Reactions of Co-ordinated Ligands. Part 16.[1] The Oxidative–Addition of Hexafluorobut-2-yne and 3,3,3-Trifluoroprop-1-yne to Tricarbonyl(1,3-diene)-iron and -ruthenium and Tricarbonyl(diphenyl-*o*-styrylphosphine)-iron Complexes: Crystal and Molecular Structure of $[Ru(CO)_2\{P(OCH_2)_3CMe\}(C_6H_8)(C_4F_6)_2]$

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Hexafluorobut-2-yne (hfb) reacts (u.v.) with buta-1,3-diene(tricarbonyl)iron, tricarbonyl(2,3-dimethylbuta-1,3-diene)iron, or tricarbonyl(diphenyl-*o*-styrylphosphine)iron to form Fe^{II} 1 : 1 adducts in which the acetylene links the iron and dienes as in, for example, $CH_2{\cdots}CH{\cdots}CH{\cdot}CH_2{\cdot}C(CF_3){=}C(CF_3)Fe(CO)_3$. Similar reactions with 3,3,3-trifluoroprop-1-yne gave the corresponding adducts, in which the arrangement $FeC(CF_3){=}CH–$ is present. In contrast tricarbonyl(cyclohexa-1,3-diene)ruthenium forms on irradiation with hfb a 1 : 2 adduct. Replacement of co-ordinated CO in the adduct by $P(OCH_2)_3CMe$ gave crystals of (9) $[Ru(CO)_2\{P(OCH_2)_3CMe\}(C_6H_8)(C_4F_6)_2]$ suitable for *X*-ray crystallography. Crystals of (9) are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions: $a = 8.875(5)$, $b = 17.841(9)$, $c = 16.517(5)$ Å, $\beta = 94.51(3)°$. The *X*-ray diffraction study (*R* 0.078, 2 418 observed intensities, measured by diffractometer) shows that formal insertion of a hfb molecule has occurred between the Ru atom and each carbon atom of one of the original olefinic bonds of the cyclohexadiene system. A new seven-membered ruthenacyclohepta-1,5-diene ring is generated. The co-ordination state of the Ru atom is close to octahedral, the ring system occupying three facial sites.

Reaction of $CH_2{\cdots}C(Me){\cdots}C(Me)CH_2C(CF_3){=}C(CF_3)Fe(CO)_3$ with carbon monoxide affords an acyl species; however, with heat in the absence of CO an interesting reductive–elimination reaction occurs with formation of a substituted tricarbonyl(cyclohexa-1,3-diene)iron complex. A similar ring closure reaction occurs with the adduct from $[Fe(1,3\text{-}C_4H_6)(CO)_3]$ and hfb.

IN continuing our study of the reactions of hexafluorobut-2-yne (hfb) with iron(0),[2] ruthenium(0),[3] and osmium(0) [3] complexes we have observed that reaction of hfb with complexes of the type $[M(CO)_3(1,3\text{-diene})]$ (M = Fe and Ru) leads to an interesting oxidative reaction, in which the acetylene links the metal to the C_4-skeleton of the original 1,3-diene. Some aspects of this work have been reported [4] in a preliminary communication, and in this paper are described details of the investigation, an extension to the corresponding reactions with 3,3,3-trifluoroprop-1-yne, and a study of the carbonylation and thermal isomerisation of the 1 : 1 adducts.

Hexafluorobut-2-yne reacts on u.v. irradiation with tricarbonyl(isoprene)iron and tricarbonyl(*cis*- or *trans*-penta-1,3-diene)iron to afford moderate yields of the known [5] tricarbonyl[tetrakis(trifluoromethyl)cyclopentadienone]iron complex. However, irradiation of a hexane solution of hfb and buta-1,3-diene(tricarbonyl)iron, tricarbonyl(2,3-dimethylbuta-1,3-diene)iron, or tricarbonyl(diphenyl-*o*-styrylphosphine)iron [6] afforded the yellow crystalline 1 : 1 adducts (1), (2), and (3). Both the mass- and i.r.-spectra confirmed the presence in these adducts of an iron tricarbonyl group, and in addition to the terminal carbonyl bands a band in the 1 630 cm^{-1} region was observed, which may be assigned to the arrangement $FeC(CF_3){=}C(CF_3)$. In the case of the first two adducts the ^1H n.m.r. spectrum showed resonances and coupling constants characteristic of an η^3-allyl system. For example, the spectrum of (1) is fully consistent with the illustrated structure; a doublet of doublets centred at τ 7.12 is assigned to the inner (*anti*) terminal proton H^1, the outer (*syn*) terminal allyl proton H^2 appearing as a doublet of doublets centred at τ 5.98. The central allylic proton H^3 appeared as a doublet of doublets of doublets at τ 5.14, and the remaining allylic proton H^4 occurred as a multiplet centred at τ 5.34. Double irradiation of H^1 or H^2 collapsed the resonance assigned to H^3 into a triplet and a doublets of doublets respectively. Irradiation of H^3 collapsed H^1 and H^2 into singlets. The methylene protons H^5 and H^6 appeared as a multiplet centred at τ 6.88, and ^1H-$\{^1H\}$ and ^1H-$\{^{19}F\}$ decoupling experiments demonstrated the presence of coupling to both H^4 and a trifluoromethyl group. The ^1H spectrum of (2) showed the expected features, the H^5 and H^6 protons appearing as a quartet arising from a similar ^1H–^{19}F coupling.

The ^{19}F spectrum of both (1) and (2) confirmed these structural features, and showed two resonances of equal intensity, the low-field resonance appearing as a triplet of quartets arising from ^1H–^{19}F coupling to the equivalent † protons H^5 and H^6, and ^{19}F–^{19}F coupling. The low-field resonance, which shows $^4J_{HF}$ coupling, is

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† Examination of molecular models shows that both H^5 and H^6 form identical dihedral angles with the α-CF_3 group.

[1] Part 15, M. Green, S. M. Heathcock, D. M. P. Mingos, and T. W. Turney, *J.C.S. Dalton*, 1977, 204.

[2] R. Burt, M. Cooke, and M. Green, *J. Chem. Soc.* (*A*), 1970, 2981.

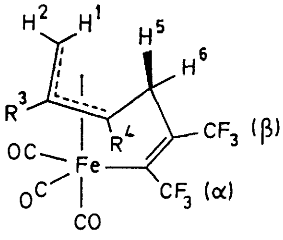
[3] M. Cooke, M. Green, and T. A. Kuc, *J. Chem. Soc.* (*A*), 1971, 1200.

[4] M. Bottrill, M. Green, R. Goddard, R. P. Hughes, and P. Woodward, *J.C.S. Chem. Comm.*, 1975, 253.

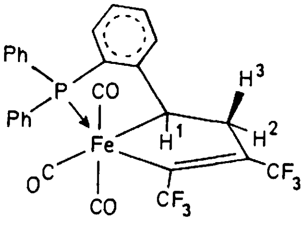
[5] J. L. Boston, D. W. A. Sharp, and G. Wilkinson, *J. Chem. Soc.*, 1962, 3488; R. S. Dickson and D. B. W. Yawney, *Austral. J. Chem.*, 1967, **20**, 77; *Inorg. Nuclear Chem. Letters*, 1967, **3**, 209.

[6] M. A. Bennett, R. S. Nyholm, and J. D. Saxby, *J. Organometallic Chem.*, 1966, **10**, 301; M. A. Bennett, G. B. Robertson, I. B. Tomkins, and P. O. Whimp, *Chem. Comm.*, 1971, 341.

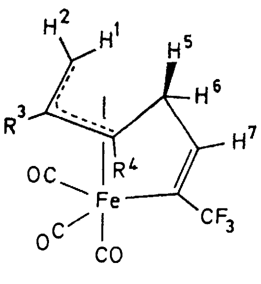
assigned to the α-CF_3 adjacent to the iron atom. The adduct (3) formed in high yield from hexafluorobut-2-yne and tricarbonyl(diphenyl-*o*-styrylphosphine)iron showed the expected features in the ^1H n.m.r. spectrum. It is interesting that H^3 and H^2 exhibit unequal $^4J_{HF}$ coupling to the α-CF_3. The ^{19}F spectrum, which showed two resonances, confirmed these couplings, and in addition a ^{31}P–^{19}F coupling between the ^{31}P nucleus of the diphenylphosphino-ligand and the α-CF_3 was observed, providing confirmation of the assignment of the ^{19}F chemical shifts.



