The Oxidative Reaction of Fluoro-olefins with Tricarbonyl(cyclobutadiene)-iron Complexes

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Tetrafluoroethylene and hexafluoropropene react on irradiation with $Fe(\pi\text{-}C_4R_4)(CO)_3$ (R = H or Me) to give π-cyclobutenyl complexes, in which the fluorocarbon links the metal and the C_4 ring. A similar reaction occurs with hexafluorobuta-1,3-diene, but a 1,3-fluorine shift also takes place. Hexafluoroacetone reacts with $Fe(\pi\text{-}C_4Me_4)(CO)_3$ to give $\overline{FeC(CF_3)_2O}(CO)_2(\pi\text{-}C_4Me_4)$, which reacts with phosphites or phosphines to give π-cyclobutenyl complexes.

We have previously shown that complexes of the general type $M(CO)_3L_2$ (M = Fe,[1] Ru,[1,2] Os;[3] L = phosphine or phosphite) undergo oxidative-elimination reactions on treatment with molecules such as fluoro-olefins and fluoroketones (A=B) forming the three-membered ring compounds $\overline{MAB}(CO)_2L_2$. In principle, such reactions should take place with other d^8 systems, for example, tricarbonyl(cycloheptatriene)-, -(cyclo-octatetraene)-, or -(cyclobutadiene)-iron. However, our observation[4] that the electrophilic molecule tetracyanoethylene undergoes an *exo*-1,3-addition reaction with tricarbonyl(cycloheptatriene)-iron to form a complex, in which the tricarbonyliron unit is bonded in the 1,2,3,6-*hapto*-form, suggested that more complex reactions may occur, and that a detailed survey was merited. In this paper we report some reactions of fluoro-olefins and hexafluoroacetone with tricarbonyl-(tetramethylcyclobutadiene)- and -(cyclobutadiene)-iron.[5] The new compounds described were

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[1] R. Burt, M. Cooke, and M. Green, *J. Chem. Soc.* (*A*), 1970, 2975.

[2] M. Cooke and M. Green, *J. Chem. Soc.* (*A*), 1969, 651.

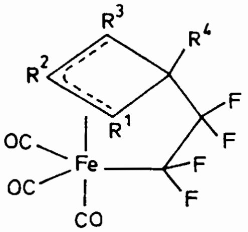
[3] M. Cooke, M. Green, and T. A. Kuc, *J. Chem. Soc.* (*A*), 1971, 1200.

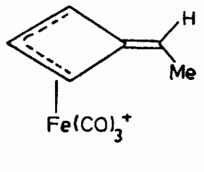
[4] M. Green, S. Tolson, J. Weaver, D. C. Wood, and P. Woodward, *Chem. Comm.*, 1971, 222.

[5] A. Bond and M. Green, *Chem. Comm.*, 1971, 12.

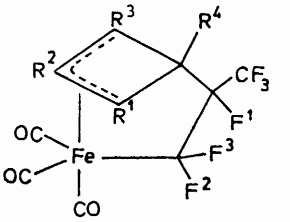
characterised by elemental analysis, i.r. and mass spectroscopy, and ^{1}H and ^{19}F n.m.r. spectroscopy.

(I) R = H
(IV) R = Me

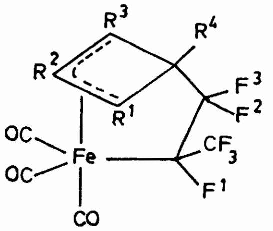




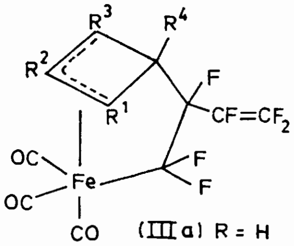
(XII)



