Reactions of Co-ordinated Ligands. Part VI.[1] The Addition of Hexafluoropropene, Trifluoroethylene, and Chlorotrifluoroethylene to Tricarbonyl(diene)iron or Ruthenium Complexes and to Tricarbonyl(*o*-styryldiphenylphosphine)iron †

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U.v. irradiation of a solution of hexafluoropropene and tricarbonyl(buta-1,3-diene)iron, tricarbonyl(isoprene)-iron, tricarbonyl(2,3-dimethylbuta-1,3-diene)iron, and tricarbonyl(cyclohexa-1,3-diene)ruthenium affords 1 : 1 π-allylic adducts, in which the fluoro-olefin links the iron atoms and the hydrocarbon chain. An *X*-ray crystal-structure determination of the isoprene adduct established the direction of addition as $FeCF(CF_3)CF_2$, and comparison of n.m.r. data suggests the same direction of addition for the other systems studied. Reaction of tricarbonyl(cyclohexa-1,3-diene)iron affords a 1 : 1 adduct formulated as an *endo*-$CF_2{\cdot}CHF(CF_3)$ substituted tricarbonyl(cyclohexa-1,3-diene)iron complex, a π-allylic complex in which an additional hexafluoropropene links the C_6 ring and iron atom, and a third product a tetracarbonylferracyclopentane. Related reactions of tricarbonyl(tricyclo[4.2.0]octa-1,3-diene)iron and tricarbonyl(cyclo-octa-1,3-diene)iron are reported. Similar oxidative-linking reactions occur between chlorotrifluoroethylene and tricarbonyl(2,3-dimethylbuta-1,3-diene)-iron, and trifluoroethylene with tricarbonyl(cyclohexa-1,3-diene or bicyclo[4.2.0]octa-1,3-diene)iron. The reaction of tricarbonyl(*o*-styryldiphenylphosphine)iron with hexafluoropropene, chlorotrifluoroethylene, and trifluoroethylene also leads to 1 : 1 adducts, formulated as ferracyclopentanes. The mechanism of formation of these compounds is discussed.

As described in the preceding paper [1] tetrafluoroethylene reacts on u.v. irradiation with tricarbonyl(1,3-diene)iron, tricarbonyl(norbornadiene)iron, tetra- or tri-carbonyl-(*trans*-cinnamaldehyde)iron to form iron(II) complexes in which the fluoro-olefin becomes bonded to the co-ordinated organic ligand. With a view to identifying the reaction paths involved in such reactions the related processes with unsymmetrical fluoro-olefins have been studied, and are described in this paper. The crystalline complexes obtained have been identified in two cases by *X*-ray crystallography, otherwise by elemental analysis, i.r. and mass spectroscopy, and ^{19}F and ^{1}H n.m.r. spectroscopy.

RESULTS

Tricarbonyl(buta-1,3-diene)iron, tricarbonyl(isoprene)-iron, or tricarbonyl(2,3-dimethylbuta-1,3-diene)iron react with an excess of hexafluoropropene on u.v. irradiation to afford respectively the crystalline 1 : 1 adducts (I), (II), and (III).

Comparison of the i.r. and ^{1}H and ^{19}F n.m.r. spectra of these complexes with those observed for the corresponding tetrafluoroethylene adducts suggested the illustrated structures. However, the unambiguous assignment of the orientation and position of the trifluoromethyl group was clearly of fundamental importance in determining the mechanism of formation of these adducts. A single crystal *X*-ray diffraction study of (II) was therefore undertaken.

The yellow orthorhombic crystals of the adduct have $a = 23{\cdot}020$, $b = 8{\cdot}497$, $c = 6{\cdot}546$ Å, space group $P2_12_12_1$ with four molecules in the unit cell. Least-squares refinement of 1245 monochromated diffractometer data gave a final *R* value of 0·036. The *X*-ray analysis shows that the central carbon atom of the hexafluoropropene molecule has become σ-bonded to the iron atom (Fe–C = 2·107 Å) while

Table 1

Final co-ordinates and standard deviations in Å

	X	*Y*	*Z*
Fe	3·5284(6)	2·0134(6)	−0·0352(9)
F(1)	3·4080(47)	−1·2974(38)	−0·8082(46)
F(2)	3·2067(55)	−0·2726(49)	−2·6619(46)
F(3)	1·5733(47)	−1·3827(44)	−1·8846(51)
F(4)	1·6897(38)	−0·5261(37)	1·1630(40)
F(5)	−0·0381(37)	−0·2174(42)	−0·1252(49)
F(6)	1·2694(36)	1·3033(38)	−1·8211(38)
O(1)	4·7006(46)	2·1870(50)	−2·7140(48)
O(2)	4·7516(48)	−0·1881(46)	1·4651(53)
O(3)	5·9272(45)	3·3865(57)	0·9549(63)
C(1)	4·2611(56)	2·0821(61)	−1·6817(65)
C(2)	4·2363(53)	0·6083(57)	0·8550(62)
C(3)	4·9610(56)	2·9227(65)	0·6009(64)
C(4)	2·0770(53)	0·7045(57)	−0·8235(59)
C(5)	1·1079(57)	0·3928(60)	0·3355(65)
C(6)	0·7543(56)	1·6337(72)	1·0685(72)
C(7)	2·0111(48)	2·3956(57)	1·4750(62)
C(8)	2·4142(56)	3·5846(61)	0·8792(70)
C(9)	2·2884(66)	3·7164(61)	−0·5380(70)
C(10)	3·0702(69)	4·6750(62)	1·7001(86)
C(11)	2·5653(70)	−0·5733(67)	−1·5118(69)
H(6A)	0·15(8)	2·14(8)	0·38(8)
H(6B)	0·25(8)	1·49(9)	1·88(9)
H(7)	2·17(7)	2·30(8)	2·42(8)
H(9A)	2·90(8)	4·48(9)	−0·92(9)
H(9B)	1·65(8)	3·28(9)	−1·03(8)
H(10A)	3·45(9)	4·30(9)	2·62(9)
H(10B)	3·68(8)	5·21(9)	1·11(9)
H(10C)	2·34(8)	5·32(9)	1·90(9)

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† No reprints available.

[1] Part V, A. Bond, B. Lewis, and M. Green, *J.C.S. Dalton*, preceding paper.

the CF_2 group was added to one double bond of the isoprene unit leaving the remainder of this unit bonded to iron in a π-allylic manner with the three almost equal Fe–C distances of 2·132, 2·166, and 2·175 Å.

TABLE 2

Anisotropic temperature factors $U_{ij} \times 10^4$ (Å^2) and standard deviations. Form used: $\exp -2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13})$

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
Fe	279(5)	296(6)	348(5)	−13(11)	89(17)	−9(13)
F(1)	914(48)	446(35)	733(51)	276(78)	−94(83)	−104(95)
F(2)	1193(66)	780(58)	593(47)	−346(109)	−361(100)	716(97)
F(3)	832(48)	641(44)	908(57)	−539(82)	−582(99)	−127(98)
F(4)	607(39)	508(35)	564(39)	−189(66)	296(72)	135(72)
F(5)	465(30)	823(43)	797(52)	−588(65)	−146(111)	63(81)
F(6)	561(38)	577(37)	488(38)	−149(67)	193(76)	−344(69)
O(1)	633(44)	737(58)	483(42)	−138(103)	205(102)	269(78)
O(2)	648(47)	557(48)	661(54)	406(88)	277(99)	−168(92)
O(3)	458(47)	860(68)	868(71)	−499(103)	174(142)	−65(109)
C(1)	407(50)	499(66)	480(49)	46(111)	265(125)	−20(90)
C(2)	348(50)	382(47)	458(60)	52(90)	64(102)	6(102)
C(3)	388(48)	514(61)	477(60)	−279(100)	10(120)	34(95)
C(4)	405(49)	372(50)	375(57)	−141(90)	19(107)	65(97)
C(5)	382(48)	439(54)	561(76)	−291(90)	−78(100)	−146(94)
C(6)	344(52)	585(72)	580(69)	−103(103)	−160(130)	69(106)
C(7)	287(39)	385(46)	479(47)	21(75)	−80(93)	64(75)
C(8)	408(62)	399(56)	596(70)	231(110)	−26(126)	−193(124)
C(9)	560(70)	371(57)	541(67)	132(112)	179(122)	−144(121)
C(10)	598(62)	357(54)	757(79)	−8(97)	−211(119)	−234(125)
C(11)	647(60)	501(56)	426(56)	−136(105)	−146(110)	47(103)

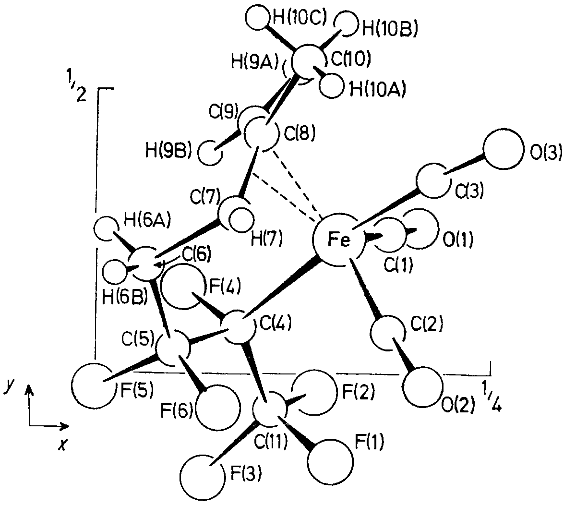
The results of the analysis are summarised in Table 1 (atomic co-ordinates), 2 (thermal parameters of the heavy atoms), 3 (some important intramolecular distances and angles), and 4 (some torsion angles). A drawing of the molecule projected down [*c*] showing the labelling of the atoms for the *X*-ray work appears in the Figure. The final list of observed and calculated structure factors are listed in Supplementary Publication No. SUP 21319 (10 pp., 1 microfiche).*

TABLE 3

Some important bond lengths (Å) and angles (°) in the complex

Fe–C(1)	1·804(6)	C(4)–Fe–C(2)	88·4(2)
Fe–C(2)	1·808(6)	Fe–C(1)–O(1)	176·7(6)
Fe–C(3)	1·812(6)	Fe–C(2)–O(2)	173·8(5)
Fe–C(4)	2·107(6)	Fe–C(3)–O(3)	173·2(6)
Fe–C(7)	2·175(6)	Fe–C(4)–F(6)	113·2(4)
Fe–C(8)	2·132(6)	Fe–C(4)–C(5)	106·1(4)
Fe–C(9)	2·166(7)	Fe–C(4)–C(11)	117·8(4)
C(11)–F(1)	1·315(8)	C(5)–C(4)–F(6)	104·9(4)
C(11)–F(2)	1·351(9)	C(11)–C(4)–F(6)	102·6(5)
C(11)–F(3)	1·334(8)	C(5)–C(4)–C(11)	116·7(5)
C(4)–F(6)	1·416(7)	C(4)–C(11)–F(1)	115·0(6)
C(5)–F(4)	1·367(7)	C(4)–C(11)–F(2)	110·4(5)
C(5)–F(5)	1·378(7)	C(4)–C(11)–F(3)	113·3(6)
C(1)–O(1)	1·127(8)	F(1)–C(11)–F(2)	105·9(6)
C(2)–O(2)	1·128(8)	F(2)–C(11)–F(3)	104·5(6)
C(3)–O(3)	1·129(8)	F(3)–C(11)–F(1)	107·0(6)
C(11)–C(4)	1·531(9)	C(4)–C(5)–F(4)	108·9(5)
C(4)–C(5)	1·543(8)	C(4)–C(5)–F(5)	111·2(5)
C(5)–C(6)	1·484(9)	C(6)–C(5)–F(4)	111·4(5)
C(6)–C(7)	1·525(9)	C(6)–C(5)–F(5)	109·7(5)
C(7)–C(8)	1·390(8)	C(4)–C(5)–C(6)	110·6(5)
C(8)–C(9)	1·429(9)	F(5)–C(5)–C(5)	105·0(5)
C(8)–C(10)	1·514(10)	C(5)–C(6)–C(7)	110·7(5)
C(1)–Fe–C(2)	108·7(3)	C(6)–C(7)–C(8)	123·5(5)
C(1)–Fe–C(3)	88·9(3)	C(7)–C(8)–C(9)	118·6(6)
C(2)–Fe–C(3)	84·7(3)	C(7)–C(8)–C(10)	120·6(6)
C(3)–Fe–C(4)	170·9(3)	C(9)–C(8)–C(10)	120·6(6)
C(4)–Fe–C(1)	87·8(3)		