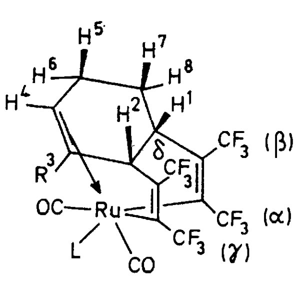
(1) $R^3 = R^4 = H$
(2) $R^3 = R^4 = Me$



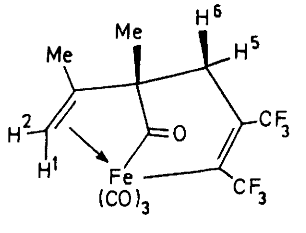
(3)



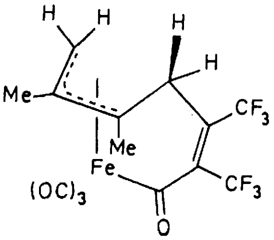
(4) $R^3 = R^4 = H$
(5) $R^3 = R^4 = Me$
(6a) $R^3 = Me$, $R^4 = H$
(6b) $R^3 = H$, $R^4 = Me$



(7) L = CO, $R^3 = H$
(8) L = CO, $R^3 = Me$
(9) L = $P(OCH_2)_3CMe$, $R^3 = H$



(10a)



(10b)

Thus, the reaction of hfb with co-ordinated 1,3-dienes involves an oxidative coupling reaction, in which the acetylene links the metal and C_4-skeleton of the diene, the metal being stabilised by co-ordination onto an η^3-allyl system. In order to obtain insight into the nature of the reaction path (paths) followed in the formation of these adducts the corresponding reactions with the unsymmetrical acetylene 3,3,3-trifluoroprop-1-yne (tfp) were examined. U.v. irradiation of hexane solutions of tfp and buta-1,3-diene(tricarbonyl)iron, tricarbonyl(2,3-dimethylbuta-1,3-diene)iron, or tricarbonyl(isoprene)iron gave the yellow crystalline 1 : 1 adducts (4), (5), and (6), which showed the expected features in their mass- and i.r.-spectra.

Examination of the ^1H and ^{19}F spectra confirmed that a parallel reaction had occurred, and that these adducts were Fe^{II} η^3-allyl complexes as illustrated. In the case of the reaction of co-ordinated isoprene two isomeric complexes (6a) and (6b) were formed differing only in the position of attachment of the tfp. The major isomer [(6a) : (6b), 2.5 : 1] was that arising from formal attack on the unsubstituted olefinic bond, the methyl group occupying the central allylic position.

Clearly the structural feature of principal importance in these three complexes is the relative orientation of the trifluoromethyl group.

The ^{19}F spectrum of, for example, (5) showed a single resonance, a doublet of triplets centred at 59.7 p.p.m. arising from coupling with the olefinic proton H^7 and the equivalent protons H^5 and H^6. The latter coupling (4.0 Hz) is similar to that observed between H^5 and H^6, and the α-CF_3 in the hfb adducts, suggesting that in the complexes formed with tfp the trifluoromethyl group is adjacent to the iron. Additional support for this assignment is that the proton H^7 exhibits a chemical shift (τ 3.65) typical of an olefinic resonance; a vinylic hydrogen adjacent to a metal would be expected to have a shift at lower field. Also, in the ^{31}C n.m.r. spectrum the C^1 carbon, which appeared as a quartet [$J(^{13}C$–$^{19}F) = 10$ Hz], exhibits a ^{13}C chemical shift (−145.5 p.p.m.) typical of an olefinic carbon not bonded directly to a metal. Finally, the ^1H–^1H coupling (4.0 Hz) between H^5/H^6 and H^7 is too great to be assigned to a $^3J_{HH}$ allylic coupling, which is normally close to zero.

An extension of the study with hexafluorobut-2-yne to the reactions with co-ordinated cyclic 1,3-dienes resulted in the observation of a different, but related type of reaction. U.v. irradiation of a solution of hfb (excess) and tricarbonyl(cyclohexa-1,3-diene)ruthenium or tricarbonyl(2-methylcyclohexa-1,3-diene)ruthenium gave respectively the colourless crystalline complexes (7) and (8). Elemental analyses and mass-spectroscopy showed that the complexes were adducts formed from the 1,3-diene complex and two molecules of hexafluorobut-2-yne. Although examination of the ^1H n.m.r. spectrum revealed the presence in both complexes of a co-ordinated olefin, and the ^{19}F spectrum showed in each case four resonances with different couplings between two pairs, there were insufficient data to define the structures of these complexes. Accordingly a single-crystal *X*-ray diffraction study on the complex (9), obtained on reaction of (7) with the ligand 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, was undertaken. Comparison of n.m.r. data showed that replacement of a terminal bonded carbon monoxide in (7) by $P(OCH_2)_3CMe$ did not cause structural changes.

The results of this study are illustrated in Figure 1, which also shows the crystallographic numbering system. Structural parameters are in Tables 1 and 2, and the contents of one unit cell are illustrated in Figure 2. It is at once apparent that the two hexafluorobut-2-yne molecules have each been inserted between the ruthenium atom and one of the carbon atoms, C(03) and C(04), which formed an olefinic bond in the original cyclohexa-1,3-diene system. The other

TABLE 1

Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Ru	0.101 35(14)	0.185 03(7)	0.506 23(7)
Phosphite group			
P	0.261 1(5)	0.113 9(2)	0.593 0(2)
O(1)	0.398 4(13)	0.153 6(6)	0.639 9(7)
O(2)	0.336 5(14)	0.045 2(6)	0.554 2(6)
O(3)	0.176 7(13)	0.077 2(7)	0.663 2(7)
C(1)	0.486 8(21)	0.106 9(12)	0.698 9(12)
C(2)	0.434 6(24)	−0.005 5(11)	0.612 0(11)
C(3)	0.268 7(24)	0.030 3(11)	0.717 9(10)
C(4)	0.432 3(19)	0.027 4(9)	0.697 9(9)
C(5)	0.523 9(25)	−0.023 6(10)	0.755 6(11)
H(11)	0.595	0.107	0.683
H(12)	0.487	0.129	0.753
H(21)	0.531	0.053	0.610
H(22)	0.383	−0.003	0.595
H(31)	0.267	−0.019	0.719
H(32)	0.227	−0.019	0.719
H(51)	0.562	0.003	0.805
H(52)	0.489	−0.068	0.756
H(53)	0.522	0.009	0.709
Carbonyl groups			
C(6)	−0.068 4(21)	0.121 6(10)	0.527 7(9)
O(6)	−0.167 4(16)	0.086 9(8)	0.540 3(8)
C(7)	0.146 6(19)	0.120 4(8)	0.421 1(9)
O(7)	0.165 6(17)	0.080 0(9)	0.371 3(7)
C_6 ring			
C(01)	−0.024 1(20)	0.246 9(10)	0.617 6(10)
C(02)	0.118 4(19)	0.273 3(8)	0.610 0(9)
C(03)	0.143 9(16)	0.345 7(9)	0.564 4(9)
C(04)	−0.005 6(18)	0.371 9(10)	0.515 5(10)
C(05)	−0.135 8(18)	0.366 1(10)	0.572 4(10)
C(06)	−0.165 7(18)	0.286 9(10)	0.593 9(9)
H(01)	−0.124	0.231	0.247
H(02)	0.208	0.247	0.635
H(03)	0.150	0.387	0.604
H(04)	0.005	0.414	0.496
H(051)	−0.223	0.393	0.622
H(052)	−0.107	0.388	0.543
H(061)	−0.249	0.255	0.551
H(062)	−0.229	0.276	0.646
Hexafluorobutyne ligands			
C(31)	0.267 9(16)	0.327 4(12)	0.509 7(10)
C(32)	0.265 8(19)	0.250 3(12)	0.487 4(9)
C(33)	0.360 4(17)	0.396 7(10)	0.495 3(11)
F(331)	0.402 4(14)	0.405 1(7)	0.419 4(7)
F(332)	0.489 8(12)	0.403 0(7)	0.541 7(7)
F(333)	0.289 3(13)	0.461 6(6)	0.506 5(10)
C(34)	0.399 5(19)	0.238 1(10)	0.431 1(11)
F(341)	0.533 4(12)	0.273 9(8)	0.443 7(8)
F(342)	0.363 7(14)	0.247 3(8)	0.350 7(6)
F(343)	0.442 7(14)	0.168 1(7)	0.437 0(8)
C(41)	−0.044 0(16)	0.333 1(8)	0.435 0(8)
C(42)	−0.036 2(16)	0.259 2(9)	0.425 4(9)
C(43)	−0.101 0(19)	0.389 1(10)	0.369 2(10)
F(431)	−0.249 1(12)	0.400 9(7)	0.370 6(7)
F(432)	−0.039 4(16)	0.455 7(6)	0.379 4(7)
F(433)	−0.078 0(13)	0.368 9(6)	0.295 7(6)
C(44)	−0.106 5(19)	0.221 1(10)	0.349 7(10)
F(441)	−0.229 9(12)	0.254 7(7)	0.314 4(6)
F(442)	−0.011 8(12)	0.212 7(6)	0.291 6(5)
F(443)	−0.157 0(13)	0.151 2(6)	0.365 2(6)