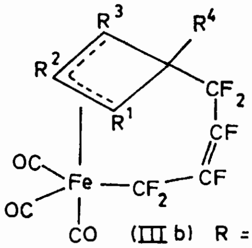
(IIa) R = H
(Va) R = Me



(IIb) R = H
(Vb) R = Me

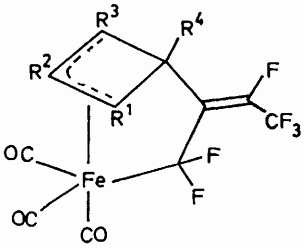


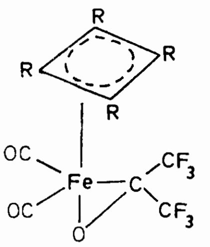
(IIIa) R = H
(VIa) R = Me



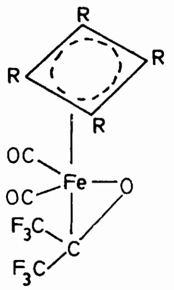
(IIIb) R = H
(VIb) R = Me

(IIIc) R = H
(VIc) R = Me

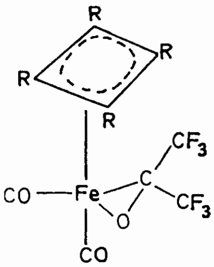




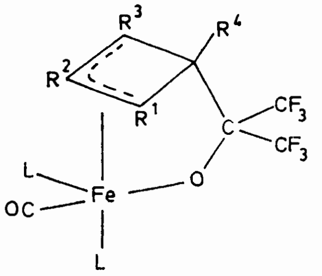
(VIIa) R = Me



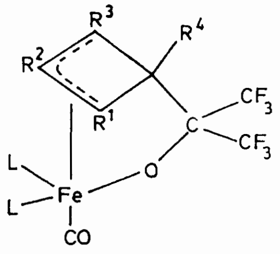
(VIIb) R = Me



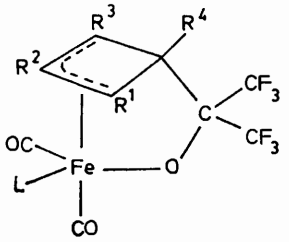
(VIIc) R = Me



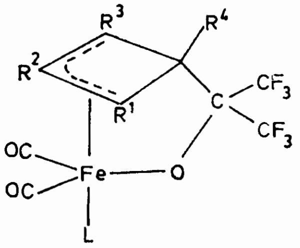
(VIII) R = Me, L = (MeO)$_3$P
(IX) R = Me, L = (EtO)$_3$P
(Xa) R = Me, L = PhMe$_2$P



(Xb) R = Me, L = PhMe$_2$P



(XIa) R = Me, L = Et$_3$P



(XIb) R = Me, L = Et$_3$P

Tetrafluoroethylene and hexafluoropropene do not react thermally with either tricarbonyl(cyclobutadiene)-iron or the tetramethyl derivative, but on u.v. irradiation of a hexane solution of the reactants the yellow, crystalline, 1 : 1 adducts (I), (II), (IV), and (V) were formed in good yield. The i.r. spectra of these compounds showed three strong terminal carbonyl bands *ca.* 30 cm^{-1} to higher wavenumber than in the parent system, indicating the presence of a tricarbonyliron unit attached to an electron-withdrawing group. The presence of an Fe(CO)$_3$ unit was confirmed by the appearance in the mass spectrum of a parent peak and peaks assignable to the consecutive loss of three carbon monoxide molecules.

The ^{1}H n.m.r. spectrum of the adduct (I) showed three resonances of relative intensity 1 : 2 : 1; the low-field resonances (H^2) and (H^1, H^3) appearing as singlets and the high-field signal (H^4) as a triplet (J_{HF} 5·0 Hz) due to ^{1}H–^{19}F coupling, *i.e.* a CHCF$_2$ group. The spectrum of adduct (IV), the tetramethyl derivative, showed a similar 1 : 2 : 1 spectrum except that the high-field signal did not show ^{1}H–^{19}F coupling. These observations are compatible with the illustrated π-cyclobutenyl structures, which have a symmetry plane, resulting in H^1 and H^3 being in identical environments. The chemical shifts of H^1, H^2, and H^3 are similar to those reported[6] for the cation (XII), taking into account a shift to low field due to the presence of a positive charge. It is interesting that in both compounds (I) and (XII) there is no evidence for ^{1}H–^{1}H coupling between vicinal hydrogens.

The ^{19}F n.m.r. spectrum of adducts (I) and (IV) showed two resonances of equal intensity with chemical shifts of 66·1 and 118·0, and 70·8 and 120·8 p.p.m. respectively. The resonances in the spectrum of (IV) appeared as triplets (J_{FF} 3·0 Hz) due to ^{19}F–^{19}F coupling. However, there was no evidence of such coupling in the case of compound (I), but the low-field signal at 66·1 p.p.m.

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[6] R. Pettit, J. D. Fitzpatrick, and L. Watts, *Tetrahedron Letters*, 1966, 2069.

appeared as a doublet (J_{HF} 5·0 Hz); the coupling constant corresponding to that observed in the ^1H spectrum and confirming the presence of the arrangement CF_2CH. Thus the C_2F_4 effectively links the C_4 ring and the iron atom. As a CF_2 group bonded directly to a transition metal normally has a ^{19}F resonance at low field, typically[7] at 40—70 p.p.m., the low-field shift in the spectrum of (I) and (IV) would be assigned to $FeCF_2$. However, the ^1H–^{19}F coupling described above strongly indicates that such an assignment is incorrect, and that the signals at 118·0 and 120·8 p.p.m. should be assigned to $FeCF_2$*CF*$_2$ in the adducts (I) and (IV). Such high shifts are not completely without precedent, in metallo-octafluorocyclopentanes, shifts as high as 112 p.p.m. have been observed[8] for M*CF*$_2CF_2$.

The plane of symmetry present in the C_2F_4 adducts is absent in the products (II) and (V) of the reaction of $Fe(\pi\text{-}C_4R_4)(CO)_3$ (R = H or Me) with hexafluoropropene. In addition there is a problem as to whether the fluoro-olefin links the C_4 ring and the iron atom as in structures (IIa) and (Va) or (IIb) and (Vb). The ^1H n.m.r. spectrum of compound (II) showed a doublet (J_{HF} 3·0 Hz) at τ 3·62 (1H), which is assigned to the central π-allylic hydrogen H^2. Double irradiation experiments established that the doublet splitting is not due to ^1H–^1H coupling, but to ^1H–^{19}F coupling, *i.e.* a long range effect possibly due to the C*F*(CF_3) nucleus. The spectrum also showed doublets at τ 4·92 (1H) and 5·85 (1H) and a broad singlet at τ 6·30 (1H). The two low-field signals are assigned[9] to the π-allylic protons H^1 and H^3 (or *vice versa*). Double irradiation of either signal collapsed the other to a singlet establishing a transannular ^1H–^1H coupling of 10·0 Hz. A similar (9·0 Hz) transannular coupling was observed[6] in compound (XII). Again as in the case of the C_2F_4 adducts there was no evidence for vicinal ^1H–^1H coupling. The high-field signal at τ 6·30 is assigned to C*H*·$CF(CF_3)$.