The molecule is asymmetric and so, since the space group is $P\,2_12_12_1$, individual crystals contain molecules of the same chirality. The carbon atoms of the carbonyl groups and of the CF group occupy four octahedral sites with respect to the iron atom and the remaining two sites are taken up by the π-allyl group. The Fe–C(carbonyl) bond lengths are essentially equal, 1·806(6) Å, so that there is no lengthening of the Fe–C(3) bond by the *trans* σ-bonded fluoro-alkyl group. A *trans* lengthening effect has been observed in the 1 : 1 complex of tetracyanoethylene with tricarbonyl(cycloheptatriene)iron [2] and a *trans* shortening effect in the tricarbonyl(1—3η-hexen-5-one)iron cation.[3] The Fe–C(4) bond length of 2·107(6) Å is within the range of values quoted for this bond in a recent review.[4] The carbon–carbon bond lengths correspond fairly well to their expected values.[5] The C–F bonds vary from 1·315(8) to 1·416(7) Å with a



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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[2] J. Weaver and P. Woodward, *J. Chem. Soc.* (*A*), 1971, 3521.

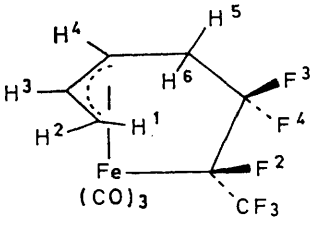
[3] A. D. V. Hardy and G. A. Sim, *J.C.S. Dalton*, 1972, 2305.

[4] M. R. Churchill, 'Perspectives in Structural Chemistry,' Vol. III, 1970, p. 91.

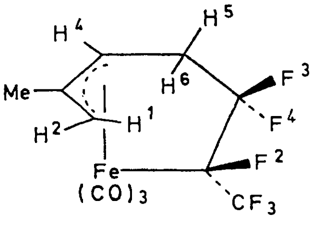
[5] *Chem. Soc. Special Publ.*, No. 18, London, 1965.

mean of 1·360 Å, however the fluorine atoms undergo considerable thermal motion so that the true mean is probably a little greater than this; the standard value is 1·379 Å.

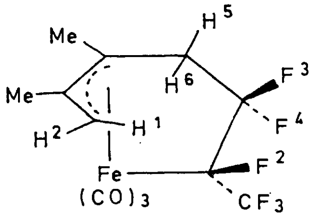
The observed geometry in (II) differs only slightly from the idealised case,[6,7] the central Fe–C distance of 2·132(6) Å is typically [2,3,8] slightly less than the remaining two, whose average length is 2·170(7) Å, the C–C lengths are 1·390(8) and 1·429(9) Å, and the C–C–C angle is 118·6(6)°. The relation of the metal–allyl system to the other ligands may be described in various ways, *e.g.* the dihedral angle of 114·4° between the C(7)–C(8)–C(9) plane and the Fe–C(1)–C(2) plane. The isoprenoid group is not planar; the methyl group is displaced by 0·105 Å from the C(7)–C(8)–C(9) allyl plane and lies on the same side of the plane as the iron atom, the carbon atom of the methylene group, C(6), lies on the other side of this plane 0·828 Å away. The non-orthogonality of the ligand σ-framework with the orbitals of the metal atom has also been used [9] to explain non-planarities in cyclic C_nR_n systems complexed with the metal atom, and the argument may be extended to π-allyl systems.



(I)

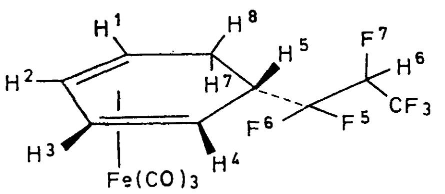


(II)

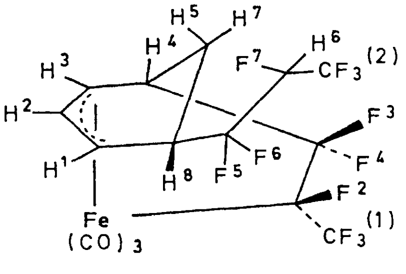


(III)

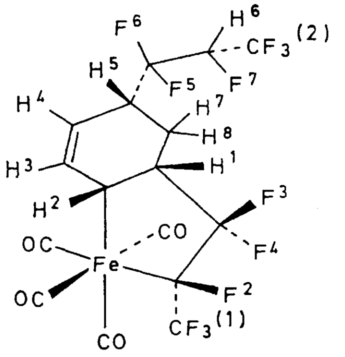
Steric relations across the bonds of the carbon chain are given by the torsion angles in Table 4. Considering only the carbon atoms in the chain, the arrangement about C(4)–C(5) is (−) anti-periplanar, while about C(5)–C(6) it is (+) syn-clinal,[10] so that the chain branches at C(6) to join up with the π-allyl group.



(IV)



(V)



(VI)

Thus the establishment of the illustrated structure of (II) allowed the firm assignment of chemical-shift and coupling-constant data listed in the Experimental section, and hence the confirmation of the direction of addition of hexafluoropropene to the other systems studied.

The irradiation of a hexane solution of hexafluoropropene and tricarbonyl(cyclohexa-1,3-diene)iron led to the formation of three complexes (IV), (V), and (VI), which were separated by column chromatography. Complex (IV), an oil which analysed for a 1 : 1 adduct, showed in the i.r. three terminal carbonyl bands at 2063, 2000, and 1987 cm^{-1}, which are at lower frequency than those observed for a normal Fe^{II} adduct, *i.e.* complexes (I)—(III).

Examination of the n.m.r. spectra of (IV) suggested the illustrated structure, arising from the formal insertion of a molecule of hexafluoropropene into a methylenic carbon–hydrogen bond of co-ordinated cyclohexa-1,3-diene. The ^{1}H n.m.r. spectrum showed in addition to resonances assigned to CH_2CH and $CF_2CHF(CF_3)$, four resonances with chemical shifts and coupling constants typical of a co-ordinated 1,3-diene. The ^{19}F spectrum firmly established the presence of a hexafluoropropyl group $CF_2CHF(CF_3)$ with inequivalent CF_2 nuclei, the inequivalence arising from the conformational rigidity of the side chain, which was clearly seen on examination of a molecular model. The overlap of the ^{1}H n.m.r. signals due to H^5, H^7, and H^8 did not allow the

TABLE 4

Some torsion angles (°) with standard deviations

(*a*) C–C–C–C	
C(11)–C(4)–C(5)–C(6)	−174·4(5)
C(4)–C(5)–C(6)–C(7)	51·7(4)
C(5)–C(6)–C(7)–C(8)	−107·9(6)
C(6)–C(7)–C(8)–C(9)	40·7(5)
C(6)–C(7)–C(8)–C(10)	−143·9(6)
(*b*) F–C–C–F	
F(6)–C(4)–C(11)–F(1)	−176·7(5)
F(6)–C(4)–C(11)–F(2)	−56·9(4)
F(6)–C(4)–C(11)–F(3)	59·8(4)
F(6)–C(4)–C(5)–F(4)	−162·5(5)
F(6)–C(4)–C(5)–F(5)	−47·0(4)

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[6] K. Vrieze, C. MacLean, P. Cossee, and C. W. Hilbers, *Rec. Trav. chim.*, 1966, **85**, 1077.

[7] G. Debrouckere, *Theor. Chim. Acta*, 1970, **19**, 310.

[8] P. F. Lindley and O. S. Mills, *J. Chem. Soc.* (*A*), 1970, 38.

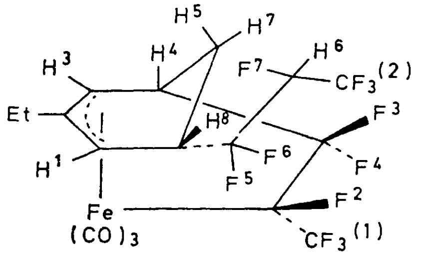
[9] S. F. A. Kettle, *Inorg. Chim. Acta*, 1967, **1**, 303.

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

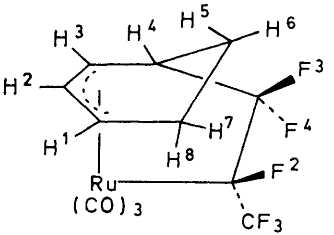
assignment of the configuration of the $CF_2CHF(CF_3)$ group relative to the iron atom; however, this feature was established crystallographically (see later).

Elemental analysis established that both the complexes (V) and (VI), which are mononuclear, contain two molecules of hexafluoropropene. Further, the i.r. and mass spectra showed that, whereas, (V) was an $Fe(CO)_3$ species, complex (VI) contained an $Fe(CO)_4$ unit.

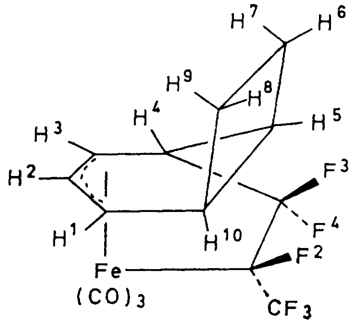
Comparison of ^{19}F chemical shifts and decoupling experiments showed that in both (V) and (VI) the two hexafluoropropene molecules were not joined together; the data was, however, compatible with the presence of a $CF_2CHF(CF_3)$ group as present in (IV), and a second molecule of hexafluoropropene linking the iron to the C_6 ring in the way established for the species (I)—(III). In agreement with the illustrated structures the ^1H n.m.r. spectrum of (V) showed typical allylic resonances, whereas the spectrum of (VI) showed two low-field signals (τ 3·68, 4·16) assignable to the H^3 and H^4 protons of an unco-ordinated double bond, as required by a structure, in which an $Fe(CO)_4$ unit is incorporated into a ferracyclopentane ring system. As might be expected, the ^{19}F chemical shifts of the nuclei of the $CF(CF_3)CF_2$ unit, which is part of the ferracyclopentane ring, differ from the corresponding shifts observed for (I), (II), (III), and (V).