TABLE 2

Bond lengths (Å) and angles (°)

(*a*) Distances			
(i) Phosphite group			
Ru–P	2.314 (4)	C(1)–C(4)	1.50(3)
P–O(1)	1.562 (12)	C(2)–C(4)	1.54(2)
P–O(2)	1.558 (12)	C(3)–C(4)	1.51(3)
P–O(3)	1.572 (13)	C(4)–C(5)	1.51(2)
O(1)–C(1)	1.46(2)		
O(2)–C(2)	1.54(2)		
O(3)–C(3)	1.44(2)		
(ii) Carbonyl groups			
Ru–C(6)	1.939 (19)	Ru–C(7)	1.886 (15)
C(6)–O(6)	1.11(2)	C(7)–O(7)	1.12(2)
(iii) C_6 ring			
Ru–C(01)	2.483 (18)	C(04)–C(05)	1.53(2)
Ru–C(02)	2.324 (15)	C(05)–C(06)	1.50(3)
C(01)–C(02)	1.37(2)	C(06)–C(01)	1.47(2)
C(02)–C(03)	1.52(2)	C(04)–C(41)	1.51(2)
C(03)–C(04)	1.57(2)	C(03)–C(31)	1.51(2)
(iv) Hexafluorobutyne ligands			
Ru–C(32)	1.912 (19)	Ru–C(42)	2.184 (15)
C(31)–C(32)	1.42(3)	C(41)–C(42)	1.33(2)
C(31)–C(33)	1.51(3)	C(41)–C(43)	1.53(2)
C(33)–F(331)	1.34(2)	C(43)–F(431)	1.33(2)
C(33)–F(332)	1.33(2)	C(43)–F(432)	1.31(2)
C(33)–F(333)	1.34(2)	C(43)–F(433)	1.30(2)
C(32)–C(34)	1.58(2)	C(42)–C(44)	1.51(2)
C(34)–F(341)	1.35(2)	C(44)–F(441)	1.34(2)
C(34)–F(342)	1.35(2)	C(44)–F(442)	1.36(2)
C(34)–F(343)	1.31(2)	C(44)–F(443)	1.33(2)
(*b*) Angles			
(i) Phosphite group			
Ru–P–O(1)	118.4(4)	O(1)–C(1)–C(4)	112.1(14)
Ru–P–O(2)	116.0(4)	O(2)–C(2)–C(4)	107.5(14)
Ru–P–O(3)	112.4(5)	O(3)–C(3)–C(4)	112.9(14)
O(1)–P–O(2)	102.5(6)	C(1)–C(4)–C(2)	110.2(14)
O(2)–P–O(3)	102.7(7)	C(2)–C(4)–C(3)	107.3(14)
O(3)–P–O(1)	102.8(6)	C(3)–C(4)–C(1)	106.2(14)
P–O(1)–C(1)	115.4(10)	C(1)–C(4)–C(5)	113.9(14)
P–O(2)–C(2)	116.7(10)	C(2)–C(4)–C(5)	107.9(14)
P–O(3)–C(3)	115.2(11)	C(3)–C(4)–C(5)	111.1(15)
(ii) Co-ordination around Ru			
Ru–C(6)–O(6)	178.3(17)	C(32)–Ru–C(6)	178.0(8)
Ru–C(7)–O(7)	175.9(16)	C(42)–Ru–C(6)	93.5(6)
C(6)–Ru–C(7)	89.6(7)	C(01,02)–Ru–C(6)	89.2(6)
C(6)–Ru–P	90.8(5)	C(32)–Ru–C(7)	92.4(7)
C(7)–Ru–P	88.3(5)	C(42)–Ru–C(7)	93.2(6)
C(32)–Ru–P	89.8(5)	C(01,02)–Ru–C(7)	163.5(7)
C(42)–Ru–P	175.5(4)	C(42)–Ru–C(32)	85.9(7)
C(01,02)–Ru–P	89.6(5)	C(01,02)–Ru–C(32)	88.3(7)
		C(01,02)–Ru–C(42)	89.0(6)
(iii) C_6 ring			
C(01)–C(02)–C(03)	120.9(14)	C(03)–C(04)–C(41)	116.2(13)
C(02)–C(03)–C(04)	110.9(12)	C(05)–C(04)–C(41)	112.5(13)
C(02)–C(03)–C(31)	104.8(14)	C(04)–C(05)–C(06)	112.3(15)
C(04)–C(03)–C(31)	112.2(13)	C(05)–C(06)–C(01)	109.8(14)
C(03)–C(04)–C(05)	107.2(13)	C(06)–C(01)–C(02)	126.1(16)
(iv) Hexafluorobutyne ligands			
Ru–C(32)–C(31)	122.8(12)	Ru–C(42)–C(41)	124.0(10)
Ru–C(32)–C(34)	129.0(13)	Ru–C(42)–C(44)	114.0(11)
C(31)–C(32)–C(34)	106.9(15)	C(41)–C(42)–C(44)	121.5(13)
C(32)–C(31)–C(03)	111.6(15)	C(42)–C(41)–C(04)	123.2(13)
C(32)–C(31)–C(33)	138.2(15)	C(42)–C(41)–C(43)	125.3(13)
C(33)–C(31)–C(03)	110.2(16)	C(43)–C(41)–C(04)	111.3(13)
C(31)–C(33)–F(331)	115.5(15)	C(41)–C(43)–F(431)	111.2(14)
C(31)–C(33)–F(332)	115.6(15)	C(41)–C(43)–F(432)	112.9(13)
C(31)–C(33)–F(333)	114.7(14)	C(41)–C(43)–F(433)	114.5(14)
F(331)–C(33)–F(332)	103.7(13)	F(431)–C(43)–F(432)	104.9(15)
F(332)–C(33)–F(333)	104.0(14)	F(432)–C(43)–F(433)	106.1(14)
F(333)–C(33)–F(331)	101.5(15)	F(433)–C(43)–F(431)	106.8(13)
C(32)–C(34)–F(341)	122.5(15)	C(42)–C(44)–F(441)	115.3(14)
C(32)–C(34)–F(342)	115.6(14)	C(42)–C(44)–F(442)	113.8(13)
C(32)–C(34)–F(343)	108.5(15)	C(42)–C(44)–F(443)	112.2(13)
F(341)–C(34)–F(342)	103.2(14)	F(441)–C(44)–F(442)	106.0(12)
F(342)–C(34)–F(343)	103.6(15)	F(442)–C(44)–F(443)	105.7(13)
F(343)–C(34)–F(341)	101.0(14)	F(443)–C(44)–F(441)	102.7(13)

C(*m*,*n*) is the midpoint of the line joining C(*m*) to C(*n*).

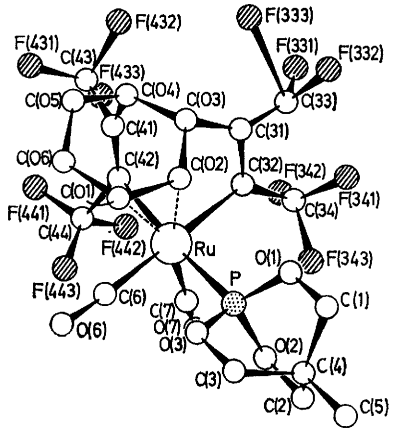


FIGURE 1 Molecular structure of $[Ru(CO)_2\{P(OCH_2)_3CMe\}(C_6H_8)(C_4F_6)_2]$

olefinic bond of the C_6 ring, C(01)–C(02), remains bonded to the ruthenium atom, while C(05) and C(06) each retain their two hydrogen atoms. The C_6 ring is nearly planar, but there is considerable variation in size among the bond angles (Table 2).