The ^1H n.m.r. spectrum of the adduct (V) showed as expected for an analogous π-cyclobutenyl system, four resonances at τ 7·80, 8·21, 8·38, and 8·88. As required by the illustrated structures for the hexafluoropropene complexes (II) and (V), the ^{19}F n.m.r. spectra show four resonances of relative intensity 3 : 1 : 1 : 1, and except for the one exception noted below, the signals appeared as well resolved multiplets. The low-field signal can be assigned both on the basis of chemical shift and the relative intensity to the CF_3 group; similar coupling constants (see Experimental section) were found for both the adducts (II) and (V). The resonances at 111·8 and 120·2 p.p.m., in for example, the spectrum of compound (II), both show a large (244 Hz) geminal ^{19}F–^{19}F coupling [240 Hz in the case of compound (VI)] allowing assignment[10,11] to F^2 and F^3. Thus, the high-field resonance, which appears at 143·5 p.p.m. in compound (II) and 155·0 p.p.m. in (V), is assigned[10] to the C*F*(CF_3) fluorine, *i.e.* F^1.

The chemical shift for the C*F*(CF_3) fluorine is lower than that observed in compounds where the $CF(CF_3)$ group is bonded to a transition metal, for example, in $(CF_3)_2CFMn(CO)_5$ the C*F*(CF_3) resonance occurs at 163·7 p.p.m.[12,13] It is also interesting that the C*F*(CF_3) shift is dependent on the nature of the substituents on the C_4 ring; a difference of some 12 p.p.m. being observed between compounds (II) and (V). Thus these points suggest that the hexafluoropropene complexes, which are formed stereospecifically, have the structure (IIa) and (Va).

Examination of the coupling-constant data is less conclusive in deciding between the two structures. In the ^{19}F spectrum of (V) the C*F*(CF_3) resonance appears as a well resolved 10-line multiplet, from which the coupling constants detailed in the Experimental section are derived. However, the corresponding signal for compound (II) is very complex because of ^1H–^{19}F coupling between C*F*(CF_3) and the central π-allylic proton H^2, which as noted above appears as a doublet (J_{HF} 3·0 Hz). In structure (IIa) such coupling can be readily envisaged, but if coupling through the iron atom is assumed then structure (IIb) is equally compatible. A more tenuous argument is that in the ^1H spectrum of compound (II) there is no evidence of ^1H–^{19}F coupling >0·5 Hz in the high-field resonance at τ 6·30 assigned to the C*H* group attached to the fluorocarbon chain. This contrasts with the coupling (J_{HF} 5·0 Hz) observed in adduct (I) where the arrangement $CHCF_2$ is present, suggesting that adduct (II) does not have the structural feature $CHCF_2$, as present in structure (IIb). Thus, consideration of these various points leads us to tentatively favour structures (IIa) and (Va).

Hexafluorobuta-1,3-diene reacts with d^8 and d^{10} zero-valent complexes to form either $1,4\text{-}(\overline{MCF_2CF{=}CFCF_2})$[14–17] or $1,2\text{-}(\overline{MCF_2C}FCF{=}CF_2)$[18] addition products. Irradiation of hexane solutions of $Fe(\pi\text{-}C_4R_4)(CO)_3$ (R = H or Me) and hexafluorobuta-1,3-diene gave good yields of the yellow crystalline compounds (III) and (VI). The presence of three terminal carbonyl bands in the i.r. spectra and the appearance in the mass spectra of peaks

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[7] J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, 1965, **4**, 93; J. B. Wilford, P. M. Treichel, and F. G. A. Stone, *J. Organometallic Chem.*, 1964, **2**, 119; E. Pitcher, A. D. Buckingham, and F. G. A. Stone, *J. Chem. Phys.*, 1962, **36**, 124.

[8] C. S. Cundy, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 1647.

[9] L. A. Fedovov, *Russ. Chem. Rev.*, 1970, **39** (8), 655.

[10] C. H. Dungan and J. R. Van Wazer, 'Compilation of Reported ^{19}F N.m.r. Chemical Shifts,' Wiley–Interscience, New York, 1970, Section C10.

[11] J. W. Emsley, J. Feeney, and C. H. Sutcliff, 'High Resolution N.m.r. Spectroscopy,' Pergamon, Oxford, 1971, vol. 7.

[12] W. R. McClellan, *J. Amer. Chem. Soc.*, 1961, **83**, 1598.

[13] M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Adv. Organometallic Chem.*, 1965, **3**, 1.

[14] R. C. Hunt, D. M. Roundhill, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1967, 982; P. B. Hitchcock and R. Mason, *Chem. Comm.*, 1967, 242.

[15] J. Browning, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 453.

[16] M. Green, S. K. Shakshooki, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 2828.

[17] M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2525.

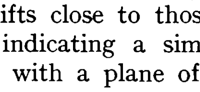
[18] M. Green, N. Mayne, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 902, and references therein.

corresponding to the consecutive loss of three carbon monoxides suggests that compounds (III) and (VI) also contain an $-Fe(CO)_3$ moiety bonded to an electronegative group.