(VII)



(VIII)



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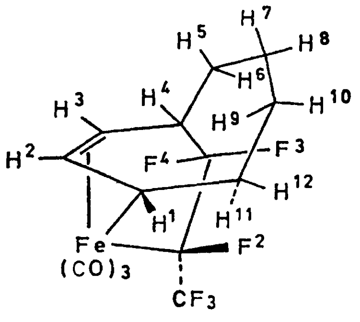
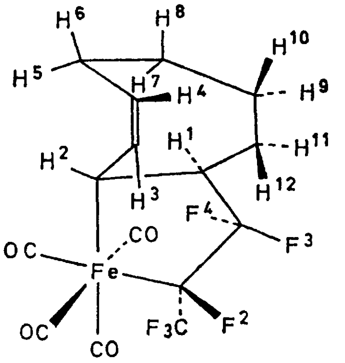


(X)



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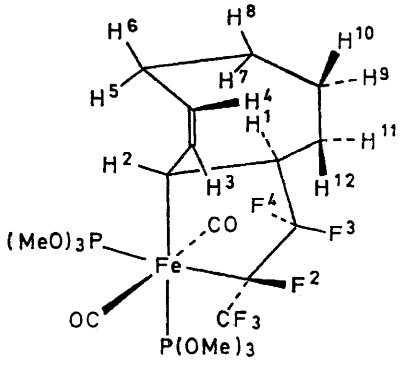

(XII)

As in the case of (IV) the spectroscopic evidence does not allow a firm decision between various structures differing as to whether the $CF_2{\cdot}CHF(CF_3)$ group has an *exo*- or *endo*-configuration relative to the iron atom. However, an X-ray crystallographic study [11] of the complex (VI) has firmly established the illustrated structure, and shows that the $CF_2CHF(CF_3)$ side chain has an *endo*-configuration relative to the ferracyclopentane ring.

An analogous reaction on u.v. irradiation of hexafluoropropene with tricarbonyl(2-ethylcyclohexa-1,3-diene)iron afforded as the only product the 1 : 2 adduct (VII), which by comparison of i.r. carbonyl frequencies and n.m.r. data is assigned the structure shown. The position of the ethyl substituent was apparent from the absence of a low-field signal in the ^1H n.m.r. spectrum corresponding to a central allylic proton.

In contrast with the iron system, u.v. irradiation of tricarbonyl(cyclohexa-1,3-diene)ruthenium with hexafluoropropene afforded the 1 : 1 adduct (VIII), formulated as a π-allylic complex. There was no evidence for the formation of ruthenium compounds analogous to (IV), (V), or (VI). The ^1H n.m.r. chemical-shift data for (VIII) compared well with those observed for (V) and (VII), and in addition decoupling experiments established typical coupling constants; the long-range coupling (4·5 Hz) between F^4 and H^2 also being observed. The ^{19}F spectrum showed shifts and coupling constants similar to those observed for (II), and on this basis the illustrated structure and stereochemistry is assigned.

The reaction of hexafluoropropene with tricarbonyl(bicyclo[4.2.0]octa-2,4-diene)iron gave only the π-allylic complex (IX), there being no evidence for products arising from an *endo*-insertion reaction into a carbon–hydrogen bond. As required by the structure shown the ^1H and ^{19}F n.m.r. shifts and coupling constants correlate well with those of the analogous cyclohexadiene adducts. In the ^1H spectrum of (IX) the protons H^5–H^{10} appear as overlapping signals in the range τ 7·2—8·6. In this reaction there was no evidence for disrotatory ring opening of the bicyclic system to give a cyclo-octatriene adduct.

The reaction of tricarbonyl(cyclo-octa-1,3-diene)iron with hexafluoropropene gave the allylic 1 : 1 adduct (X), which

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[11] R. Goddard and P. Woodward, unpublished observations, currently R = 0·055.

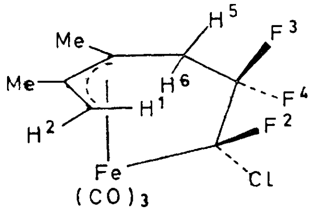
exhibited the expected spectroscopic characteristics. When heated (80 °C) in hexane solution for 6 h, the yellow crystalline adduct is transformed *via* a π- to σ-allyl conversion and the co-ordination of a fourth molecule of carbon monoxide (released by thermal decomposition) into colourless needles of the substituted ferracyclopentane (XI), which showed four terminal carbonyl bands in the i.r. spectrum characteristic of an $Fe(CO)_4$ unit, in addition to a weak absorption at 1622 cm^{-1} identified as a $\nu_{C=C}$ stretching frequency of the unco-ordinated double-bond. The ^1H n.m.r. spectrum confirmed the presence of a free double-bond, exhibiting two overlapping low-field multiplets in the range τ 4·0—4·3. The ^{19}F n.m.r. spectrum showed resonances similar to those observed for (VI).

A related reaction occurred on refluxing (X) with trimethyl phosphite to give the diphosphite complex (XII), whose parameters correlated well with those of (XI). In the ^1H n.m.r. spectrum the resonance due to the unco-ordinated double-bond occur at τ 4·06 and 4·41, and display a mutual *cis* coupling of 10·5 Hz. The H^1 signal (τ 7·57) is also well separated from the complex methylenic resonance and exhibits a large (41·0 Hz) coupling to F^3. Although, there are alternative structures for this complex, in which the phosphite ligands occupy positions *cis* to the iron–carbon σ-bonds of the ferracyclopentane ring, examination of molecular models suggests that in such isomeric structures there would be considerable non-bonding interactions, and therefore the illustrated structure is preferred.

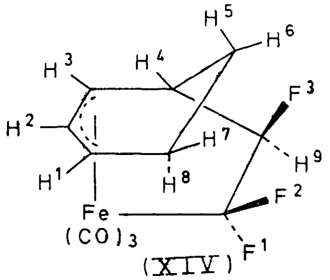
The reactions of hexafluoropropene described are stereospecific, there being no evidence for the formation of isomeric products. It was therefore important to examine related reactions of other unsymmetrical fluoro-olefins.

Whereas, the u.v. irradiation of solutions of chlorotrifluoroethylene with tricarbonyl(isoprene)iron afforded very low yields of products, the corresponding reaction of tricarbonyl(2,3-dimethylbuta-1,3-diene)iron afforded a moderate yield of (XIII). The i.r. and ^1H n.m.r. spectra are similar to those observed for the C_2F_4 and C_3F_6 adducts thus establishing a π-allylic structure. The orientation of addition of C_2F_3Cl is established by the ^{19}F n.m.r. chemical shifts and ^1H–^{19}F coupling constants. Furthermore, observation of a through-space ^1H–^{19}F coupling (5·0 Hz) to H^1 confirmed the stereochemistry at the CFCl group; the chlorine, as in the case of the CF_3 group in the corresponding hexafluoropropene adduct, occupies an outside position in the spiral formed by the carbon chain.

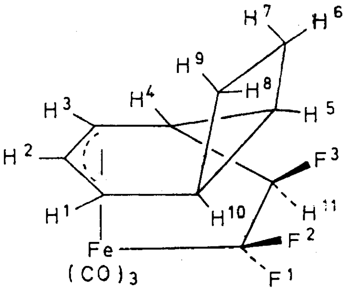
Trifluoroethylene reacts with tricarbonyl(cyclohexa-1,3-diene)iron and tricarbonyl(bicyclo[4.2.0]octa-2,4-diene)iron to give (XIV) and (XV) as stable crystalline compounds. Interestingly, tricarbonyl(cyclo-octa-1,3-diene)iron did not react with trifluoroethylene.



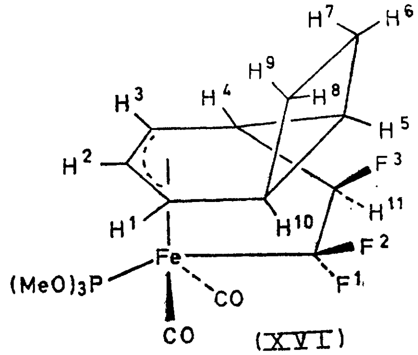
(XIII)



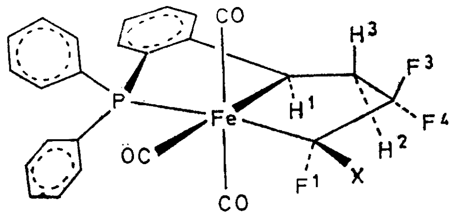
(XIV)



(XV)



(XVI)

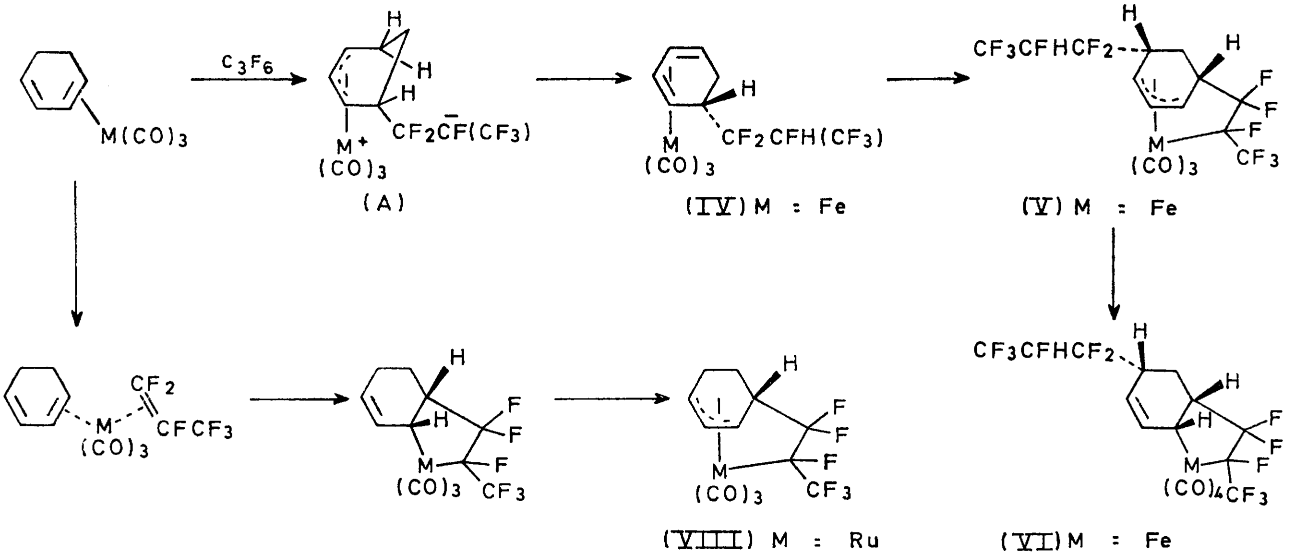


(XVII) X = CF_3
(XVIII) X = H
(XIX) X = Cl

The ^1H n.m.r. spectrum of (XIV) was well resolved, and, although containing many features in common with that of the corresponding tetrafluoroethylene adduct,[1] shows one significant change concerning the couplings associated with the central allylic proton H^2. Unlike the C_2F_4 adduct of tricarbonyl(cyclohexa-1,3-diene)iron this proton does not display a ^1H–^{19}F coupling, suggesting that the CF_2CFH proton H^9 occupies the position assumed by F^4 in the C_2F_4 adduct. The H^9 resonance at τ 5·48 shows one large (52·0 Hz) geminal ^1H–^{19}F coupling and two smaller vicinal couplings. Analysis of the remaining allylic and methylenic resonances parallel the C_2F_4 adduct case. As required by the illustrated structure, the ^{19}F n.m.r. spectrum exhibits low-field signals (44·9 and 87·3 p.p.m.) typical of an $FeCF_2$ group. The fact that this group averages a substantially lower chemical shift than the C_2F_4 adduct is attributed to the presence of the adjacent CHF group. The F^2 resonance was readily distinguishable by its through-space coupling to H^8, and F^3 resonated at high field (177·8 p.p.m.) typical of a CH*F* group.

