(HF^2) 15.0, *J*(HF^1) 6.0 Hz], 7.84(s, 3 H), 8.24(s, 3 H), 8.33(s, 3 H), and 8.88(s, 3 H); ^{19}F, 51.4[m, 1 F, F^2, *J*(F^{1}F^2) 220, *J*(F^{2}F^3) 11.0, *J*(F^{2}H) 15.0], 69.0[m, 1 F, F^1, *J*(F^{1}F^2) 220, *J*(F^{1}F^3) 2.0, *J*(F^{1}H) 6.0], and 191.0 p.p.m. [m, 1 F, F^3, *J*(F^{2}F^3) 11.0, *J*(F^{1}F^3) 2.0, *J*(F^{3}H) 54.0 Hz]. The mass spectrum (base peak *m/e* 128) showed peaks at *m/e* 330 (*P*, 1%), 311 (*P* − F, 1%), 302 (*P* − CO, 1%), 283 (*P* − CO − F, 5%), 274 (*P* − 2CO, 18%), 255 (*P* − 2CO − F, 1%), 246 (*P* − 3CO, 15%), and 227 (*P* − 3CO − F, 18%).

* Throughout this paper: 1 eV ≃ 1.60 × 10^{-19} J; 1 atm = 101 325 Pa.

[26] J. Potenza, R. Johnson, D. Mastropaolo, and A. Efraty, *J. Organometallic Chem.*, 1974, **64**, C13.

Prolonged irradiation (4 d) followed by chromatography (elution with hexane) gave starting material, complex (3), and a yellow band. Recrystallization (−78 °C) from hexane gave pale yellow *crystals* of (4) (0.08 g, 20%), m.p. 100 °C (Found: C, 47.3; H, 4.0; F, 17.3. $C_{13}H_{13}F_3FeO_3$ requires C, 47.4; H, 3.9; F, 17.3%), ν(CO) (hexane) at 2 056m, 1 995s, and 1 977s cm^{-1}. N.m.r. spectra in $CDCl_3$: ^1H, τ 8.12(s, 3 H), 8.14(s, 6 H), 9.16(s, 3 H), and 10.2[q, 1 H, $CHCF_3$, J(HF) 12.0 Hz]; ^{19}F, 55.7 p.p.m. [d, 3 F, $CHCF_3$, J(FH) 12.0 Hz]. The mass spectrum (base peak m/e 346) showed peaks at m/e 330 (P, 1%), 302 (P − CO, 25%), 274 (P − 2CO, 100%), and 247 (P − 3CO, 100%); metastable peaks occurred at 248 [(P − CO) ⟶ (P − 2CO)] and 211 [(P − 2CO) ⟶ (P − 3CO)].

TABLE 7

Final atomic co-ordinates (fractional; ×10^5, Fe; ×10^4, C, O, F; ×10^3, H) in complex (1)

Atom	x	y	z
Fe	642(4)	24 590(5)	18 553(3)
C(1)	903(3)	1 982(5)	993(3)
O(1)	1 431(3)	1 764(5)	443(3)
C(2)	−1 147(3)	1 825(5)	1 164(3)
O(2)	−1 904(3)	1 375(5)	758(3)
C(3)	106(4)	4 318(5)	1 380(3)
O(3)	144(4)	5 496(4)	1 077(3)
F(101)	1 019(2)	−744(3)	1 614(2)
F(102)	1 139(3)	−1 749(3)	3 040(2)
F(103)	−314(2)	−1 730(3)	2 027(2)
C(10)	504(3)	−897(4)	2 372(3)
C(11)	209(2)	564(4)	2 789(2)
C(12)	−670(2)	535(3)	3 353(2)
C(13)	−996(3)	−844(4)	3 837(3)
F(131)	−1 271(2)	−570(3)	4 729(2)
F(132)	−256(2)	−1 861(3)	4 062(2)
F(133)	−1 768(2)	−1 555(4)	3 271(2)
C(41)	− 997(2)	1 659(4)	3 131(2)
C(42)	604(3)	3 064(4)	3 333(2)
C(43)	−506(2)	3 169(4)	3 138(2)
C(44)	−1 060(2)	1 894(4)	3 495(2)
C(411)	2 127(3)	1 348(5)	3 285(3)
C(421)	1 280(3)	4 365(5)	3 720(3)
C(431)	−983(3)	4 712(4)	3 165(3)
C(441)	−1 929(3)	2 223(5)	4 025(3)
H(411)	241(4)	100(7)	390(5)
H(412)	229(5)	61(8)	281(5)
H(413)	249(4)	208(6)	305(4)
H(421)	97(4)	523(7)	347(4)
H(422)	199(5)	421(8)	364(5)
H(423)	139(4)	437(7)	441(5)
H(431)	−168(4)	472(6)	280(4)
H(432)	−101(4)	491(7)	357(5)
H(433)	−58(4)	547(6)	288(4)
H(441)	−233(4)	149(7)	406(4)
H(442)	−170(4)	251(7)	466(5)
H(443)	−238(5)	293(7)	371(5)