Around the ruthenium atom the co-ordination is almost ideally octahedral, but whereas one of the hexafluorobut-2-yne ligands [C(42)] lies *trans* to the phosphite ligand, the other [C(32)] lies *trans* to a carbonyl group [C(6)–O(6)]. In consequence, and also because of possible steric interactions, the two hexafluorobut-2-yne ligands differ in their structural details, especially bond angles (Table 2). Thus, Ru–C(42) at 2.184(15) Å is decidedly longer than Ru–C(32) [1.912(19) Å], and the bending away of the trifluoromethyl groups from the direction of the original acetylenic linkages shows considerable variation, with angles at C(42) of 121.5(13), at C(41) 125.3(13), at C(32) 106.9(15), and at C(31) 138.2(15)°. The distortion in the second ligand may arise as a result of its position *cis* to the phosphite. As is usual in co-ordinated fluorocarbons, the CF_3 groups all have F–C–F angles less than the ideal tetrahedral value.

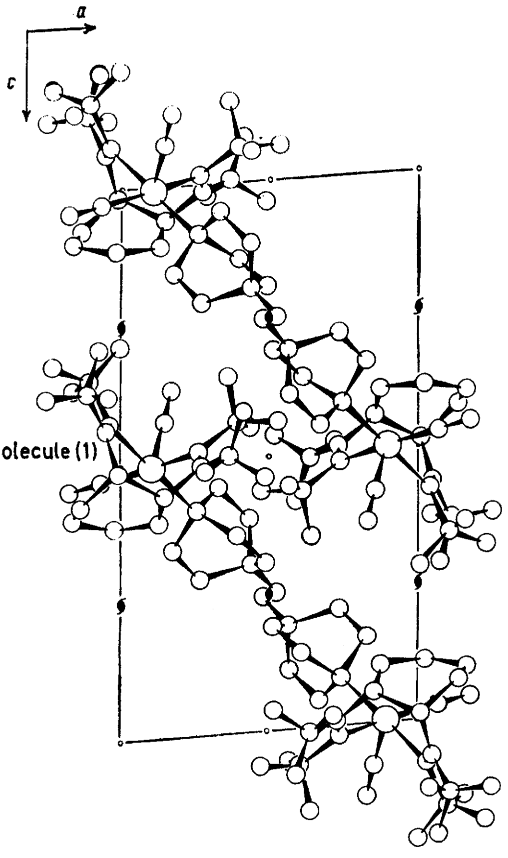
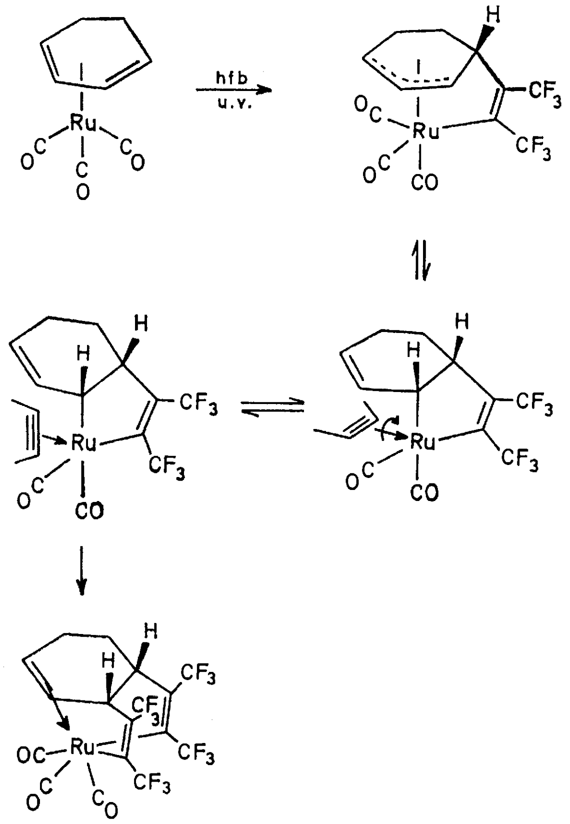


FIGURE 2 Contents of one unit cell seen in projection along *b* looking towards the origin

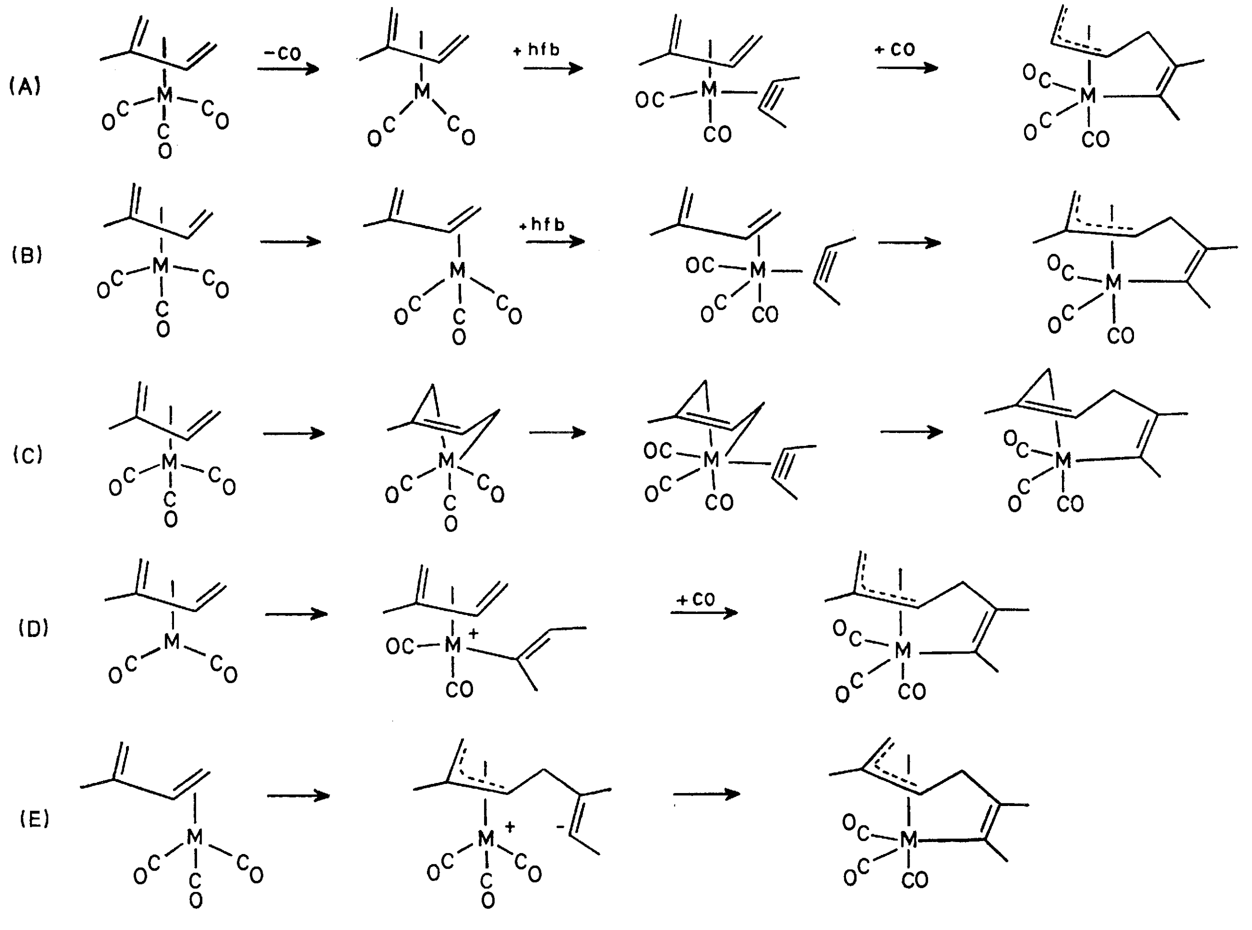


SCHEME 1

In the cyclohexene ring, the bonding from the olefinic link [C(01)–C(02)] to the ruthenium atom is somewhat asymmetric (Table 2), but of course the attachments of the hexafluorobut-2-yne ligands to the ring are not symmetrically related to this bond. The structural geometry of the carbonyl and phosphite ligands is as expected, and in the crystal there are no abnormally short intermolecular contacts.