The corresponding spectra of the adduct (XV) closely paralleled those of (XIV); the protons H^5–H^{10} in the ^{1}H spectrum appearing as a complex pattern at τ 7·2—8·6. Reaction of (XV) with trimethyl phosphite led to the displacement of one molecular equivalent of carbon monoxide and the formation of the π-allylic complex (XVI). In the ^{19}F spectrum of (XVI) the signals at 48·8 and 81·7 p.p.m. (assigned to F^2 and F^1, respectively) are considerably broadened relative to those in (XV), whereas the signal at 177·3 p.p.m. (F^3) showed no evidence of ^{19}F–^{31}P coupling. Since the ^{31}P atom of the phosphite ligand would be expected to couple more strongly with the α-CF_2 nuclei this observation substantiates the previously made assignments.

As described in the preceding paper,[1] tricarbonyl(*o*-styryldiphenylphosphine)iron, [(sp)Fe(CO)$_3$], reacts with C_2F_4 to form a ferracyclopentane. It was clearly important to study the related reactions of unsymmetrical fluoro-olefins. Irradiation of a solution of [(sp)Fe(CO)$_3$] and hexafluoropropene, trifluoroethylene, or chlorotrifluoroethylene afforded respectively the crystalline 1 : 1 adducts (XVII), (XVIII), and (XIX) in high yield. In each case an analysis of the ^{1}H and ^{19}F n.m.r. spectra of these adducts established both the illustrated orientation of the addend and the stereochemistry at the asymmetric carbon atom. Significantly, whereas the orientation of the addenda in (XVII) and (XIX) coincide with those exhibited by the other adducts formed by these fluoro-olefins, the trifluoroethylene orientation is opposite to that encountered in (XIV) and (XV).

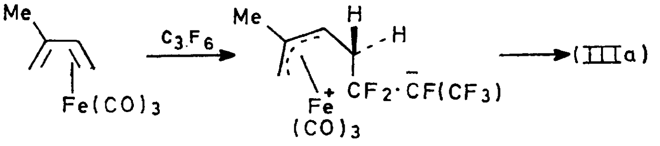


Scheme 2

DISCUSSION

The direction of addition established by *X*-ray crystallography for the reaction of hexafluoropropene to tricarbonyl(isoprene)iron, and inferred by comparison of n.m.r. parameters for the other adducts, is that found for the reaction of CF_2=CFX (X = H, Cl, or CF_3) with a wide range of nucleophiles, suggesting that the formation of these adducts involves electrophilic attack by the fluoro-olefin at the least-substituted carbon atom of the 1,3-diene. The observed stereochemistry is not that which would be expected if the reaction involved initial attack by the nucleophilic zerovalent iron atom on the fluoro-olefin followed by collapse of the resultant dipolar species.

However, the direction of addition found for (I), (II), and (III) is consistent with the mechanism proposed [1] for the corresponding reaction of C_2F_4, in which *endo*-attack by the hexafluoropropene or chlorotrifluoroethylene on a co-ordinated double bond of a *cisoid*-1,2-η bonded diene affords a dipolar species, which collapses to give the adduct; the orientation of the substituent on the diene being governed by steric rather than electronic effects (Scheme 1).



Scheme 1

As mentioned in the preceding paper tricarbonyl(cyclohexa-1,3-diene)iron shows a higher reactivity towards C_2F_4 than might be expected, and it is reasonable to extend the suggestion that there is an alternative reaction path available for the formation of these adducts to the reactions with hexafluoropropene. However, the formation of the complexes (IV), (V), and (VI) where the important structural feature of an *endo*-CF_2·CFH(CF_3) side chain has been established by *X*-ray crystallography,[11] suggests that the ionic pathway plays a dominant role, possibly because of the greater susceptibility of hexafluoropropene to nucleophilic attack. As illustrated in Scheme 2 *endo*-attack by C_3F_6 on [C_6H_8Fe(CO)$_3$] leads to the formation of the ionic intermediate (A), which because of the coplanarity of the π-allylic system would be so orientated that a 1,5 interaction would be facilitated, leading to proton abstraction by the carbanion and formation of (IV). The formation of (V) and (VI) from (IV), a sequence which was established in separate experiments, could then occur either by further reaction of (IV) *via* the ionic pathway, or by a reaction path involving co-ordination of the hexafluoropropene to the iron atom (Scheme 2).

The alternative reaction path which can be envisaged, does not involve ionic intermediates, and is illustrated (Scheme 2) for the formation of the ruthenium adduct (VIII), and similarly for (VII), (IX), and (X), *etc.* Such a reaction involves initial co-ordination of both the diene (as a mono-olefin) and fluoro-olefin followed by an electronic rearrangement to give a metallocyclopentane. Similar processes have been proposed to explain olefin metathesis,[12] valence isomerisation of cubane to *syn*-tricyclo-octadiene,[13] cyclo-addition reactions of norbornadiene,[14] and rearrangement of *exo*-tricyclo-[3.2.1.0^{2,4}]octene.[15] Recently, the isolation and structural characterisation of [Ir(nbd)$_3$(acac)] as a metallocyclopentane has been described,[16] and Whitesides has commented on the thermal stability of platinacyclopentanes.[17]

Clearly, on the present evidence it is not possible to assess the relative importance of the two reaction paths, however, the direction of addition of trifluoroethylene to [(sp)Fe(CO)$_3$] is interesting, and possibly reflects a change of mechanism.

EXPERIMENTAL

Spectroscopic data were obtained by the methods outlined in the preceding paper.[1]

Reactions of Hexafluoropropene.—(*a*) *With* (*buta*-1,3-*diene*) *tricarbonyliron.* An excess of hexafluoropropene (0·45 g, 3·0 mmol) was condensed (−196 °C) into a Carius tube (100 ml) containing (buta-1,3-diene)tricarbonyliron (0·50 g, 2·5 mmol) in hexane (20 ml). U.v. irradiation (250 W Hanovia lamp) of the tube and contents (24 h), followed by removal of the volatile material *in vacuo* gave a crystalline solid. Chromatography on alumina and elution with hexane gave, on recrystallisation (−78 °C) from hexane, yellow *crystals* of (I) (0·01 g, 5%), m.p. 75 °C (Found: C, 35·1; H, 1·8; F, 33·3. $C_{10}H_6F_6FeO_3$ requires C, 34·9; H, 1·7; F, 33·2%), ν_{CO} (hexane) 2091s, 2038m, and 2021s cm^{-1}. The mass spectrum (base *m/e* 316) showed peaks at *m/e* 344 (*P*, 4%), 316 (*P* − CO, 100%), 297 (*P* − CO − F, 6%), 288 (*P* − 2CO, 30%), 269 (*P* − 2CO − F, 18%), 260 (*P* − 3CO, 60%), and 241 (*P* − 4CO − F, 50%). The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 4·75 [m, 1H, H^3, $J_{1,3}$ 13, $J_{2,3}$ 8·0, $J_{3,4}$ 7·5, $J(\mathrm{H^3F^2}) = J(\mathrm{H^3F^4})$ 3·5 Hz], 5·34 (ddd, 1H, H^4, $J_{4,5} = J_{4,6} = J_{4,3}$ 7·5 Hz), 6·38 (dd, 1H, H^2, $J_{1,2}$ 2·5, $J_{2,3}$ 8·0 Hz), 6·82 [ddd, 1H, H^1, $J_{1,2}$ 2·5, $J_{1,3}$ 13·0, $J_{1,2}$ 2·5 $J(\mathrm{H^1F^2})$ 6·5 Hz], 7·41 [ddd, 1H, H^5, $J_{4,5}$ 7·5, $J_{5,6} = J(\mathrm{H^5F^3})$ 15·0 Hz], and 8·10 [dm, 1H, H^6, $J_{5,6}$ 15·0, $J_{4,6}$ 7·5, $J(\mathrm{H^6F^3})$ 37·0 Hz]. The ^{19}F n.m.r. spectrum (CDCl$_3$) showed resonances at 66·1 p.p.m. [ddd, 3F, CF$_3$, $J(\mathrm{CF_3F^2})$, $J(\mathrm{CF_3F^3}) = J(\mathrm{CF_3F^4})$ 11·0 Hz], 98·0 [dm, 1F, F^4, $J_{3,4}$ 229, $J(\mathrm{CF_3F^4})$ 11·0, $J(\mathrm{F^4H^3})$ 3·5 Hz], 116·8 [ddm, 1F, F^3, $J_{3,4}$ 229, $J(\mathrm{CF_3F^3})$ 11·0, $J(\mathrm{CF_3H^6})$ 37·0, $J(\mathrm{CF_3H^5})$ 15·0 Hz], and 177·5 [m, 1F, F^2, $J(\mathrm{CF_3F^2})$ 11·0, $J(\mathrm{F^2H^3})$ 3·5, $J(\mathrm{F^2H^1})$ 6·5 Hz].

(*b*) *With tricarbonyl*(*isoprene*)*iron.* Similarly, u.v. irradiation (46 h) of a solution of tricarbonyl(isoprene)iron (0·40 g, 2·0 mmol) and an excess of hexafluoropropene (0·90 g, 6·0 mmol) in hexane (15 ml) and removal of volatile material *in vacuo* gave, on recrystallisation (0 °C) of the residue from methylene chloride–hexane, yellow *crystals* of (II) (0·11 g, 16%), m.p. 97—98 °C (Found: C, 37·1; H, 2·7; F, 31·6. $C_{11}H_8F_6FeO_3$ requires C, 36·8; H, 2·3; F, 31·8%), ν_{CO} (hexane) 2088s, 2035s, and 2014s cm^{-1}. The mass spectrum (base *m/e* 202) showed peaks at *m/e* 358 (*P*, 3%), 330 (*P* − CO, 95%), 311 (*P* − CO − F, 6%), 302 (*P* − 2CO, 23%), 283 (*P* − 2CO − F, 15%), 274 (*P* − 3CO, 15%), and 255 (*P* − 3CO − F, 52%). The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 6·51 (ddd, 1H, H^4, $J_{4,5} = J_{4,6}$ 7·5, $J_{2,4}$ 4·0 Hz), 6·52 (dd, 1H, H^2, $J_{2,4}$ 4·0, $J_{1,2}$ 3·0 Hz), 6·86 [dd, 1H, H^1, $J_{1,2}$ 3·0, $J(\mathrm{H^1F^2})$ 8·0 Hz], 7·45 [ddd, 1H, H^5, $J_{5,6} = J(\mathrm{H^5F^3})$ 14·5, $J_{4,5}$ 7·5 Hz], 7·91 (s, 3H, Me), and 8·20 [m, 1H, H^6, $J_{5,6}$ 14·5, $J_{4,6}$ 7·5, $J(\mathrm{H^6F^3})$ 39·0, $J(\mathrm{H^6F^4})$ 10·5 Hz]. The ^{19}F n.m.r. spectrum (CHCl$_3$) showed resonances at 65·9 p.p.m. [ddd, 3F, CF$_3$, $J(\mathrm{CF_3F^2}) = J(\mathrm{CF_3F^3}) = J(\mathrm{CF_3F^4})$ 10·5 Hz], 101·2 [ddq, 1F, F^4, $J_{3,4}$ 232, $J(\mathrm{CF_3F^4}) = J(\mathrm{F^4H^6})$ 10·5 Hz], 117·0 [dm, 1F, F^3, $J_{3,4}$ 232, $J(\mathrm{CF_3F^3}) = J_{2,3}$ 10·5, $J(\mathrm{F^3H^6})$ 39·0, $J(\mathrm{F^3H^5})$ 14·5 Hz], and 178·3 [m, 1F, F^2, $J(\mathrm{CF_3F^2}) = J_{2,3}$ 10·5, $J(\mathrm{F^2H^1})$ 8·0 Hz].