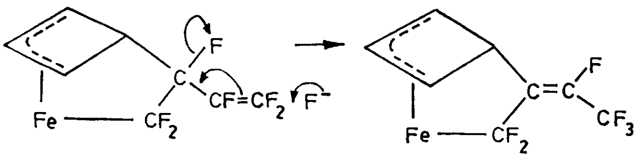
The i.r. spectrum showed in addition to the carbonyl bands a band at 1727m cm^{-1}, which may be attributed [19] to the arrangement [$FeCF_2C{=}C$].

The ^1H n.m.r. spectrum of compound (III) showed three singlet resonances at τ 3·62 (1H), 5·36 (2H), and 6·34 (1H) with shifts close to those observed for the C_2F_4 adduct (I), indicating a similar π-cyclobutenyl structure for (III) with a plane of symmetry passing through the iron atom, the central π-allylic carbon and the carbon atom to which the fluorocarbon chain is attached. The tetramethyl derivative (VI) showed resonances at τ 7·80, 8·32, and 8·90 (1 : 2 : 1) as required by structure (VI).

The ^{19}F n.m.r. spectra of adducts (III) and (VI) showed three resonances. For example, in the case of (III) multiplets at 68·1 p.p.m. (3F), 94·8 (1F), and 95·8 (2F) were observed. This establishes the presence of CF_3, CF, and CF_2 groups, and is clearly incompatible with either a simple 1,2-insertion [structures (IIIa) and (VIa)] or a 1,4-insertion [(IIIb) and (VIb)]. Of the various alternative structures containing these features, structures (IIIc) and (VIc) fit the evidence most satisfactorily. In particular, the i.r. band at 1727 cm^{-1} can be assigned to a C=C stretching frequency of $FeCF_2C{=}CF(CF_3)$, and the coupling constants $J(CF_2{-}CF_2)$ 15 Hz, $J(CF_3{-}CF)$ 11·0 Hz, and $J(CF_2{-}CF)$ 5·0 Hz are what might be expected [10,11] for the arrangement,



Moreover, a simple reaction path is available to explain the formation of (IIIc) and (VIc). This involves an initial 1,2-insertion to give, for example, (IIIa), which then undergoes a fluoride anion catalysed 1,3-fluorine shift (S_N2'): [18,19]



The direction indicated for the 1,2-insertion is preferred, because in the alternative the structural feature $CRCF_2C{=}C$ would occur, and in the case of compound (III; R = H) a $^1H{-}^{19}F$ coupling would be expected in the resonance of the proton attached to the C_4 ring carbon carrying the fluorocarbon chain.

Hexafluoroacetone reacts with $M(CO)_3L_2$ (M = Ru or Os; L = phosphine or phosphite) to form the three-ring complexes $\overline{\mathrm{MC(CF_3)_2O}}\mathrm{(CO)_2L_2}$.[1-3] Irradiation of a hexane solution of $Fe(\pi{-}C_4Me_4)(CO)_3$ with an excess of hexafluoroacetone gave a high yield of the red crystalline complex (VII). In contrast with the fluoro-olefin adducts the i.r. spectrum showed two terminal carbonyl bands at 2041 and 1999 cm^{-1}, and the mass spectrum showed the loss of only two carbon monoxide molecules, suggesting that complex (VII) is a dicarbonyl derivative containing a rigid three-membered ring system $\overline{\mathrm{FeC(CF_3)_2O}}$;[1-3] the C_4 ring remaining intact. There are three possible structures (VIIa), (VIIb), and (VIIc) which have these structural features, and examination of the temperature-invariant ^1H and ^{19}F n.m.r. spectra showed that at least two isomers are formed. The ^1H spectrum showed singlet resonances at τ 8·40 and 8·80 in the ratio 3 : 2, while the ^{19}F spectrum showed two resonances at 82·8 and 80·0 p.p.m. in the ratio 3 : 2. The low-field resonance was a sharp singlet indicating that this isomer had chemically equivalent CF_3 groups as required by isomeric structures (VIIa) and (VIIb); the other resonance was broad suggesting slightly non-equivalent CF_3 groups as in structure (VIIc). The chemical shifts of the CF_3 groups in complex (VII) are higher than those observed in other systems containing the arrangement $\overline{\mathrm{MC(CF_3)_2O}}$, however, the presence of a ring current due to the co-ordinated tetramethylcyclobutadiene makes comparison difficult.

Treatment of complex (VII) with carbon monoxide (80°, 100 atm., 6 h) led to the displacement of hexafluoroacetone and the formation of tricarbonyl(tetramethylcyclobutadiene)iron. However, the corresponding reaction with phosphines or phosphites gave complexes in which the hexafluoroacetone links the iron atom to the C_4 ring, analogous to the fluoro-olefin adducts. Trimethyl and triethylphosphite and dimethylphenylphosphine reacted with complex (VII) to give respectively the crystalline monocarbonyl derivatives (VIII), (IX), and (X), characterised as bis-phosphite or -phosphine substituted complexes. The i.r. spectra showed a single terminal carbonyl band. The ^1H n.m.r. spectra of complexes (VIII) and (IX) showed four singlet methyl resonances with chemical shifts similar to those observed for the hexafluoropropene adduct (V); in the case of (X) coincidence of methyl resonances occurred. In addition the $POCH_3$ resonance in the ^1H spectrum of complex (VIII) appeared as an apparent doublet indicating [20] a low value for $|J_{PP'}|$, *i.e.* a relative *cis*-configuration for the phosphite ligand. This evidence is consistent with the illustrated π-cyclobutenyl structures, the asymmetry of which is due to the presence of *cis*-phosphites, one of the phosphites occupying a position *trans* to the oxygen of the hexafluoroacetone.