Thus, the formation of (7) and (8) involves formally the addition of two hfb molecules to *one* olefinic double bond, which is incorporated into a ruthenacyclohepta-2,6-diene ring. With the establishment of the identity of these complexes it was then possible to interpret the n.m.r. spectral data (see Experimental section), and from this it became clear that in the reaction of the co-ordinated 2-methylcyclohexa-1,3-diene to form (8) only the unsubstituted double-bond is involved in the reaction with the two hfb molecules. The same preferential attack on the unsubstituted double bond was observed in the reaction of 3,3,3-trifluoroprop-1-yne with tricarbonyl(isoprene)iron and it is suggested that the formation of (7) and (8) involves the intermediacy of a 1 : 1 adduct; the second acetylene molecule inserting into a σ-allyl bond as illustrated in Scheme 1.

If this reasonable assumption is accepted then it is clear that in the reaction with the first acetylene molecule, attack takes place on the face of the co-ordinated cyclohexa-1,3-diene to which the metal is bonded. Clearly this is of importance in considering possible reaction paths for the oxidative reaction of hfb with co-ordinated 1,3-dienes. Other observations which must be taken into account are (i) the preferential attack on the unsubstituted double bond and (ii) the regiospecificity of the 3,3,3-trifluoroprop-1-yne reactions in the sense that the acetylenic carbon atom carrying the trifluoromethyl substituent becomes bonded to the iron atom. However, a crucial question is, what is the effect of the u.v. irradiation?



SCHEME 2

There are two obvious possibilities, (A) and (B), which are illustrated in Scheme 2. The first involves loss of carbon monoxide on irradiation to give a 16-electron species, which is captured by the acetylene, recombination with CO initiating an oxidative reaction and the formation of a metallocyclopent-2-ene. The second alternative (B) requires the formation on irradiation of a 1,2-η^2-bonded 1,3-diene species, which is captured by hfb. Metallocyclopent-2-ene formation is then promoted by re-co-ordination of the second double bond of the diene. Neither reaction path provides an explanation for the regiospecificity of the 3,3,3-trifluoroprop-1-yne reaction. Regarding the effect of substituents on the diene; path (B) provides a readier explanation, in that alkyl substituents on olefin complexes are known to have a destabilising effect on π-complex formation.

Since in the related reaction of hexafluoroacetone (hfa) with $[Fe(\eta^4-C_4Me_4)(CO)_3]$ a complex $[Fe(\eta^4-C_4H_4)(CO)_2\{(CF_3)_2CO\}]$ is formed, which on treatment with phosphine or phosphite ligands affords a linked Fe^{II} η^3-cyclobutenyl complex,[7] it could be argued that this provides evidence for the last stage of path (A). However, such an interpretation is not unambiguous since it is possible that phosphite or phosphine displaces hfa to give $[Fe(\eta^4-C_4Me_4)(CO)_2L]$, which then reacts *via* a different reaction path with the displaced hfa.

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[7] A. Bond and M. Green, *J.C.S. Dalton*, 1972, 763.

A further difficulty with regard to distinguishing between paths (A) and (B) is that at the present time we do not know what the relative reactivities are of η^4-bonded-1,3-diene-$Fe(CO)_2$ and η^2-bonded-1,3-diene-$Fe(CO)_3$ towards an acetylene, and of their relative ease of formation.

Recently, a perturbation m.o. analysis has suggested that because of the even-alternant properties of the bonding networks generated by butadiene p_π orbitals and metal d_π orbitals the canonical forms represented in Scheme 3[8] provide an accurate description of the bonding in metal–butadiene complexes. With this assumption the path (C) can be envisaged.

Scheme 3

It is easy to eliminate path (D) involving the intermediacy of a dipolar species[2,9-11] formed by attack of the nucleophilic metal centre on the acetylene, since it is known that 3,3,3-trifluoroprop-1-yne reacts with both metallic[12] and non-metallic[13] nucleophiles at the acetylenic carbon which does not carry a CF_3 substituent. However, the other ionic path (E) has the merit of explaining both the direction of reaction of $CF_3C{\equiv}CH$, and also the effect of substituents on the 1,3-diene.

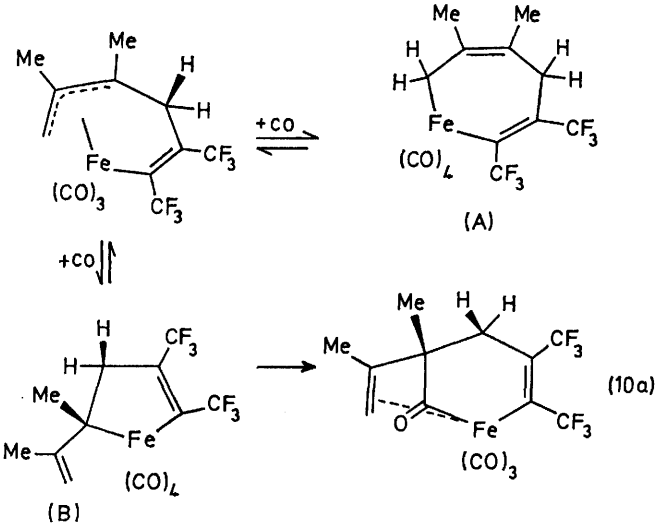
In summary, it can be seen that it is difficult at the present time to distinguish with certainty between various possible reaction paths, and as we have previously discussed for the related reactions with fluoro-olefins[14] and hexafluoroacetone[15] there may be competing processes.

It was suggested that complexes (7) and (8) were formed *via* a further reaction of a 1 : 1 adduct. This implied that other insertion reactions might be possible. When the complex (2) was heated under a pressure of carbon monoxide (50 atm) a bright yellow crystalline complex (10) was formed. Elemental analysis and mass-spectroscopy showed that (10) was a 1 : 1 adduct of (2) and carbon monoxide. The i.r. spectrum of (10) confirmed the presence of an $Fe(CO)_3$ unit, and in addition showed a new band at 1 704 cm^{-1} typical of a metal acyl [Fe–C(O)–] group. The apparent occurrence of a ' carbonyl insertion ' reaction suggested two possible structures (10a) and (10b) for this new complex.

Comparison of the ^{1}H n.m.r. spectra of (10) and (2) showed that, whereas in the spectrum of (2) there is little difference (τ 7.92 and 8.02) in the chemical shifts of the methyl groups, the methyl substituents in (10) show resonances at τ 8.25 and 8.70, suggesting rather different chemical environments. Such a feature is present in structure (10a). An additional point is that the $^4J_{HF}$ coupling observed in the ^{1}H and ^{19}F spectra of (2) is not present in the corresponding spectra of (10), the protons H^5 and H^6 appearing as doublets centred at τ 8.32 and 8.90. Furthermore, the carbonylation reaction had little effect on the two chemical shifts of the α- and β-CF_3 groups.

Thus, the formation of (10) can be seen as a carbonyl insertion reaction of a σ-allyl system (Scheme 4) formed on reaction with carbon monoxide. It might be argued that the terminal-bonded σ-allyl (A) would be formed preferentially; however, it is possible that the rate-determining step is the ' carbonyl insertion ' (*i.e.* alkyl migration) reaction, and then in view of the expected relative migratory aptitudes of the groups adjacent to the iron, *viz.* t-alkyl > primary alkyl > trifluoromethyl-substituted vinyl group, the formation of (10a) can be understood.

Examination of the i.r. spectra of minor products formed in the reaction of (2) with carbon monoxide suggested that the thermolysis of (2) should be studied.



Scheme 4

In refluxing hexane the adduct (2) was transformed (47% yield) into the yellow crystalline isomer (11). A similar thermolysis reaction of (1), but in refluxing heptane, led to an analogous reaction (14% yield) and the formation of the crystalline complex (12). Elemental analysis and mass spectroscopy showed that (11) and (12) were respectively isomeric with (2) and (1). The mass spectra showed the corresponding parent ions, and ions resulting from the stepwise loss of three carbon monoxide ligands. In both cases the i.r. spectra showed a typical $Fe(CO)_3$ pattern, which was shifted to lower (30 cm^{-1}) wavelength compared with the parent complexes. There was no indication of bands correspond-

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[8] D. M. P. Mingos, *J.C.S. Dalton*, 1977, 20, 26, 31.

[9] A. Nakamura and S. Otsuka, *J. Amer. Chem. Soc.*, 1973, **95**, 5091.