(*c*) *With tricarbonyl*(2,3-*dimethylbuta*-1,3-*diene*)*iron.* Similarly, u.v. irradiation (40 h) of a solution of tricarbonyl-(2,3-dimethylbuta-1,3-diene)iron (0·40 g, 1·8 mmol) and $CF_3CF{=}CF_2$ (0·62 g, 4·0 mmol) in hexane afforded yellow crystals. Removal of volatile material *in vacuo* and recrystallisation (0 °C) from methylene chloride–hexane gave yellow *needles* of (III) (0·11 g, 16%), m.p. 85—86 °C (Found: C, 38·3; H, 2·6; F, 30·8. $C_{12}H_{10}F_6FeO_3$ requires C, 38·7; H, 2·7; F, 30·6%), ν_{CO} (hexane) 2084s, 2031s, and 2009s cm^{-1}. The mass spectrum (base *m/e* 288) showed peaks at *m/e* 372 (*P*, 3%), 352 (*P* − HF, 6%), 344 (*P* − CO, 61%), 324 (*P* − CO − HF, 21%), 316 (*P* − 2CO, 2%), 296 (*P* − 2CO − HF, 23%), 288 (*P* − 3CO, 100%), and 268 (*P* − 3CO − HF, 4%). The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 6·68 (d, 1H, H^2, $J_{1,2}$ 3·0 Hz), 7·13 [dd, 1H, H^1, $J_{1,2}$ 3·0, $J(\mathrm{H^1F^2})$ 7·0 Hz], 7·72 [dd, 1H, H^5, $J_{5,6} = J(\mathrm{H^5F^3})$ 15·0 Hz], 7·87 (s, 3H, Me), 8·02 (s, 3H, Me), and 8·09 [dm, 1H, H^6, $J_{5,6}$ 15·0, $J(\mathrm{H^6F^3})$ 37·0 Hz]. The ^{19}F n.m.r. spectrum (CHCl$_3$) showed resonances at 66·2 p.p.m. [ddd, 3F, CF$_3$, $J(\mathrm{CF_3F^2}) = J(\mathrm{CF_3F^3}) = J(\mathrm{CF_3F^4})$ 19·5 Hz], 98·8 [dm, 1F, F^4, $J_{3,4}$ 233, $J(\mathrm{F^4CF_3})$ 10·5 Hz], 118·6 [dm, 1F, F^3, $J_{3,4}$ 233, $J(\mathrm{F^3CF_3})$ 10·5, $J(\mathrm{F^3H^6})$ 37·0, $J(\mathrm{F^3H^5})$ 15·0 Hz], and 179·0 [m, 1F, F^2, $J(\mathrm{F^2CF_3})$ 10·5, $J(\mathrm{F^2H^1})$ 7·0 Hz].

(*d*) *With tricarbonyl*(*cyclohexa*-1,3-*diene*)*iron.* Irradiation (3 days) of a solution of tricarbonyl(cyclohexa-1,3-diene)iron (1·0 g, 4·5 mmol) and hexafluoropropene (1·5 g, 10 mmol) in hexane (15 ml) gave initially a deposit of crystals followed by an oil. Volatile material was removed *in vacuo* and the residue chromatographed on alumina. Elution with hexane gave a yellow *oil* (IV) (0·30 g, 18%), m.p. *ca.* −40 °C (Found: C, 38·9; H, 2·2; F, 30·4. $C_{12}H_8F_6FeO_3$ requires C, 38·9; H, 2·2; F, 30·8%), ν_{CO} (hexane) 2063s, 2000s, and

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1978s cm^{-1}. The mass spectrum (base *m/e* 113) showed peaks at *m/e* 370 (*P*, 7%), 342 (*P* − CO, 79%), 314 (*P* − 2CO, 32%), 295 (*P* − 2CO − F, 2%), 286 (*P* − 3CO, 65%), and 267 (*P* − 2CO − F, 8%). The ^{1}H n.m.r. spectrum (C_6F_6) showed resonances at τ 5·43 (m, 1H, H^2, $J_{2,3}$ 4·5 Hz), 5·64 (dd, 1H, H^3, $J_{3,4}$ 6·5, $J_{2,3}$ 4·5 Hz), 7·40 (m, 1H, H^1), 7·44 [dd, 1H, H^4, $J_{3,4}$ 6·5, $J(H^4F)$ 34·0 Hz], and 8·06—8·94 (complex m, 3H, $H^{5,7,8}$). The ^{19}F n.m.r. spectrum (toluene) showed resonances at 74·0 p.p.m. [dddd, 3F, CF_3, $J(CF_3F^6) = J(CF_3F^7) = J(CF_3H^6)$ 11·0, $J(CF_3F^5)$ 6·0 Hz], 115·9 [dm, 1F, F^6, $J_{5,6}$ 245, $J(F^6CF_3)$ 11·0 Hz], 121·4 [dm, 1F, F^5, $J_{5,6}$ 245, $J(F^5CF_3)$ 6·0 Hz], and 211·0 [m, 1F, F^7, $J(F^7CF_3)$ 11·0, $J(F^7H^6)$ 43·0 Hz]. Elution with methylene chloride–hexane (1 : 2), followed by recrystallisation from the same solvent system gave yellow *needles* of (V) (0·06, 3%), m.p. 129—131 °C (Found: C, 34·8; H, 1·5; F, 43·9. $C_{15}H_8F_{12}FeO_3$ requires C, 34·6; H, 1·5; F, 43·8%), ν_{CO} (hexane) 2090s, 2037s, and 2020ms cm^{-1}. The mass spectrum (base *m/e* 127) showed peaks at *m/e* 520 (*P*, 1%), 492 (*P* − CO, 10%), 473 (*P* − CO − F, 1%), 464 (*P* − 2CO, 9%), 445 (*P* − 2CO − F, 2%), 436 (*P* − 3CO, 10%), 342 (*P* − C_3F_6 − CO, 40%), and 323 (*P* − C_3F_6 − CO − F, 10%). The ^{1}H n.m.r. spectrum ([$^{2}H_6$]acetone) showed resonances at τ 3·96 [ddd, 1H, H^2, $J_{1,2} = J_{2,3} = J(H^2F^4)$ 5·0 Hz], 4·52 [dm, 1H, H^6, $J(H^6F^7)$ 43·0, $J(H^6F^{5\text{ or }6})$ 16·0, $J(H^6CF_3^{(2)})$ 11·0 Hz], 4·75 (ddd, 1H, H^3, $J_{2,3} = J_{3,4}$ 5·0, $J_{1,3}$ 1·5 Hz), 5·10 (m, 1H, H^1, $J_{1,2}$ 5·0, $J_{1,3}$ 1·5 Hz), 6·50 (m, 1H, H^4, $J_{3,4}$ 5·0 Hz), and 7·03—7·62 (complex m, 3H, $H^{5,7,8}$). The ^{19}F n.m.r. spectrum (acetone) showed resonances at 65·4 p.p.m. [ddd, 3F, $CF_3^{(1)}$, $J(CF_3^{(1)}F^3)$ 17·0, $J(CF_3^{(1)}F^2) = J(CF_3^{(1)}F^4)$ 9·0 Hz], 73·5 [dddd, 3F, $CF_3^{(2)}$, $J(CF_3^{(2)}F^6) = J(CF_3^{(2)}F^7) = J(CF_3^{(2)}H^6)$ 11·0, $J(CF_3^{(2)}F^5)$ 6·0 Hz], 90·3 [dm, 1F, F^4, $J_{3,4}$ 248, $J(F^4CF_3^{(1)})$ 9·0, $J(F^4H^2)$ 5·0 Hz], 108·9 [dm, 1F, F^3, $J_{3,4}$ 248, $J(F^3CF_3^{(1)})$ 7·0 Hz], 112·8 [m, 2F, $F^{5,6}$, $J(F^6CF_3^{(2)})$ 11·0, $J(F^5CF_3^{(2)})$ 6·0, $J(F^{5\text{ or }6}H^6)$ 16·0 Hz], 188·5 [m, 1F, F^2, $J(F^2CF_3^{(1)})$ 9·0 Hz], and 211·2 [dm, 1F, F^7, $J(F^7CF_3^{(2)})$ 11·0, $J(F^7H^6)$ 43·0 Hz].

Finally, elution with methylene chloride–hexane (2 : 1) and subsequent recrystallisation (0 °C) from the same solvent gave large colourless *prisms* of (VI) (0·30 g, 12%), m.p. 97·9 °C (Found: C, 35·1; H, 1·5; F, 41·7. $C_{16}H_8F_{12}FeO_4$ requires C, 35·0; H, 1·5; F, 41·6%), ν_{CO} (hexane) 2131m, 2072vs, and 2046s cm^{-1}; $\nu_{C=C}$ (Nujol) 1627w cm^{-1}. The mass spectrum (base *m/e* 191) showed peaks at *m/e* 548 (*P*, 4%), 520 (*P* − CO, 1%), 492 (*P* − 2CO, 10%), 473 (*P* − 2CO − F, 1%), 464 (*P* − 2CO, 10%), 445 (*P* − 3CO − F, 2%), 436 (*P* − 4CO, 40%), 417 (*P* − 4CO − F, 2%), 342 (*P* − C_3F_6 − 2CO, 72%), and 323 (*P* − C_3F_6 − 2CO − F, 2%). The ^{1}H n.m.r. spectrum ([$^{2}H_6$]acetone) showed resonances at τ 3·68 (m, 1H, H^3, $J_{3,4}$ 11·0 Hz), 4·16 [dm, 1H, H^6, $J(H^6F^7)$ 43·0, $J(H^6CF_3^{(2)})$ 11·0 Hz], 4·17 (d, 1H, H^4, $J_{3,4}$ 11·0 Hz), 6·01 (m, 1H, H^2), 7·00 (m, 2H, $H^{1,5}$), and 7·95 (m, 2H, $H^{7,8}$). The ^{19}F n.m.r. spectrum (acetone) showed resonances at 66·7 [dddd, 3F, $CF_3^{(1)}$, $J(CF_3^{(1)}F^2) = J(CF_3^{(1)}F^3) = J(CF_3^{(1)}F^4)$ 10·0, $J(CF_3^{(1)}H)$ 4·5 Hz], 74·2 [ddddd, 3F, $CF_3^{(2)}$, $J(CF_3^{(2)}F^5) = J(CF_3^{(2)}F^6) = J(CF_3^{(2)}F^7) = J(CF_3^{(2)}H^6)$ 11·0, $J(CF_3^{(2)}H)$ 6·5 Hz], 110·8 [dm, 1F, F^4, $J_{3,4}$ 247, $J_{2,4} = J(F^4CF_3^{(1)})$ 10·0, $J(F^4H)$ 18·0 Hz], 114·7 [dm, 1F, F^3, $J_{3,4}$ 247, $J(F^3CF_3^{(1)})$ 10·0 Hz], 117·4 [complex m, 2F, $F^{5,6}$, $J(F^5CF_3^{(2)}) = J(F^6CF_3^{(2)})$ 11·0, $J_{5,7}$ or $J_{6,7}$ 43·0 Hz], 162·8 [dq, 1F, F^2, $J_{2,4} = J(F^2CF_3^{(1)})$ 10·0 Hz], and 212·5 [ddq, 1F, F^7, $J_{5,7}$ or $J_{6,7} = J(F^7H^6)$ 43·0, $J(F^7CF_3^{(2)})$ 11·0 Hz].