Carbonylation of Complex (4).—A solution of (4) (0.20 g, 0.6 mmol) in hexane (30 cm^3) contained in a stainless-steel autoclave (100 cm^3, glass-lined) was heated (100 °C, 2 h) under a pressure (100 atm) of carbon monoxide. Removal of the solvent *in vacuo*, followed by chromatography on alumina [eluted with hexane–methylene chloride (1 : 1)] and crystallization (−78 °C) from hexane, gave pale yellow *needles* of (6) (0.195 g, 90%), m.p. 105—106 °C (Found: C, 46.7; H, 3.5; F, 15.8. $C_{14}H_{13}F_3FeO_4$ requires C, 46.8; H, 3.5; F, 15.9%), ν(CO) (hexane) at 2 059m, 2 001s, 1 988s, and 1 731m cm^{-1}. N.m.r. spectra in $CDCl_3$: ^1H, τ 7.82(s, 3 H, Me^b), 8.01(s, 3 H, Me^a), 8.15(s, 3 H, Me^c), 9.08(q, 3 H, Me^d), and 10.14[q, 1 H, $CHCF_3$, J(HF) 13.0 Hz]; ^{19}F, 53.9 p.p.m. [dq, 3 F, $CHCF_3$, J(FH) 13.0, J(FMe) 1.5 Hz]. The mass spectrum (base peak m/e 274) showed peaks at m/e 358 (P, 50%), 330 (P − CO, 57%), 302 (P − 2CO, 100%), 274 (P − 3CO, 100%), and metastable peaks at 304 [P ⟶ (P − CO)], 276 [(P − CO) ⟶ (P − 2CO)], and 248 [(P − 2CO) ⟶ (P − 3CO)].

Thermolysis of Complex (4).—A solution of (4) (0.40 g, 1.2 mmol) in hexane (30 cm^3) contained in a Carius tube (100 cm^3) was heated (100 °C) for 6 h. On cooling, black needles were deposited. These were collected and washed with hexane to afford black *crystals* of (5) (0.10 g, 28%), m.p. 250 °C (Found: C, 47.7; H, 3.4; F, 18.7; Fe, 18.3. $C_{24}H_{24}F_6Fe_2O_4$ requires C, 47.7; H, 3.9; F, 19.0; Fe, 18.6%), ν(CO) (Nujol) at 1 960s and 1 770s cm^{-1}. N.m.r. spectra in $CDCl_3$: ^1H, τ 8.13 (s, 6 H), and 8.39 (s, 6 H); ^{19}F, 52.0 p.p.m. (s, 3 F, CF_3). The mass spectrum (base peak m/e 301) showed peaks at m/e 602 (P, 17%), 574 (P − CO, 9%), 555 (P − CO − F, 1%), 546 (P − 2CO, 2%), 518 (P − 3CO, 1%), 490 (P − 4CO, 65%), 301 (P − 3CO − $C_5Me_4CF_3$, 100%, and metastable peaks at 518 [(P − CO) ⟶ (P − 2CO)] and 200 [$Fe_2(C_5Me_4CF_3)_2$ ⟶ $Fe(C_5Me_4CF_3)$].