Examination of the ^1H spectrum of complex (X) indicated the presence of two isomers, *i.e.* structures (Xa) and (Xb); one CH_3 resonance appearing as an apparent doublet and the other as an apparent triplet.

In agreement with the illustrated structures the ^{19}F n.m.r. spectra showed a single peak at some 10 p.p.m. to low field of the resonance in complex (VII). The

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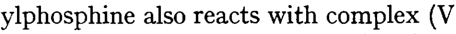
[19] W. T. Miller, J. H. Fried, and H. Goldwhite, *J. Amer. Chem. Soc.*, 1960, **82**, 3091.

[20] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 770.

signals appeared as singlets, there being no evidence of ^{19}F–^{31}P coupling suggesting that the oxygen of the hexafluoroacetone is bound to the iron.

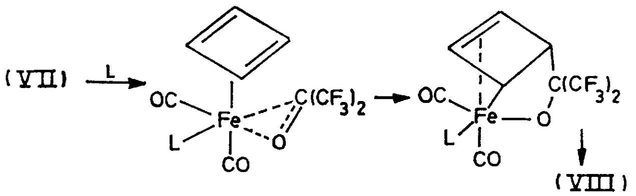
Triethylphosphine also reacts with complex (VII), but to give the mono-substituted complex (XIa) or (XIb). However, as with complexes (VIII) and (IX) the ^1H and ^{19}F n.m.r. spectra indicate that the hexafluoroacetone links the C_4 ring to the iron atom.

The conversion of complex (VII) to (VIII), (IX), or (X) is clearly related to the three- to five-membered-ring transformations recently observed in Ni [16,17,21,22] and Pd chemistry,[23] for example,



$$L_2MC(CF_3)_2O \xrightarrow{HFA} L_2MC(CF_3)_2OC(CF_3)_2O$$

the difference between the two reactions being that one hexafluoroacetone (HFA) is replaced by a co-ordinated cyclobutadiene. Co-ordination of a phosphite or phosphine activates the already co-ordinated hexafluoroacetone towards carbon–carbon bond formation with the cyclobutadiene:



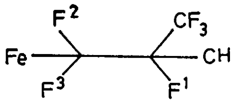
It is possible that a similar reaction path is followed in the formation of the C_2F_4, $C_2F_3CF_3$, and C_4F_6 adducts. A detailed discussion of the mechanism and synthetic implications of these and related reactions will be presented in a subsequent paper.

EXPERIMENTAL

^1H and ^{19}F N.m.r. spectra were recorded on a Varian Associates HA 100 spectrometer at 100 and 94·1 MHz respectively. Chemical shifts are relative to Me_4Si (τ 10·00) and CCl_3F (0·00 p.p.m.) internal standard. I.r. spectra were recorded with a Perkin-Elmer 257 spectrophotometer. Mass spectra were recorded on an A.E.I. MS 902 spectrometer with an ionising voltage of 70 eV. All reactions, other than those in Carius tubes, were carried out in an atmosphere of dry, oxygen-free nitrogen. Tricarbonyl(cyclobutadiene)iron and tricarbonyl(tetramethylcyclobutadiene)iron were prepared by the published methods.

Reactions of Tricarbonyl(cyclobutadiene)iron.—(a) *With tetrafluoroethylene.* An excess of tetrafluoroethylene (0·20 g, 2·0 mmol) was condensed (−196°) into a Pyrex Carius tube (100 ml) containing tricarbonyl(cyclobutadiene)iron (0·10 g, 0·52 mmol) dissolved in hexane (15 ml) and irradiated (250 W, Hanovia lamp) for 24 h. The solvent was removed *in vacuo* and the residue chromatographed on an alumina column. Elution with hexane gave $Fe(C_4H_4)(CO)_3$, and elution with hexane–benzene (3 : 2 v/v) followed by recrystallisation (−78°) from hexane gave pale yellow *crystals* of adduct (I) (0·13 g, 82%), m.p. 81° (Found: C, 37·1; H, 1·6; F, 26·2. $C_9H_4F_4FeO_3$ requires C, 37·0; H, 1·4; F, 26·1%), ν_{CO} (hexane) 2091s, 2037s, and 2016s cm^{-1}. The mass spectrum (base *m/e* 88) showed peaks at *m/e* 292 (*P*, 81%), 264 (*P* − CO, 58%), 236 (*P* − 2CO, 5%), 208 (*P* − 3CO, 11%) and metastable peaks at 238 [$P \longrightarrow (P - CO)$] and 184 [$(P - 2CO) \longrightarrow (P - 3CO)$]. The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 3·66 (s, 1H, H^2), 5·56 (s, 2H, H^1 and H^3) and 6·41 (t, 1H, H^4, J_{HF} 5·0 Hz). The ^{19}F n.m.r. spectrum ($CDCl_3$) showed resonances at 66·1 (d, 2F, $FeCF_2\mathit{CF}_2$, J_{HF} 5·0 Hz) and 118·0 p.p.m. (br, s, 2F, $Fe\mathit{CF}_2$).