(e) *With tricarbonyl*(2-*ethylcyclohexa*-1,3-*diene*)*iron*. Similarly, a Carius tube containing a solution of tricarbonyl(2-ethylcyclohexa-1,3-diene)iron (0·50 g, 2·0 mmol) and C_3F_6 (0·60 g, 4·0 mmol) in hexane (12 ml) was irradiated for 5 days. Removal of volatile products *in vacuo*, followed by chromatography on alumina, and elution with methylene chloride–hexane (1 : 2) gave pale yellow *crystals* of (VII) (0·08 g, 9%), m.p. 116—119 °C (Found: C, 37·5; H, 2·2; F, 40·9. $C_{17}H_{12}F_{12}FeO_3$ requires C, 37·2; H, 2·2; F, 41·5%), ν_{CO} (hexane) 2086s, 2032s, and 2015ms cm^{-1}. The mass spectrum (base *m/e* 370) showed peaks at *m/e* 520 (*P* − CO, 12%), 492 (*P* − 2CO, 14%), 473 (*P* − 2CO − F, 5%), 464 (*P* − 3CO, 20%), 445 (*P* − 3CO − F, 2%), 370 (*P* − C_3F_6 − CO, 100%), and 351 (*P* − C_3F_6 − CO − F, 14%). The ^{1}H n.m.r. spectrum ([$^{2}H_6$]acetone) showed resonances at τ 4·50 [dm, 1H, H^6, $J(H_6F_7)$ 43·0 $J(H^6F^{5\text{ or }6})$ 18·0, $J(H^6CF_3^{(2)})$ 12·0 Hz], 4·87 (dd, 1H, H^3, $J_{3,4}$ 8·0, $J_{1,3}$ 2·0 Hz), 5·22 (m, 1H, H^1, $J_{1,3}$ 2·0 Hz), 6·44 (m, 1H, H^4, $J_{3,4}$ 8·0 Hz), 7·20—7·76 (complex m, 3H, $H^{5,7,8}$), 7·52 [q, 2H, CH_2Me, J(HH) 7·5 Hz], and 8·63 [t, 3H, CH_2Me, J(HH) 7·5 Hz]. The ^{19}F n.m.r. spectrum (acetone) showed resonances at 65·7 p.p.m. [ddd, 3F, $CF_3^{(1)}$, $J(CF_3^{(1)}F^3)$ 16·5, $J(CF_3^{(1)}F^2) = J(CF_3^{(1)}F^4)$ 9·5 Hz], 73·7 [dddd, 3F, $CF_3^{(2)}$, $J(CF_3^{(2)}\ F^6) = J(CF_3^{(2)}F^7) = J(CF_3^{(2)}H^6)$ 12·0, $J(CF_3^{(2)}F^5)$ 6·0 Hz], 94·3 [dm, 1F, F^4, $J_{3,4}$ 255, $J(F^4CF_3^{(1)})$ 9·5 Hz], 109·3 [dm, 1F, F^3, $J_{3,4}$ 255, $J(F^3CF_3^{(1)})$ 16·5 Hz], 113·7 [complex m, 2F, $F^{5,6}$, $J(F^6CF_3^{(2)})$ 12·0, $J(F^5CF_3^{(2)})$ 6·0, $J(F^{5\text{ or }6}H^6)$ 18·0 Hz], 186·0 [m, 1F, F^2, $J(F^2CF_3^{(1)})$ 9·5 Hz], and 209·5 [dm, 1F, F^7, $J(F^7CF_3^{(2)})$ 12·0, $J(F^7H^6)$ 43·0 Hz].

(f) *With tricarbonyl*(*cyclohexa*-1,3-*diene*)*ruthenium*. U.v. irradiation (60 h) of a solution of tricarbonyl(cyclohexa-1,3-diene)ruthenium (0·50 g, 1·9 mmol) and C_3F_6 (0·60 g, 4·0 mmol) in hexane (12 ml) gave white crystals. Recrystallisation (0 °C) from methylene chloride–hexane gave colourless *needles* of (VIII) (0·15 g, 20%), m.p. 129—131 °C (Found: C, 34·7; H, 1·8; F, 27·5. $C_{12}H_8F_6O_3Ru$ requires C, 34·8; H, 1·9; F, 27·5%), ν_{CO} (hexane) 2100s, 2044s, and 2029s cm^{-1}. The mass spectrum (base *m/e* 228) showed peaks at *m/e* 415 (*P*, 1%), 387 (*P* − CO, 16%), 368 (*P* − CO − F, 1%), 359 (*P* − 2CO, 11%), 340 (*P* − 2CO − F, 1%), 331 (*P* − 3CO, 27%), and 312 (*P* − 3CO − F, 3%). The ^{1}H n.m.r. spectrum (C_6F_6) showed resonances at τ 4·12 [ddd, 1H, H^2, $J_{1,2} = J_{2,3}$ 6·5, $J(H^2F^4)$ 4·5 Hz], 4·76 (ddd, 1H, H^3, $J_{2,3} = J_{3,4}$ 6·5, $J_{1,3}$ 2·0 Hz), 5·13 (m, 1H, H^1, $J_{1,2}$ 6·5, $J_{1,3}$ 2·0 Hz), 7·04 (m, 1H, H^4, $J_{3,4}$ 6·5 Hz), 7·49 (m, 2H, $H^{5,7}$), and 8·28 (m, 2H, $H^{6,8}$). The ^{19}F n.m.r. spectrum (acetone) showed resonances at 65·9 p.p.m. [ddd, 3F, CF_3, $J(CF_3F^3)$ 17·0, $J(CF_3F^2) = J(CF_3F^4)$ 9·5 Hz], 98·0 [dm, 1F, F^4, $J_{3,4}$ 239, $J(F^4CF_3)$ 9·5, $J(F^4H^2)$ 4·5 Hz], 113·1 [dq, 1F, F^3, $J_{3,4}$ 239, $J(F^3CF_3)$ 17·0 Hz], and 193·5 [m, 1F, F^2, $J(F^2CF_3)$ 9·5 Hz].

(g) *With* (*bicyclo*[4.2.0]*octa*-2,4-*diene*)*tricarbonyliron*. Similarly, u.v. irradiation (6 days) of a solution of (bicyclo[4.2.0]octa-2,4-diene)tricarbonyliron (0·75 g, 3·0 mmol) in hexane (12 ml) in the presence of C_3F_6 (0·90 g, 6·0 mmol) gave yellow *platelets* of (IX) (0·70 g, 58%), m.p. 139—142 °C (Found: C, 42·4; H, 2·6; F, 28·7. $C_{14}H_{10}F_6FeO_3$ requires C, 42·4; H, 2·5; F, 28·8%), ν_{CO} (hexane) 2083s, 2030s, and 2012s cm^{-1}. The mass spectrum (base *m/e* 312) showed peaks at *m/e* 396 (*P*, 2%), 368 (*P* − CO, 60%), 340 (*P* − 2CO, 10%), 321 (*P* − 2CO − F, 10%), and 312 (*P* − 3CO, 100%). The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 4·25 [ddd, 1H, H^2, $J_{1,2} = J_{2,3}$ 7·0, $J(H^2F^4)$ 4·0 Hz], 5·18 (dd, 1H, H^3, $J_{2,3} = J_{3,4}$ 7·0 Hz), 5·59 (d, 1H, H^1, $J_{1,2}$ 7·0 Hz), 7·09 [m, 1H, H^4, $J_{3,4}$ 7·0, $J(H^4F^3)$ 15·0 Hz], and 7·24—8·56 (complex m, 6H, H^{5-10}). The ^{19}F n.m.r. spectrum (acetone) showed resonances at 65·5 [d of d of d, 3F, CF_3,

J(CF$_3$F^3) 15·0, J(CF$_3$F^2) = J(CF$_3$F^4) 9·0 Hz], 98·5 [dm, 1F, F^4, $J_{3,4}$ 232, J(F^{4}CF$_3$) 9·0, J(F^{4}H^2) 4·0 Hz], 114·6 [dm, 1F, F^3, $J_{3,4}$ 232, J(F^{3}CF$_3$) = $J_{2,3}$ = J(F^{3}H^4) 15·0 Hz], and 186·3 [m, 1F, F^2, $J_{2,3}$ 15·0, J(F^{2}CF$_3$) 9·0 Hz].

(h) *With tricarbonyl*(*cyclo-octa*-1,3-*diene*)*iron*. Irradiation (50 h) of a solution of tricarbonyl(cyclo-octa-1,3-diene)iron (0·75 g, 3·0 mmol) and hexafluoropropene (0·72 g, 6·0 mmol) in hexane (12 ml) gave yellow *crystals* of (X) (0·60 g, 50%), m.p. 102—105 °C (Found: C, 41·7; H, 3·1; F, 28·8. C$_{14}$H$_{12}$F$_6$FeO$_3$ requires C, 42·2; H, 3·0; F, 28·6%), ν_{CO} (hexane) 2080s, 2026s, and 2011s cm^{-1}. The mass spectrum (base *m/e* 41) showed peaks at *m/e* 370 (*P* – CO, 1%), 342 (*P* – 2CO, 2%), and 314 (*P* – 3CO, 1%). The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 5·93 (m, 2H, H^{2,3}, $J_{1,2}$ 7·0 Hz), 6·56 (m, 1H, H^1, $J_{1,2}$ = $J_{1,11}$ = $J_{1,12}$ 7·0 Hz), 6·85—7·93 (m, 1H, H^4), and 8·10—9·14 (complex m, 8H, H$^{5-12}$, $J_{1,11}$ = $J_{1,12}$ 7·0 Hz). The ^{19}F n.m.r. spectrum (CHCl$_3$) showed resonances at 65·8 p.p.m. [ddd, 3F, CF$_3$, J(CF$_3$F^3) 15·0, J(CF$_3$F^2) = J(CF$_3$F^4) 10·0 Hz], 94·3 [dm, 1F, F^4, $J_{3,4}$ 234, J(F^{4}CF$_3$) 10·0 Hz], 105·0 [dm, 1F, F^3, $J_{3,4}$ 234, J(F^{3}CF$_3$) 15·0 Hz], and 187·8 [m, 1F, F^2, J(F^{2}CF$_3$) 10·0 Hz].