TABLE 8

Final atomic co-ordinates (fractional; ×10^5, Fe; ×10^4, C, O, F; ×10^3, H) in complex (2)

Atom	x	y	z
Fe	25 671(4)	18 659(2)	16 004(3)
C(1)	1 310(3)	1 692(2)	102(2)
O(1)	457(3)	1 587(1)	−810(2)
C(2)	1 007(3)	2 376(2)	1 927(2)
O(2)	32(3)	2 732(1)	2 085(2)
C(3)	3 407(3)	2 789(2)	1 444(3)
O(3)	3 893(3)	3 362(1)	1 323(3)
C(11)	2 357(3)	862(1)	2 412(2)
C(12)	2 986(3)	1 410(1)	3 347(2)
C(116)	4 683(3)	1 325(1)	3 759(2)
C(115)	5 123(3)	857(1)	2 791(2)
C(114)	5 107(3)	1 437(2)	1 799(2)
C(113)	4 156(3)	1 214(1)	690(2)
C(112)	3 571(3)	439(1)	852(2)
C(111)	3 692(3)	367(1)	2 210(2)
C(10)	802(3)	492(2)	2 204(3)
F(101)	546(2)	22(1)	1 258(2)
F(102)	684(3)	89(1)	3 162(2)
F(103)	−393(2)	975(1)	1 957(2)
C(13)	2 268(3)	1 700(2)	4 302(2)
F(131)	2 750(3)	1 288(1)	5 324(2)
F(132)	726(2)	1 677(1)	4 006(2)
F(133)	2 679(2)	2 416(1)	4 609(2)
O(116)	5 570(3)	1 597(1)	4 647(2)
C(120)	6 667(4)	456(2)	3 238(3)
C(118)	6 380(4)	2 005(2)	2 000(3)
C(117)	4 266(4)	1 489(2)	−523(3)
O(112)	3 168(3)	−29(1)	72(2)
C(119)	3 733(4)	−438(2)	2 671(3)
H(120A)	664(5)	8(3)	384(4)
H(120B)	687(6)	23(3)	256(5)
H(120C)	745(5)	84(3)	359(4)
H(118A)	655(5)	224(3)	273(4)
H(118B)	622(5)	239(2)	142(4)
H(118C)	729(6)	177(3)	200(4)
H(117A)	516(5)	131(3)	−64(4)
H(117B)	339(5)	131(3)	−120(4)
H(117C)	425(5)	202(2)	−61(4)
H(119A)	474(4)	−72(2)	264(3)
H(119B)	372(5)	−46(3)	351(4)
H(119C)	287(5)	−71(3)	220(4)

Crystal-structure Determinations of Complexes (1) *and* (2).—Experimental details of the collection and treatment of the diffraction data for (1) and (2) follow similar lines and are therefore presented for (1) only, data in braces representing differences in respect of complex (2).

Species (1) crystallizes as small orange-red parallelopipeds {dark yellow blocks}. A single crystal was mounted on a quartz fibre with low-temperature epoxy-resin adhesive, and the unit cell and space group were determined *via* oscillation and zero- and first-layer (equi-inclination) Weissenberg photography. The specimen was then transferred to a Syntex $P2_1$ four-circle diffractometer equipped with ϕ-axis low-temperature device (N_2 stream) and slowly cooled to *ca.* 215 K.