(b) *With hexafluoropropene.* Similarly, u.v. irradiation (24 g) of a solution of $Fe(C_4H_4)(CO)_3$ (0·10 g, 0·52 mmol) and hexafluoropropene (0·20 g, 1·3 mmol) in hexane (15 ml) gave pale yellow crystals of adduct (II) (0·12 g, 27%), m.p. 104° (Found: C, 35·0; H, 1·3; F, 33·3. $C_{11}H_4F_6FeO$ requires C, 35·1; H, 1·2; F, 33·3%), ν_{CO} (hexane) 2093m, 2040s, and 2015m cm^{-1}. The mass spectrum (base *m/e* 145) showed peaks at *m/e* 342 (*P*, 1%), 323 (*P* − F, 0·5%), 314 (*P* − CO, 1%), 295 (*P* − CO − F, 3%), 286 (*P* − 2CO, 1%), 267 (*P* − 2CO − F, 1·1%), 258 (*P* − 3CO, 1·2%), and 239 (*P* − 3CO − F, 2%). The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 3·62 (d, 1H, J_{HF} 3·0 Hz), 4·92 (d, 1H, J_{HH} transannular 10·0 Hz), 5·85 (d, 1H, J_{HH} transannular 10·0 Hz), and 6·30 (s, 1H); double irradiation of the peak at τ 4·92 or at 5·85 caused the other peak to collapse to a singlet. The ^{19}F n.m.r. spectrum ($CDCl_3$) showed resonances at 69·3 p.p.m. [CF_3, $J(CF_3–F^1)$ 11·0 Hz,



$J(CF_3–F^2)$ 3·0 Hz, $J(CF_3–F^3)$ 16·0 Hz], 111·8 [F_2, $J(F^2–F^3)$, 244 Hz, $J(F^2–CF_3)$ 3·0 Hz], 120·2 [F^3, $J(F^2–F^3)$ 244 Hz, $J(F^3–CF_3)$ 16 Hz, $J(F^3–F^1)$ 9·0 Hz], and 143·5 [F^1, $J(F^1–CF_3)$ 11 Hz, $J(F^1–H)$ 3·0 Hz, $J(F^1–F^3)$ 9·0 Hz].

(c) *With hexafluorobuta-*1,3-*diene.* Similarly, u.v. irradiation (24 h) of a solution of $Fe(C_4H_4)(CO)_3$ (0·10 g, 0·50 mmol) and hexafluorobuta-1,3-diene (0·20 g, 1·2 mmol) in hexane (14 ml) gave after chromatography on alumina and elution with hexane–benzene (3 : 2 v/v) followed by recrystallisation (−78°) from hexane, pale yellow *needles* of adduct (III) (0·09 g, 47%), m.p. 101° (Found: C, 37·0; H, 1·7; F, 32·4. $C_{11}H_4F_6O_3Fe$ requires C, 37·3; H, 1·2; F, 32·2%), ν_{OO} (hexane) 2089s, 2047s, 2011m, and 1727m cm^{-1}. The mass spectrum (base *m/e* 298) showed peaks at *m/e* 354 (*P*, 1%), 326 (*P* − CO, 68%), 298 (*P* − 2CO, 100%), 279 (*P* − 2CO − F, 13%), and 270 (*P* − 3CO, 10%). The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 3·62 (s, 1H), 5·36 (s, 2H), and 6·34 (s, 1H). The ^{19}F n.m.r. spectrum ($CDCl_3$) showed resonances at 68·1 p.p.m. [CF_3, $J(CF_3–CF_2)$ 15·0 Hz, $J(CF_3–CF)$ 11·0 Hz], 94·8 [CF, $J(CF–CF_3)$ 11·0 Hz, $J(CF–CF_2)$ 5·0 Hz], and 95·8 [CF_2, $J(CF_2–CF_3)$ 15·0 Hz, $J(CF_2–CF)$ 5·0 Hz].

Reactions of Tricarbonyl(tetramethylcyclobutadiene)iron.—(a) *With tetrafluoroethylene.* Similarly, u.v. irradiation (24 h) of a solution of $Fe(C_4Me_4)(CO)_3$ (0·10 g, 0·40 mmol) in hexane (15 ml) with tetrafluoroethylene (0·10 g, 1·0 mmol) gave, on chromatography on alumina, and elution with hexane, unchanged $Fe(C_4Me_4)(CO)_3$, while further elution with hexane–benzene (3 : 2) followed by recrystallisation (−78°) from hexane gave pale yellow *crystals* of the adduct

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(IV) (0·08 g, 93%), m p. 148—150° (Found: C, 44·7; H, 3·5; F, 21·8. $C_{13}H_{12}F_4FeO_3$ requires C, 44·8; H, 3·4; F, 21·8%), ν_{CO} (hexane) 2076s, 2011s, and 1999m cm^{-1}. The mass spectrum (base *m/e* 155) showed peaks at *m/e* 348 (*P*, 0·1%), 320 (*P* – CO, 11·6%), 292 (*P* – 2CO, 4%), 264 (*P* – 3CO, 0·2%), and 245 (*P* – 3CO, 3%). The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 7·80 (s, 3H), 8·24 (s, 6H), and 8·90 (s, 3H). The ^{19}F n.m.r. spectrum ($CDCl_3$) showed resonances at 70·8 p.p.m. [t, 2F, $FeCF_2\mathit{CF}_2$, J_{FF} 3·0 Hz] and 120·8 [t, 2F, $FeCF_2CF_2$, J_{FF} 3·0 Hz].