Thermolysis of Complex (X).—A Carius tube (100 ml) containing (X) (0·30 g, 0·86 mmol) and hexane (10 ml) was maintained at 80 °C for 6 h. Filtration of the solution and cooling (0 °C) of the filtrate gave colourless *needles* of (XI) (0·10 g, 31%), m.p. 98—100 °C (Found: C, 42·3; H, 2·9; F, 26·9. C$_{15}$H$_{12}$F$_6$FeO$_4$ requires C, 42·3; H, 2·8; F, 26·8%), ν_{CO} (hexane) 2129m, 2077ms, 2060s, and 2050ms cm^{-1}; $\nu_{C=C}$ (Nujol) 1622vw cm^{-1}. The mass spectrum (base *m/e* 314) showed peaks at *m/e* 426 (*P*, 10%), 398 (*P* – CO, 20%), 370 (*P* – 2CO, 30%), 351 (*P* – 2CO – F, 5%), 350 (*P* – 2CO – HF, 10%), 342 (*P* – 3CO, 80%), 323 (*P* – 3CO – F, 12%), 322 (*P* – 3CO – HF, 16%), 314 (*P* – 4CO, 100%), and 294 (*P* – 4CO – HF, 15%). The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 3·97—4·33 (m, 2H, H^{3,4}), 6·64 (m, 1H, H^2), 7·40—8·94 [complex m, 9H, H$^{1,5-12}$, J(H^{1}F^3) 37·0 Hz].

The Reaction of Complex (X) *with Trimethyl Phosphite*.—A solution of (X) (0·30 g, 0·75 mmol) and trimethyl phosphite (1·0 g, 8·1 mmol) in hexane (15 ml) was refluxed (4 h), during which time a deposit of highly coloured crystals was formed. Recrystallisation (0 °C) of the solid from methylene chloride–hexane gave colourless *crystals* of (XII) (0·18 g, 39%), m.p. 133—135 °C (Found: C, 36·9; H, 5·1; F, 18·3; P. 10·8. C$_{19}$H$_{30}$F$_6$P$_2$FeO$_8$ requires C, 36·9; H, 5·0; F, 18·4; P, 10·0%), ν_{CO} (hexane) 2037s and 1976s cm^{-1}. The mass spectrum (base 438) showed peaks at *m/e* 494 [*P* – P(OMe)$_3$, 30%], 466 [*P* – P(OMe)$_3$ – CO, 30%], 438 [*P* – P(OMe)$_3$ – 2CO, 100%], and 418 [*P* – P(OMe)$_3$ – 2CO – HF, 90%]. The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 4·06 (ddd, 1H, H^3, $J_{3,4}$ = $J_{2,3}$ 10·5, $J_{3,5}$ 6·0 Hz), 4·41 (ddd, 1H, H^4, $J_{3,4}$ 10·5, $J_{4,5}$ = $J_{4,6}$ 8·0 Hz), 6·13 [d, 9H, POMe, J(HP) 9·5 Hz], 6·26 [d, 9H, POMe, J(HP) 10·0 Hz], 6·88 (m, 1H, H^2, $J_{2,3}$ 10·5 Hz), 7·57 [m, 1H, H^1, J(H^{1}F^3) 41·0 Hz], and 7·94—8·88 (complex m, 8H, H$^{5-12}$, $J_{4,5}$ = $J_{4,6}$ 8·0, $J_{3,5}$ 6·0 Hz). The ^{19}F n.m.r. spectrum (acetone) showed resonances at 67·3 p.p.m. [m, 3F, CF$_3$, J(CF$_3$F^2) 7·0 Hz], 104·4 (dm, 1F, F^4, $J_{3,4}$ 224, $J_{2,4}$ 18·0 Hz), 117·1 [ddm, 1F, F^3, $J_{3,4}$ 224, J(F^{3}H^1) 41·0 Hz], and 159·5 [m, 1F, F^2, $J_{2,4}$ 18·0, J(F^{2}CF$_3$) 7·0 Hz].

Reaction of Chlorotrifluoroethylene with Tricarbonyl(2,3-*dimethylbuta*-1,3-*diene*)*iron*.—Ultraviolet irradiation of a solution of tricarbonyl(2,3-dimethylbuta-1,3-diene)iron (0·40 g, 1·8 mmol) and chlorotrifluoroethylene (0·50 g, 4·2 mmol) in hexane (15 ml) gave, after removal of volatile material *in vacuo* and recrystallisation (0 °C) of the residual oil from methylene chloride–hexane, pale yellow *crystals* of (XIII) (0·10 g, 17%), m.p. 98—100 °C (Found: C, 39·0; H, 2·8; F, 16·9. C$_{11}$H$_{10}$ClF$_3$FeO$_3$ requires C, 38·9; H, 3·0; F, 16·8%), ν_{CO} (hexane) 2083s, 2031s, and 2008s cm^{-1}. The mass spectrum (base *m/e* 198) showed peaks at *m/e* 339 (*P*, 2%), 319 (*P* – HF, 8%), 311 (*P* – CO, 13%), 291 (*P* – CO – HF, 10%), 283 (*P* – 2CO, 2%), 263 (*P* – 2CO – HF, 5%), 255 (*P* – 3CO, 10%), 235 (*P* – 3CO – HF, 12%), and 198 (*P* – 3CO – HF – HCl, 100%). The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 6·78 (d, 1H, H^2, $J_{1,2}$ 3·0 Hz), 7·49 [dd, 1H, H^1, $J_{1,2}$ 3·0, J(H^{1}F^2) 5·0 Hz], 7·64 [ddd, 1H, H^5, $J_{5,6}$ 14·0, J(H^{5}F^3) 15·0, J(H^{5}F^4) 1·0 Hz], 7·93 (s, 3H, Me), 7·98 (s, 3H, Me), and 8·25 [dddd, 1H, H^6, $J_{5,6}$ 14·0, J(H^{6}F^3) 35·0, J(H^{6}F^4) = J(H^{6}F^2) 4·0 Hz]. The ^{19}F n.m.r. spectrum (CHCl$_3$) showed resonances at 104·2 p.p.m. [m, 1F, F^2, $J_{2,3}$ 11·0, $J_{2,4}$ 20·0, J(F^{2}H^1) 5·0, J(F^{2}H^6) 4·0 Hz], 104·4 [dm, 1F, F^4, $J_{3,4}$ 224, $J_{2,4}$ 10·0, J(F^{4}H^6) 4·0, J(F^{4}H^5) 1·0 Hz], and 108·8 [dddd, 1F, F^3, $J_{3,4}$ 224, $J_{2,3}$ 11·0, J(F^{3}H^6) 35·0, J(F^{3}H^5) 15·0 Hz].

Reactions of Trifluoroethylene.—(*a*) *With tricarbonyl*(*cyclohexa*-1,3-*diene*)*iron*. Similarly, irradiation (80 h) of a solution of tricarbonyl(cyclohexa-1,3-diene)iron (0·40 g, 1·8 mmol) and C$_2$F$_3$H (0·50 g, 6·1 mmol) in hexane (12 ml) afforded large crystals. Recrystallisation (0 °C) from methylene chloride–hexane gave pale yellow *crystals* of (XIV) (0·18 g, 33%), m.p. 94—96 °C (Found: C, 43·9; H, 3·0; F, 18·8. C$_{11}$H$_9$F$_3$FeO$_3$ requires C, 43·7; H, 3·0; F, 18·9%), ν_{CO} (hexane) 2080s, 2024s, and 2007s cm^{-1}. The mass spectrum (base *m/e* 218) showed peaks at *m/e* 302 (*P*, 20%), 282 (*P* – HF, 1%), 274 (*P* – CO, 50%), 254 (*P* – CO – HF, 4%), 246 (*P* – 2CO, 60%), 226 (*P* – 2CO – HF, 5%), and 218 (*P* – 3CO, 100%). The ^{1}H n.m.r. spectrum (CFCl$_3$) showed resonances at τ 4·40 (ddd, 1H, H^3, $J_{3,4}$ 7·5, $J_{2,3}$ 6·5, $J_{1,3}$ 2·0 Hz), 5·49 (dd, 1H, H^2, $J_{1,3}$ = $J_{2,3}$ 6·5 Hz), 5·48 (dddd, 1H, H^1, $J_{1,2}$ 6·5, $J_{1,7}$ = $J_{1,8}$ 3·0, $J_{1,3}$ 2·0 Hz), 7·40 [dddd, 1H, H^4, $J_{3,4}$ = $J_{4,5}$ = $J_{4,6}$ 7·5, J(H^{4}F^3) 16·0 Hz], 7·77 (m, 2H, H^{5,7}, $J_{4,5}$ 7·5, $J_{1,7}$ 3·0 Hz), and 8·71 [m, 2H, H^{6,8}, $J_{4,6}$ = J(H^{8}F^2) 7·5, $J_{1,8}$ 3·0 Hz]. The ^{19}F n.m.r. spectrum (CHCl$_3$) showed resonances at 44·9 p.p.m. [dddd, 1F, F^2, $J_{1,2}$ 252, $J_{2,3}$ 17·0, J(F^{2}H^8) 7·5, J(F^{2}H^9) 3·0 Hz], 87·3 [ddd, 1F, F^1, $J_{1,2}$ 252, $J_{1,3}$ 15·0, J(F^{1}H^9) 12·0 Hz], and 177·8 [dddd, 1F, F^3, $J_{2,3}$ 17·0, $J_{1,3}$ 15·0, J(F^{3}H^9) 52·0, J(F^{3}H^4) 16·0 Hz].

(b) *With* (*bicyclo*[4.2.0]*octa*-2,4-*diene*)*tricarbonyliron*. By the same procedure irradiation (70 h) of a solution of (bicyclo[4.2.0]octa-2,4-diene)tricarbonyliron (0·75 g, 3·0 mmol) and C$_2$F$_6$H (0·50 g, 6·1 mmol) in hexane (15 ml) afforded yellow *needles* of (XV) (0·65 g, 66%), m.p. 110—113 °C (Found: C, 47·6; H, 3·4; F, 17·0. C$_{13}$H$_{11}$F$_3$FeO$_3$ requires C, 47·6; H, 3·4; F, 17·4%), ν_{CO} (hexane) 2080s, 2026s, and 2008s cm^{-1}. The mass spectrum (base *m/e* 1%) showed peaks at *m/e* 328 (*P*, 7%), 300 (*P* – CO, 33%), 272 (*P* – 2CO, 3%), 244 (*P* – 3CO, 35%), 218 (*P* – C$_2$F$_3$H – CO, 95%), 190 (*P* – C$_2$F$_3$H – 2CO, 100%), and 162 (*P* – C$_2$F$_3$H – 3CO, 17%). The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 4·39 (dd, 1H, H^2, $J_{1,2}$ = $J_{2,3}$ 7·0 Hz), 4·54 (dd, 1H, H^3, $J_{2,3}$ = $J_{3,4}$ 7·0 Hz), 5·55 [ddd, 1H, H^{11}, J(H^{11}F^3) 54·0, J(H^{11}F^1) 12·5, J(H^{11}F^2) 3·5 Hz], 5·73 (d, 1H, H^1, $J_{1,2}$ 7·0 Hz), 7·17 [m, 1H, H^4, $J_{3,4}$ 7·0, J(H^{4}F^3) 18·0 Hz], and 7·60—8·54 [complex m, 6H, H$^{5-10}$, J(H^{10}F^2) 7·5 Hz]. The ^{19}F n.m.r. spectrum (acetone) showed resonances at 44·6 p.p.m. [dddd, 1F, F^2, $J_{1,2}$ 250, $J_{2,3}$ 18·0, J(F^{2}H^{10}) 7·5, J(F^{2}H^{11}) 3·5 Hz], 80·1 [ddd, 1F, F^1, $J_{1,2}$ 250, $J_{1,3}$ = J(F^{1}H^{11})

12·5 Hz], and 176·7 [dddd, 1F, F^3, $J_{2,3} = J(F^3H^4)$ 18·0, $J_{1,3}$ 12·5, $J(F^3H^{11})$ 54·0 Hz].