[10] M. I. Bruce, T. Blackmore, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 106.

[11] J. W. Lauher and R. Hoffmann, *J. Amer. Chem. Soc.*, 1976, **98**, 1729.

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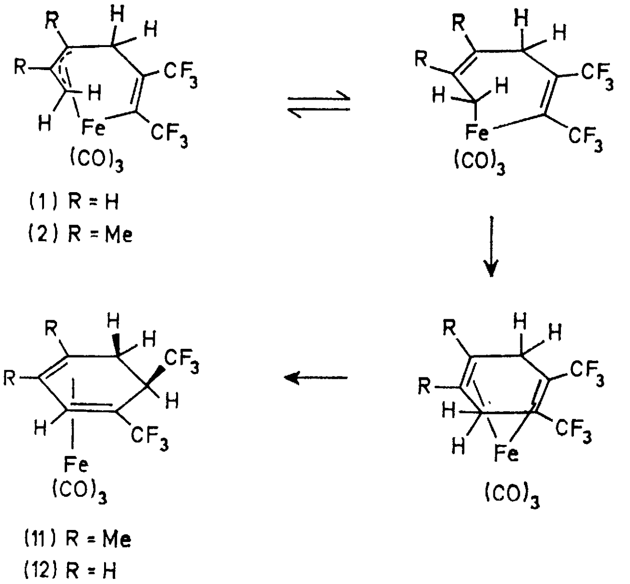
[13] R. N. Haszeldine, *J. Chem. Soc.*, 1952, 3490.

[14] M. Green, B. Lewis, J. J. Daly, and F. Sanz, *J.C.S. Dalton*, 1975, 1118.

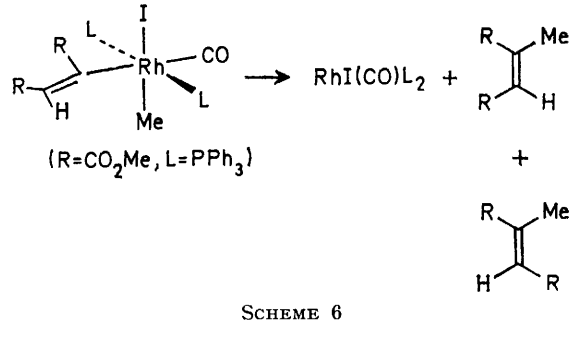
[15] M. Green and B. Lewis, *J.C.S. Dalton*, 1975, 1137.

ing to an acyl carbonyl or an unco-ordinated olefinic bond. Examination of the ^1H and ^{19}F n.m.r. spectra (see Experimental section) suggested the illustrated cyclic structures for (11) and (12). That a cyclisation reaction had in fact occurred was supported by an alternative synthesis of (12), which was achieved by refluxing $Fe_2(CO)_9$ and 1,2-bis(trifluoromethyl)cyclohexa-1,4-diene together in hexane.



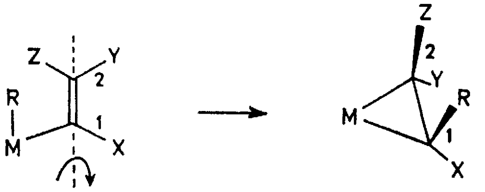
Scheme 5

The thermal rearrangement of (1) and (2) can be understood (Scheme 5) in terms of the initial formation of a terminal-bonded σ-allyl intermediate, which in the absence of carbon monoxide undergoes a reductive elimination reaction to give a tricarbonylcyclohexa-1,4-dieneiron complex. Previous studies [16,17] have shown that cyclohexa-1,4-dienes react with iron carbonyls to give cyclohexa-1,3-diene complexes and, therefore, under the reaction conditions of the cyclisation reaction (refluxing hexane or heptane) isomerisation occurs to give the 1,3-diene complex. Although the n.m.r. data do not establish the stereochemistry of the products (11) and (12) it is reasonable to assume that it is an *endo*-hydrogen (same face as the iron) which undergoes a metal-promoted 1,3-H shift.[18] It is interesting to note that in this isomerisation reaction hydrogen migrates preferentially to an electronegatively substituted olefinic carbon atom.



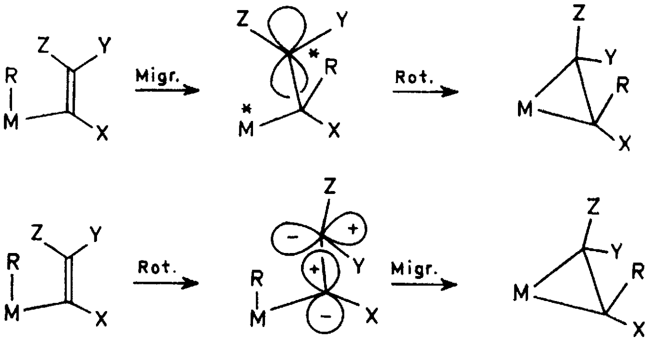
Scheme 6

There is precedent for the postulated reductive-elimination step in an investigation reported [19] by Schwartz and his co-workers, where it was shown that an alkylvinylrhodium(III) complex (Scheme 6) decomposed on heating (115 °C) to form $[RhI(CO)L_2]$ and the corresponding olefins *cis* (98%) : *trans* (2%). In both the iron and rhodium systems a formal $d^6 \rightarrow d^8$ change in oxidation state is involved; however, in the case of the iron system the newly formed olefin remains bonded to the metal.



Scheme 7

Focusing on the geometrical aspects of this reaction, and simplifying the system by treating the final π-complex as a metallocyclopropane, the reaction can be pictured as involving (Scheme 7) a rotation of the vinyl system away from the migrating R group. This poses a problem if overlap is to be maintained in a concerted process between an sp^3 orbital of the migrating R group and a π-orbital on C^1. The point can be made clearer by considering geometrical extremes for the reaction path; (i) prior migration of R or (ii) prior rotation about C^1–C^2 (Scheme 8). Clearly the latter would be facilitated by polarisation of the metal–vinyl complex, the R group then migrating to an electron-deficient centre.



Scheme 8

It is clear from this brief discussion of the problem that a detailed analysis is merited in order to gain a better understanding of this interesting reaction.

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* The intermediate here can be depicted either as a diradical or a dipolar species.

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[17] A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc.* (*A*), 1968, 332.

[18] M. Green and R. P. Hughes, *J.C.S. Dalton*, 1976, 1907.

[19] J. Schwartz, D. W. Hart, and J. L. Holden, *J. Amer. Chem. Soc.*, 1972, **94**, 9269.

EXPERIMENTAL

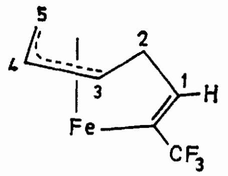
^{1}H N.m.r. spectra were recorded on a Varian Associates HA 100 spectrometer at 100 MHz with SiMe$_4$ (τ 10.00) as internal reference. ^{19}F and ^{13}C N.m.r. spectra were recorded on a JEOL PFT-100 spectrometer at 94.1 and 25.15 MHz respectively; chemical shifts are relative to CFCl$_3$ and SiMe$_4$, respectively, as external references. I.r. spectra were recorded on a Perkin-Elmer 457 spectrophotometer using Nujol mulls. The mass spectra were recorded on an A.E.I. MS902 spectrometer operating at 70 eV.* Reactions, except those in sealed tubes, were conducted in a dry oxygen-free nitrogen atmosphere.