Fifteen reflections, $18 < 2\theta < 26°$ {$14 < 2\theta < 23°$}, were taken from a 30-m rotation photograph and centred in 2θ, ω, and χ. The unit cell was chosen by inspection and the orientation matrix calculated. For data collection, $2.9 \leqslant 2\theta \leqslant 60.0°$ (graphite-monochromated Mo-K_α radiation; $\lambda_{\alpha1} = 0.709\ 26$, $\lambda_{\alpha2} = 0.713\ 54$ Å). Reflections ($+h+k\pm l$ with $0kl$ and $0k\bar{l}$ reflections afterwards merged) were scanned (θ—2θ in 96 steps) at speeds between 0.042 5 {0.033 7} and 0.488 3° s^{-1} depending on an initial 2-s peak count in which 150.0 and 1 500.0 counts were used as critical values. The intensities of three check reflections, $\bar{5}2\bar{5}$, $31\bar{7}$, and $3\bar{3}1$ {$15\bar{4}$, $\bar{1}54$, and $\bar{3}\bar{3}\bar{2}$} were monitored once every 28 {33} but analysis [27] of their net counts as individual functions of time subsequently revealed no significant crystal or machine variance over the *ca.* 145- {160-} h X-ray exposure. Of 4 695 {4 946} independent reflections measured, 3 920 {4 376} had $I \geqslant 1.0\sigma(I)$ and were retained to solve and refine the structure.

Crystal data. (1) $C_{15}H_{12}F_6FeO_3$, $M = 410.10$, Monoclinic, space group $P2_1/n$, $a = 13.377(5)$, $b = 8.959(5)$, $c = 13.544(6)$ Å, $\beta = 100.54(3)°$, $U = 1\ 596.3(12)$ Å^3, $D_m = 1.71$ (flotation), $Z = 4$, $D_c = 1.707$ g cm^{-3}, $F(000) = 824$, μ(Mo-$K_{\bar{\alpha}}$) = 10.6 cm^{-1}. (2) $C_{17}H_{12}F_6FeO_5$, $M = 446.12$, Monoclinic, space group $P2_1/n$, $a = 9.031(7)$, $b = 17.865(16)$, $c = 11.519(10)$ Å, $\beta = 105.49(6)°$, $U = 1\ 791(3)$ Å^3, $D_m = 1.71$ (flotation), $Z = 4$, $D_c = 1.728$ g cm^{-3}, $F(000) = 936$, μ(Mo-$K_{\bar{\alpha}}$) = 9.6 cm^{-1}.

The observed data were corrected for Lorentz and polarization (but not for X-ray absorption) effects and the structure was solved *via* Patterson (Fe) and difference-Fourier (C, O, and F) techniques (all data), F_c values used in the latter being optimized by full-matrix (later block-diagonal) least-squares refinement. Hydrogen atoms were located from difference maps summed to a $(\sin\theta)/\lambda$ maximum of 0.5, this method employing only 1 547 {1 694} data.

F_o moduli were weighted such that $w^{-1} = xy$ with $x = b/\sin\theta$ if $\sin\theta < b$, $x = 1$ if $\sin\theta \geqslant b$, $y = F_o/a$ if $F_o > a$, and $y = 1$ if $F_o \leqslant a$, in which a and b took values of 40.0 {35.0} and 0.3 respectively. Mixed-mode refinement (Fe, C, O, and F atoms anisotropic; H atoms isotropic) continued until there was no significant change in any of the 276 {315} variables. Final residuals of R 0.065 {0.047} and R' 0.073 {0.058} were obtained at a data : variable ratio better than 14.2 {13.8} : 1. An ultimate difference-Fourier of 0.28 {0.36} Å resolution revealed a maximum residue of *ca.* 1.38 {0.52} eÅ^{-3} near −0.31, 0.44, 0.08 {0.31, 0.08, 0.24}.

Atomic-scattering factors for neutral atoms were taken from refs. 28 (Fe,F), 29 (C,O), and 30 (H), with appropriate correction for both components of anomalous dispersion.[31] Except for preliminary data treatment, all the calculations were executed by the 'X-RAY '72' crystallographic system [32] implemented on the University of London CDC 7600 computer. For complex (1), Table 7 lists the derived atomic co-ordinates, Appendix C a comparison of $|F_o|$ against F_c, and Appendix D the thermal parameters. For complex (2) the corresponding data are presented in Table 8 and Appendices E and F respectively.

We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the S.R.C. for support.

[7/1036 *Received*, 16*th June*, 1977]

[27] A. G. Modinos, 'DRSYN', a Fortran program for data analysis.

[28] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[29] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[30] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[31] 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

[32] Technical Report TR-192, the Computer Science Centre, University of Maryland, June 1972.