Reaction of Complex (XV) *with Trimethyl Phosphite.*—A solution of (XV) (0·21 g, 0·64 mmol) and trimethyl phosphite (0·50 g, 4·0 mmol) in hexane (15 ml) was refluxed (½ h). Volatile material was removed *in vacuo* and the residue recrystallised (−78 °C) from hexane to give pale yellow *crystals* of (XVI) (0·135 g, 50%), m.p. 99—101 °C (Found: C, 43·0; H, 4·8; F, 12·9; P, 7·3. $C_{15}H_{20}F_3FeO_5P$ requires C, 42·5; H, 4·7; F, 13·4; P, 7·3%), ν_{CO} (hexane) 2027s and 1975s cm^{-1}. The mass spectrum (base *m/e* 396) showed peaks at *m/e* 424 (*P*, 40%), 396 (*P* − CO, 100%), and 368 (*P* − 2CO, 50%). The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 4·68 [ddd, 1H, H^2, $J_{1,2} = J_{2,3}$ 6·5, $J(H^2P)$ 15·5 Hz], 5·07 (dd, 1H, H^3, $J_{2,3} = J_{3,4}$ 6·5 Hz), 5·60 [dm, 1H, H^{11}, $J(H^{11}F^3)$ 54·0, $J(H^{11}F^1)$ 11·5 Hz], 6·18 (m, 1H, H^1, $J_{1,2}$ 6·5 Hz), 6·40 [d, 9H, POMe, J(HP) 11·0 Hz], 7·28 [m, 1H, H^4, $J_{3,4}$ 6·5, $J(H^4F^3)$ 13·5 Hz], and 7·60—8·77 (complex m, 6H, H^{5-10}). The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at 48·8 p.p.m. (dm, 1F, F^2, $J_{1,2}$ 252, $J_{2,3}$ 17·0 Hz), 81·7 [dm, 1F, F^1, $J_{1,2}$ 252, $J_{1,3}$ 17·0, $J(F^1H^{11})$ 11·5 Hz], 177·3 [dddd, 1F, F^3, $J_{1,3} = J_{2,3}$ 17·0, $J(F^3H^{11})$ 54·0, $J(F^3H^4)$ 13·5 Hz].

Reactions of Tricarbonyl(o-*styryldiphenylphosphine*)*iron.*—(a) *With hexafluoropropene.* Irradiation (1 day) of a solution of [(sp)Fe$(CO)_3$] (0·70 g, 1·63 mmol) and hexafluoropropene (0·50 g, 3·3 mmol) in hexane (12 ml) gave cream coloured crystals. Recrystallisation from methylene chloride–hexane gave *crystals* of (XVII) (0·70 g, 74%), m.p. 182—184 °C (Found: C, 53·7; H, 2·8; F, 19·5; P, 5·6. $C_{26}H_{17}F_6FeO_3P$ requires C, 53·9; H, 2·9; F, 19·7; P, 5·4%), ν_{CO} (hexane) 2088w, 2028s, and 2014s cm^{-1}. The mass spectrum (base *m/e* 400) showed peaks at *m/e* 578 (*P*, 1%), 559 (*P* − F, 0·5%), 550 (*P* − CO, 9%), 522 (*P* − 2CO, 8%), 503 (*P* − 2CO − F, 1%), 494 (*P* − 3CO, 88%), 475 (*P* − 3CO − F, 1%), and 474 (*P* − 3CO − HF, 1%). The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·23—3·07 (complex m, 14H, C_6H_5), 6·21 [dd, 1H, H^3, $J_{2,3}$ 10·0, $J(H^3F^3)$ 7·5 Hz], 6·92 (d, 1H, H^1, $J_{1,2}$ 9·0 Hz), and 7·21 [m, 1H, H^2, $J_{2,3}$ 10·0, $J_{1,2}$ 9·0, $J(H^2F^3)$ 36·0 Hz]. The ^{19}F n.m.r. spectrum (acetone) showed resonances at 66·7 p.p.m. [dddd, 3F, CF_3, $J(CF_3F^1) = J(CF_3F^3) = J(CF_3F^4)$ 11·0, J(PF) 2·0 Hz], 108·3 [ddq, 1F, F^4, $J_{3,4}$ 236, $J_{1,4} = J(F^4CF_3)$ 11·0 Hz], 119·1 [dm, 1F, F^3, $J_{3,4}$ 236, $J_{1,3}$ 13·0, $J(F^3CF_3)$ 11·0, $J(F^3H^2)$ 36·0, $J(F^3H^3)$ 7·5 Hz], and 162·3 [m, 1F, F^1, $J_{1,3}$ 13·0, $J_{1,4} = J(F^1CF_3) = J$(PF) 11·0 Hz].

(b) *With trifluoroethylene.* Similarly, [(sp)Fe$(CO)_3$] (0·50 g, 1·17 mmol) and trifluoroethylene (0·40 g, 4·9 mmol) gave white *prisms* of (XVIII) (0·39 g, 66%), m.p. 182—194 °C (Found: C, 59·1; H, 3·34; F, 11·6; P, 6·1. $C_{25}H_{18}F_3FeO_3P$ requires C, 58·8; H, 3·5; F, 11·2; P, 6·1%), ν_{CO} (hexane) 2080w, 2015s, and 1996s cm^{-1}. The mass spectrum (base *m/e* 331) showed peaks at *m/e* 510 (*P*, 2%), 482 (*P* − CO, 3%), 462 (*P* − CO − HF, 3%), 454 (*P* − 2CO, 4%), 434 (*P* − 2CO − HF, 15%), 426 (*P* − 3CO, 70%), 407 (*P* − 3CO − F, 5%), and 406 (*P* − 3CO − HF, 15%). The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·3—3·1 (complex m, 14H, C_6H_5), 3·70 [ddd, 1H, H^4, $J(H^4F^1)$ 50·0, $J(H^4F^3)$ 22·0, $J(H^4F^4)$ 13·5 Hz], 6·17 (dd, 1H, H^1, $J_{1,2}$ 13·5, $J_{1,3}$ 5·5 Hz), 7·10 [m, 1H, H^3, $J_{2,3} = J(H^3F^4)$ 13·5, $J_{1,3}$ 5·5, $J(H^3F^3)$ 13·0 Hz], and 7·82 [ddd, 1H, H^2, $J_{1,2} = J_{2,3}$ 13·5, $J(H^2F^3)$ 35·0 Hz]. The ^{19}F n.m.r. spectrum (acetone) showed resonances at 55·2 p.p.m. [m, 1F, F^1, $J_{1,3}$ 13·0, $J_{1,4}$ 6·0, $J(F^1H^4)$ 50·0 Hz], 94·2 [d of m, 1F, F^4, $J_{3,4}$ 219, $J_{1,4}$ 6·0, $J(F^4H^3) = J(F^4H^4)$ 13·5 Hz], and 115·3 [ddddd, 1F, F^3, $J_{3,4}$ 219, $J_{1,3} = J(F^3H^3)$ 13·0, $J(F^3H^2)$ 35·0, $J(F^3H^4)$ 22·0 Hz].

(c) *With chlorotrifluoroethylene.* In a similar way, reaction of [(sp)Fe$(CO)_3$] (0·50 g, 1·17 mmol) and chlorotrifluoroethylene (0·50 g, 4·3 mmol) afforded yellow *crystals* of (XIX) (0·15 g, 24%), m.p. 177—181 °C (Found: C, 54·4; H, 3·0; F, 10·5; P, 5·8. $C_{25}H_{17}F_3O_3ClPFe$ requires C, 55·0; H, 3·1; F, 10·5; P, 4·7%), ν_{CO} (hexane) 2088w, 2025s, and 2014s cm^{-1}. The mass spectrum (base *m/e* 460) showed peaks at *m/e* 545 (*P*, 1%), 5·7 (*P* − CO, 1%), 489 (*P* − 2CO, 12%), and 461 (*P* − 3CO, 17%). The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·3—3·1 (complex m, 14H, C_6H_5), 6·08 (dd, 1H, H^1, $J_{1,2}$ 12·5, $J_{1,3}$ 5·5 Hz), 6·99 [m, 1H, H^3, $J_{2,3} = J(H^3F^3)$ 12·5, $J_{1,3}$ 5·5 Hz], and 7·25 [ddddd, 1H, H^2, $J_{1,2} = J_{2,3}$ 12·5, $J(H^2F^3)$ 35·0, $J(H^2F^1) = J(H^2F^4)$ 3·5 Hz]. The ^{19}F n.m.r. spectrum (acetone) showed resonances at 79·7 p.p.m. [m, 1F, F^1, $J_{1,3}$ 12·5, $J(F^1H^2)$ 3·5 Hz], 106·2 [dddd, 1F, F^3, $J_{3,4}$ 225, $J_{1,3} = J(F^3H^3)$ 12·5, $J(F^3H^2)$ 35·0 Hz], and 115·9 [dm, 1F, F^4, $J_{3,4}$ 225, $J(F^4H^2)$ 3·5 Hz].

Crystal Data.—$C_{11}H_8F_6FeO_3$, $M = 358{\cdot}0$, yellow orthorhombic crystals, $a = 23{\cdot}020(12)$, $b = 8{\cdot}497(5)$, $c = 6{\cdot}546(4)$ Å, $U = 1280{\cdot}4$ Å^3, $D_c = 1857$ kg m^{-1}, $Z = 4$. Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å; $\mu(\text{Mo-}K_\alpha) = 1299$ m^{-1}. Space group $P2_12_12_1$ from systematic absences.

Unit-cell dimensions were obtained from zero-layer precession photographs by a least-squares procedure and the standard deviations quoted above are estimates to allow for systematic errors. The intensities were measured round (*b*) on a linear diffractometer equipped with a graphite monochromator; the 1245 strongest measured reflections were used in the analysis. The diffracted intensities decreased steadily with time and the change was compensated for by an appropriate alteration of the overall scale factor.

Structure Determination and Refinement.—The position of the heavy iron atom was found close to (0·153, *b*/4,0) from a three-dimensional Patterson function whose further interpretation was difficult. Therefore a three-dimensional Fourier, based on the phases from the iron atom, was calculated. This map had two false mirror planes arising from the ' special ' position of the iron atom but a reasonable trial structure was eventually obtained and successfully refined with isotropic and then anisotropic temperature factors in a least squares block-diagonal (3 × 3, and 1 × 1 or 6 × 6) process. Hydrogen-atom positions were found from a difference map and refinement continued till $R\ (= \Sigma|\Delta|/\Sigma|F_o|)$ was 0·036. Hydrogen atoms attached to C(6), C(7), C(9), and C(10) were given temperature factors of $U_{iso} = 0{\cdot}06$, 0·05, 0·06, and 0·07, respectively.

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