Reactions of Hexafluorobut-2-yne.—(a) *With (buta-*1,3-*diene)tricarbonyliron.* Hexafluorobut-2-yne (0.48 g, 3.0 mmol) was condensed (−196 °C) into a Carius tube (100 cm^3) containing buta-1,3-diene(tricarbonyl)iron (0.50 g, 2.5 mmol) dissolved in hexane (20 cm^3). The tube and contents were irradiated (250 W, Hanovia u.v. lamp) for 24 h. The solvent was removed *in vacuo*, and the residue chromatographed on an alumina-packed column (20 × 2 cm). Elution with benzene–hexane (1 : 9) gave, after recrystallisation (−40 °C) from hexane, pale yellow *crystals* of (1) (0.07 g, 8%), m.p. 38 °C (Found: C, 37.1; H, 1.7; F, 31.0. $C_{11}H_6F_6FeO_3$ requires C, 37.1; H, 1.7; F, 31.2%), ν_{CO} (hexane) 2 068s, 2 034s, and 2 021m cm^{-1}, $\nu_{C=C}$ (Nujol) 1 631 cm^{-1}. The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 5.14 (ddd, 1 H, H^3, J_{13} 13 Hz, $J_{23} = J_{34} = 8.0$ Hz), 5.34 (complex m, 1 H, H^4, J_{34} 8.0 Hz), 5.98 (dd, 1 H, H^2, J_{23} 8.0 Hz, J_{12} 1.5 Hz), 6.88 (complex m, 2 H, H^5 and H^6, J_{HCF_3} 3.0 Hz), and 7.12 (dd, 1 H, H^1, J_{12} 1.5 Hz, J_{13} 13.0 Hz). The ^{19}F n.m.r. spectrum (CH$_2$Cl$_2$) showed resonances at 54.0 p.p.m. (qt, 3 F, α-CF$_3$, $J_{\alpha\beta}$ 14.0 Hz, $J_{\alpha CF_3H^5} = J_{\beta CF_3H^6} = 3.5$ Hz) and 58.5 (q, 3 F, β-CF$_3$, $J_{\alpha\beta}$ 14.0 Hz).

(b) *With tricarbonyl(*2,3-*dimethylbuta-*1,3-*diene)iron.* Similarly, irradiation (8 days) of a solution of tricarbonyl-(2,3-dimethylbuta-1,3-diene)iron (1.50 g, 6.8 mmol) and hexafluorobut-2-yne (1.50 g, 8.8 mmol) in hexane (20 cm^3) gave after removal of the solvent *in vacuo* and chromatography [elution with CH$_2$Cl$_2$–hexane (1 : 1)] a yellow solid. Recrystallisation (0 °C) from hexane gave yellow *crystals* of (2) (1.50 g, 58%), m.p. 45—47 °C [Found: C, 40.8; H, 2.6; F, 29.6%; *M*, 391 (osmometry in CHCl$_3$). $C_{13}H_{10}F_6FeO_3$ requires C, 40.6; H, 2.6; F, 29.6%; *M*, 384], ν_{CO} (hexane) 2 080s, 2 025s, and 2 007s cm^{-1}, $\nu_{C=C}$ (Nujol) 1 631m cm^{-1}. The mass spectrum (base peak *m/e* 191) showed peaks at *m/e* 356 (*P* − CO, 3%), 328 (*P* − 2CO, 18%) ,300 (*P* − 3CO, 40%), and 281 (*P* − 3CO − F, 4%). The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 6.27 (d, 1 H, H^2, J_{12} 1.5 Hz), 6.89 (q, 2 H, H^5 and H^6, $J_{\alpha CF_3H}$ 3.5 Hz), 7.40 (d, 1 H, H^1, J_{12} 1.5 Hz), 7.92 (s, 3 H, CH$_3$), and 8.02 (s, 3 H, CH$_3$). The ^{19}F n.m.r. spectrum (CH$_2$Cl$_2$) showed resonances at 53.2 p.p.m. (qt, 3 F, α-CF$_3$, $J_{\alpha\beta}$ 14.0 Hz, $J_{\alpha CF_3H^5} = J_{\alpha CF_3H^6} = 3.5$ Hz) and 59.2 (q, 3 F, β-CF$_3$, $J_{\alpha\beta}$ 14.0 Hz).

(c) *With tricarbonyl(diphenyl-*o*-styrylphosphine)iron.* Similarly, irradiation (1 day) of a solution of [Fe(CO)$_3$(sp)] (0.40 g, 0.9 mmol) and hexafluorobut-2-yne (0.50 g, 3.1 mmol) in hexane (20 cm^3) afforded small colourless *crystals* of (3) (0.41 g, 75%), m.p. 141—145 °C (Found: C, 55.2; H, 2.9; F, 19.4; P, 5.4. $C_{27}H_{17}F_6FeO_3P$ requires C, 54.8; H, 2.9; F, 19.3; P, 5.3%), ν_{CO} (hexane) 2 079w, 2 016s, and 2 008s cm^{-1}; $\nu_{C=C}$ (Nujol) 1 614m cm^{-1}. The mass spectrum (base peak *m/e* 506) showed peaks at *m/e* 590 (*P*, 1%), 562 (*P* − CO, 45%), 543 (*P* − CO − F, 1%), 534 (*P* − 2CO, 82%), 515 (*P* − 2CO − F, 3%), 506 (*P* − 3CO, 100%), and 487 (*P* − 3CO − F, 3%). The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 2.21—3.00 (complex m, 16 H, aryl), 5.58 (dd, 1 H, H^1, J_{12} 11.0 Hz, J_{13} 7.5 Hz), 6.12 (ddq, 1 H, H^3, J_{23} 17.0 Hz, J_{13} 7.5 Hz, $J_{\alpha CF_3H}$ 2.5 Hz), and 6.71 (m, 1 H, H^2, J_{23} 17.0 Hz, J_{12} 11.0 Hz, $J_{\alpha CF_3H}$ 4.0 Hz). The ^{19}F n.m.r. spectrum (C$_6$H$_5$Cl) showed resonances at 53.4 p.p.m. (m, 3 F, α-CF$_3$, $J_{\alpha\beta}$ 14.0 Hz, $J_{\alpha CF_3H}$ 4.0 Hz, $J_{\alpha CF_3H} = J_{PF} = 2.5$ Hz) and 57.7 (q, 3 F, β-CF$_3$, $J_{\alpha\beta}$ 14.0 Hz).

Reactions of 3,3,3-*Trifluoropropyne.*—(a) *With buta-*1,3-*diene(tricarbonyl)iron.* A solution of buta-1,3-diene(tricarbonyl)iron (1.50 g, 7.5 mmol) and 3,3,3-trifluoropropyne (10 mmol) in hexane (30 cm^3) contained in a Carius tube (100 cm^3) was irradiated (7 days). The solvent was removed *in vacuo*, and the residue chromatographed on an alumina-packed column. Elution with hexane gave first unchanged [Fe(CO)$_3$(C$_4$H$_6$)] followed by a yellow band. Removal of solvent followed by recrystallisation (−78 °C) from hexane gave pale yellow *crystals* of (4) (0.25 g, 11%), m.p. 44 °C (Found: C, 41.6; H, 2.6. $C_{10}H_7F_3FeO_3$ requires C, 41.7; H, 2.4%), ν_{CO} (hexane) 2 079s, 2 022s, and 2 007s cm^{-1}; $\nu_{C=C}$ (Nujol) 1 630w cm^{-1}. The mass spectrum (base peak *m/e* 44) showed peaks at *m/e* 288 (*P*, 2%), 260 (*P* − CO, 11%), 232 (*P* − 2CO, 37%), and 204 (*P* − 3CO, 27%). The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 3.7 (m, 1 H, H^7, $J_{\alpha CF_3H}$ 2.0 Hz, $J_{67} = J_{57} = 4.0$ Hz), 5.1 (m, 2 H, H^3 and H^4, J_{13} 12.0 Hz, J_{23} 8.0 Hz), 6.1 (d, 1 H, H^2, J_{23} 8.0 Hz), 7.25 (d, 1 H, H^1, J_{13} 12.0 Hz), and 7.40 (m, 2 H, H^{5,6}, $J_{\alpha CF_3H}$ 4.0 Hz). The ^{19}F n.m.r. spectrum ([^{2}H$_6$]acetone) showed a resonance at 59.9 p.p.m. (dt, 3 F, αCF$_3$, $J_{\alpha CF_3H^7}$ 2.0 Hz, $J_{\alpha CF_3H^5}$ 4.0 Hz). The ^{13}C n.m.r. spectrum (CDCl$_3$) showed resonances at −145.0 p.p.m. (q, C^1, J_{CF} 10.0 Hz), −96.7 (s, C^4), −80.9 (s, C^3), −64.4 (s, C^5), and −34.8 (s, C^2).