(b) *With hexafluoropropene.* U.v. irradiation (24 h) of a solution of $Fe(C_4Me_4)(CO)_3$ (0·10 g, 0·40 mmol) and hexafluoropropene (0·20 g, 1·35 mmol) in hexane (20 ml) gave pale yellow *crystals* of the adduct (V) (0·12 g, 72%), m.p. 123° (Found: C, 42·4; H, 3·1; F, 28·4. $C_{14}H_{12}F_6FeO_3$ requires C, 42·2; H, 3·0; F, 28·6%), ν_{CO} (hexane) 2076s, 1023s, and 1996m cm^{-1}. The mass spectrum (base *m/e* 370) showed peaks at 398 (*P*, 26%), 376 (*P* – F, 1%), 370 (*P* – CO, 100%), 351 (*P* – CO – F, 58%), 342 (*P* – 2CO, 8%), 323 (*P* – 2CO – F, 43%), 314 (*P* – 3CO, 50%), and 295 (*P* – 3CO – F, 62%). The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 7·80 (s, 3H), 8·21 (s, 3H), 8·38 (s, 3H), and 8·88 (s, 3H). The ^{19}F n.m.r. spectrum ($CDCl_3$) showed resonances at 69·3 p.p.m. [CF_3, $J(CF_3–F^1)$ 11·0 Hz, $J(CF_3–F^2)$ 3·0 Hz, $J(CF_3–F^3)$ 17·0 Hz], 107·5 [F^2, $J(F^2–F^3)$ 240 Hz, $J(F^2–CF^3)$ 3·0 Hz, $J(F^2–F^1)$ 11·0 Hz], 123·0 [F^3, $J(F^2–F^3)$ 240 Hz, $J(F^3–CF_3)$ 17·0 Hz, $J(F^3–F^1)$ 8·0 Hz], and 155·0 [F^1, $J(F^1–CF_3)$ 11·0 Hz, $J(F^1–F^3)$ 8·0 Hz, $J(F^1–F^2)$ 11·0 Hz].

(c) *With hexafluorobuta*-1,3-*diene.* Similarly, irradiation (24 h) of a solution of $Fe(C_4Me_4)(CO)_3$ (0·20 g, 0·81 mmol) and hexafluorobuta-1,3-diene (0·30 g, 1·80 mmol) in hexane (30 ml) gave on chromatography and elution with hexane–benzene (3 : 2) followed by recrystallisation (–78°) from hexane, pale yellow *crystals* of the adduct (VI) (0·12 g, 37%), m.p. 136° (Found: C, 43·8; H, 3·2; F, 27·7. $C_{15}H_{12}F_6FeO_3$ requires C, 43·9; H, 3·0; F, 27·8%), ν_{CO} (hexane) 2074s, 2021s, and 2001s, and 1727m cm^{-1}. The mass spectrum (base *m/e* 354) showed peaks at 410 (*P*, 4%), 382 (*P* – CO, 50%), 363 (*P* – CO – F, 13%), 354 (*P* – 2CO, 100%), 335 (*P* – 2CO – F, 0·3%), 326 (*P* – 3CO, 40%), and 307 (*P* – 2CO – F, 13%). The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 7·80 (s, 3H), 8·32 (s, 6H), and 8·90 (s, 3H). The ^{19}F n.m.r. spectrum ($CDCl_3$) showed resonances at 68·2 p.p.m. [CF_3, $J(CF_3–CF_2)$ 16 Hz, $J(CF_3–CF)$ 11·0 Hz], 94·8 [CF, $J(F–CF_3)$ 11·0 Hz, $J(F–CF_2)$ 8·0 Hz], and 96·8 [CF_2, $J(CF_2 – CF_3)$ 16 Hz, $J(CF_2 – CF)$ 8·0 Hz].

(d) *With hexafluoroacetone.* Hexafluoroacetone (0·20 g, 1·2 mmol) was condensed (–196°) into a Carius tube containing $Fe(C_4Me_4)(CO)_3$ (0·10 g, 0·40 mmol) dissolved in hexane (15 ml) and irradiated for 24 h. The solvent was removed *in vacuo* and the residue was chromatographed on alumina. Elution with hexane–benzene (8 : 2) followed by recrystallisation (–78°) from hexane gave red *crystals* of the complex (VII) (0·12 g, 80%), m.p. 61° (Found: C, 40·5; H, 2·2; F, 29·9. $C_{13}H_{12}F_6FeO_3$ requires C, 40·4; H, 3·1; F, 29·6%), ν_{CO} (hexane) 2041s and 1999s cm^{-1}. The mass spectrum (base *m/e* 108) showed peaks at 386 (*P*, 0·2%), 358 (*P* – CO, 6%), 330 (*P* – 2CO, 12%), 311 (*P* – 2CO – F, 14%), 220 (*P* – HFA, 26%), 192 (*P* – HFA – CO, 20%), 164 (*P* – HFA – 2CO, 80%), and metastable peaks at 304 [(*P* – 2CO) $\longrightarrow$ (*P* – 2CO)], 292 [(*P* – 2CO) $\longrightarrow$ (*P* – 2CO – F)], 168 [(*P* – HFA) $\longrightarrow$ (*P* – HFA – CO)], and 140 [(*P* – HFA – CO) $\longrightarrow$ (*P* – HFA – 2CO)]. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 8·40 (s, 12H) and 8·80 (s, 12H) in the ratio 3 : 2. The ^{19}F n.m.r. spectrum ($CDCl_3$) showed resonances at 80·0 p.p.m. (s, 6F) and 82·8 (broad s, 6F) in the ratio 2 : 3.

Reactions of Hexafluoroacetone(cis-*dicarbonyl*)(π-*tetramethylcyclobutadiene*)*iron* (VII).—(a) *With trimethyl phosphite.* A solution of complex (VII) (0·10 g, 0·33 mmol) and an excess of trimethyl phosphite (3 ml) in methylcyclohexane (20 ml) was heated under reflux (20 min). The solvent was removed *in vacuo*, and the yellow solid was chromatographed on alumina. Elution with methylene chloride–hexane (2 : 5) gave, on recrystallisation (–40°) from hexane, yellow *needles* of the complex (VIII) (0·08 g, 43%), m.p. 124° (Found: C, 36·4; H, 5·1; F, 19·3. $C_{18}H_{30}F_6FeO_8P_2$ requires C, 35·6; H, 5·0; F, 18·8%), ν_{CO} (hexane) 1936s and 1935sh cm^{-1}. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 6·65 (d, 18H, $POCH_3$, $|J|_{POCH}$ 10·0 Hz), 8·16 (s, 3H), 8·21 (s, 3H), 8·27 (s, 3H), and 8·88 (s, 3H). The ^{19}F n.m.r. spectrum ($CDCl_3$) showed a resonance at 71·4 p.p.m. (s, CF_3).

(b) *With triethyl phosphite.* Similarly, the complex (VII) (0·10 g, 0·33 mmol) and an excess of triethyl phosphite (3 ml) were heated (10 min) under reflux in methylcyclohexane (20 ml). Chromatography on alumina and elution with diethyl ether–hexane (1 : 9) followed by recrystallisation (–78°) from hexane gave orange *needles* of the complex (IX) (0·09 g, 38%), m.p. 158° (Found: C, 42·0; H, 6·1; F, 17·0. $C_{24}H_{42}F_6FeO_8P_2$ requires C, 42·0; H, 6·1; F, 16·6%), ν_{CO} (hexane) 1934s and 1922sh cm^{-1}. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 5·90 (d of q, 12H, $POCH_2$, J_{HH} 7·0 Hz), 8·18 (s, 3H), 8·25 (s, 6H), 8·73 (t, 18H, $POCH_2\mathit{CH}_3$, J_{HH} 7·0 Hz), and 8·90 (s, 3H). The ^{19}F n.m.r. spectrum ($CDCl_3$) showed a resonance at 71·1 p.p.m. (s, CF_3).

(c) *With dimethylphenylphosphine.* In a similar manner, complex (VII) (0·10 g, 0·33 mmol) and an excess of dimethylphenylphosphine (2 ml) were heated under reflux (10 min) in hexane (20 ml). Chromatography on alumina and elution with diethyl ether–hexane (1 : 9) gave, on recrystallisation (–40°) from hexane, red *plates* of complex (X) (0·03 g, 17%), m.p. 148° (Found: C, 53·3; H, 5·21; F, 18·1. $C_{28}H_{34}F_6FeO_2P_2$ requires C, 53·1; H, 5·4; F, 18·0%), ν_{CO} (hexane) 1887s cm^{-1}. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·65 (m, 10H, C_6H_5), 8·22 (s, 3H), 8·40 (t, 6H, PCH_3, $|J|_{PCH}$ 10·0 Hz), 8·70 (d, 6H, PCH_3, $|J|_{PCH}$ 8·0 Hz), and 8·88 (broad s, 6H). The ^{19}F n.m.r. spectrum ($CDCl_3$) showed a resonance at 70·4 p.p.m. (s, CF_3).

(d) *With triethylphosphine.* Similarly, a solution of complex (VII) (0·10 g, 0·33 mmol) and an excess of triethylphosphine (2 ml) were heated under reflux (5 min) in hexane. Chromatography on alumina followed by elution with hexane–diethyl ether (9 : 1) and recrystallisation (–78°) from hexane gave orange *crystals* of the complex (IX) (0·08 g, 44%), m.p. 142° (decomp.) (Found: C, 45·4; H, 5·4; F, 22·4. $C_{19}H_{27}F_6FeO_3P$ requires C, 45·3; H, 5·4; F, 22·6%), ν_{CO} (hexane) 2016s and 1945s cm^{-1}. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 8·12 (broad m, 9H, overlapping signals), 8·72 (s, 3H), 8·80 (s, 3H), 8·86 (t, 9H, $PCH_2\mathit{CH}_3$, J_{HH} 5·0 Hz), and 8·94 (s, 3H). The ^{19}F n.m.r. spectrum ($CDCl_3$) showed a resonance at 72·4 p.p.m. (s, CF_3).

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