(b) *With tricarbonyl(*2,3-*dimethylbuta-*1,3-*diene)iron.* Similarly, irradiation (6 days) of tricarbonyl(2,3-dimethyl-buta-1,3-diene)iron (1.50 g, 6.8 mmol) and 3,3,3-trifluoropropyne (10.0 mmol) in hexane (30 cm^3) gave on elution from an alumina-packed column first unchanged [Fe(CO)$_3$-(C$_6$H$_{10}$)] followed by a yellow band. Removal of solvent and recrystallisation (−78 °C) from hexane gave pale yellow *crystals* of (5) (0.80 g, 38%), m.p. 62 °C (Found: C, 45.8; H, 3.7. $C_{12}H_{11}F_3FeO_3$ requires C, 45.6; H, 3.5%), ν_{CO} (hexane) 2 072s, 2 015s, and 1 987s cm^{-1}; $\nu_{C=C}$ (Nujol) 1 630mw cm^{-1}. The mass spectrum (base peak *m/e* 123) showed peaks at *m/e* 316 (*P*, 4%), 288 (*P* − CO, 34%), 260 (*P* − 2CO, 87%), and 232 (*P* − 3CO, 77%). The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 3.65 (dq, 1 H, H^7, J_{57} 4.0 Hz, $J_{\alpha CF_3H^7}$ 2.0 Hz), 6.30 (s, 1 H, H^2), 7.3 (q, 2 H, H^5 and H^6, $J_{\alpha CF_3H}$ 4.0 Hz, J_{57} 4.0 Hz), 7.45 (s, 1 H, H^1), 7.9 (s, 3 H, CH$_3$), and 8.0 (s, 3 H, CH$_3$). The ^{19}F n.m.r. spectrum ([^{2}H$_6$]acetone) showed a resonance at 59.7 p.p.m. (dt, 3 F, α-CF$_3$, $J_{\alpha CF_3H^7}$ 2.0 Hz, $J_{\alpha CF_3H^5}$ 4.0 Hz). The ^{13}C n.m.r. spectrum (CDCl$_3$) showed resonances

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* 1 eV ≈ 1.60 × 10^{-19} J.

at −145.5 p.p.m. (q, C^1, J_{CF} 10.0 Hz), −112.0 (s, C^7), −97.0 (s, C^6), −62.1 (s, C^5), −43.6 (s, C^2), −27.3 (s, C^3), and −24.2 (s, C^4).

(c) *With tricarbonyl(isoprene)iron.* Irradiation (6 days) of a solution of tricarbonyl(isoprene)iron (0.50 g, 0.5 mmol) and 3,3,3-*trifluoro*propyne (0.94 g, 10 mmol) in hexane (30 cm^3) gave after chromatography and recrystallisation (−78 °C) from hexane pale yellow *crystals* of (6a) and (6b) (0.25 g, 31%), m.p. 54 °C (Found: C, 44.2; H, 3.3. $C_{11}H_9F_3FeO_3$ requires C, 43.8; H, 3.0%), ν_{CO} (hexane) 2 076s, 2 019s, and 2 002 cm^{-1}; $\nu_{C=C}$ (Nujol) 1 630mw cm^{-1}. The mass spectrum (base peak *m/e* 246) showed peaks at *m/e* 302 (*P*, 5%), 288 (*P* − CH_2, 24%), 274 (*P* − CO, 44%), 260 (*P* − CO − CH_2, 38%), 246 (*P* − 2CO, 100%), 232 (*P* − 2CO − CH_2, 26%), and 218 (*P* − 3CO, 85%). The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances due to two isomers [(6a)/(6b) = 2.5/1]; isomer (6a) τ 3.75 (m, 1 H, H^7, $J_{\alpha CF_3H^7}$ 2.0 Hz), 5.20 (m, 1 H, H^4, J_{45} 6.0 Hz), 6.30 (s, 1 H, H^2), 7.25 (m, 2 H, H^5 and H^6), 7.30 (s, 1 H, H^1), and 8.00 (s, 3 H, CH_3); isomer (6b) τ 3.70 (m, 1 H, H^7, $J_{\alpha CF_3H^7}$ 2.0 Hz), 5.25 (m, 1 H, H^3, J_{13} 14.0 Hz, J_{23} 8.0 Hz), 6.30 (d, 1 H, H^2, J_{23} 8.0 Hz), 7.20 (m, 2 H, H^5 and H^6), 7.45 (d, 1 H, H^1, J_{13} 14.0 Hz), and 7.90 (s, 3 H, CH_3). The ^{19}F n.m.r. spectrum ([$^2H_6$]acetone) showed resonances at 59.8 p.p.m. [m, 3 F, α-CF_3 (isomer 6a), $J_{\alpha CF_3H^7}$ 2.0 Hz, $J_{\alpha CF_3H^6}$ 4.0 Hz] and 60.2 [m, 3 F, α-CF_3 (isomer 6b), $J_{\alpha CF_3H^7}$ 2.0 Hz, $J_{\alpha CF_3H^6}$ 4.0 Hz]. The ^{13}C n.m.r. spectrum ($CDCl_3$) showed resonances due to (6a) at −144.5 p.p.m. (q, C^1, J_{CF} 10.0 Hz), −113.7 (s, C^6), −80.2 (s, C^3), −65.3 (s, C^5), −35.9 (s, C^2), and −29.2 (s, C^4); and (6b) at −144.5 p.p.m. (q, C^1, J_{CF} 10.0 Hz), −97.1 (s, C^4), −59.2 (s, C^5), −40.2 (s, C^2), and −29.7 (s, C^3).

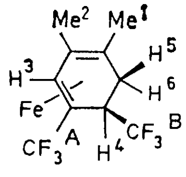
*Reaction of Tricarbonyl(cyclohexa-*1,3-*diene)ruthenium with Hexafluorobut-*2-*yne.*—Similarly, irradiation (40 h) of a solution of tricarbonyl(cyclohexa-1,3-diene)ruthenium (0.50 g, 1.9 mmol) and hexafluorobut-2-yne (0.70 g, 4.3 mmol) in hexane (12 cm^3) afforded on recrystallisation (0 °C) from CH_2Cl_2–hexane colourless *crystals* of (7) (0.10 g, 9%), m.p. 180—182 °C (Found: C, 34.7; H, 1.4; F, 37.9. $C_{17}H_8F_{12}O_3Ru$ requires C, 34.6; H, 1.4; F, 38.6%), ν_{CO} (CH_2Cl_2) 2 124s and 2 066vs cm^{-1}; $\nu_{C=C}$ (Nujol) 1 620w cm^{-1}. The mass spectrum (base peak *m/e* 20) showed peaks at *m/e* 589 (*P*, 1%), 561 (*P* − CO, 21%), 533 (*P* − 2CO, 7%), 514 (*P* − 2CO − F, 2%), 505 (*P* − 3CO, 21%), 486 (*P* − 3CO − F, 4%), and 485 (*P* − 3CO − HF, 4%). The ^1H n.m.r. spectrum ([$^2H_6$]acetone) showed resonances at τ 3.16 (d, 1 H, H^3, J_{34} 8.5 Hz), 3.42 (dd, 1 H, H^4, J_{34} 8.5 Hz, J_{45} 5.5 Hz), 5.94 (m, 1 H, H^2), 6.60 (m, 1 H, H^1), 7.32 (m, 2 H, H^7 and H^8), and 7.96 (m, 2 H, H^5 and H^6, J_{45} 5.5 Hz). The ^{19}F n.m.r. spectrum ([$^2H_6$]acetone) showed resonances at 46.8 p.p.m. (q, 3 F, αCF_3, $J_{\alpha\beta}$ 18.0 Hz), 53.2 (q, 3 F, γCF_3, $J_{\gamma\delta}$ 14.0 Hz), 58.1 (q, 3 F, δCF_3, $J_{\gamma\delta}$ 14.0 Hz), and 58.7 (q, 3 F, βCF_3, $J_{\alpha\beta}$ 18.0 Hz).

*Reaction of Tricarbonyl(*2-*methylcyclohexa-*1,3-*diene)-ruthenium with Hexafluorobut-*2-*yne.*—Irradiation (3 days) of a solution of tricarbonyl(2-methylcyclohexa-1,3-diene)-ruthenium (0.50 g, 1.8 mmol) and hexafluorobut-2-yne (0.70 g, 4.3 mmol) in hexane (12 cm^3) afforded colourless *crystals* of (8) (0.15 g, 14%), m.p. 192—195 °C (Found: C, 36.3; H, 1.8; F, 37.8. $C_{18}H_{10}F_{12}O_3Ru$ requires C, 35.8; H, 1.7; F, 37.9%), ν_{CO} (CH_2Cl_2) 2 124s and 2 066vs cm^{-1}; $\nu_{C=C}$ (Nujol) 1 620m cm^{-1}. The mass spectrum (base peak *m/e* 195) showed peaks at *m/e* 575 (*P* − CO, 10%), 556 (*P* − CO − F, 5%), 547 (*P* − 2CO, 35%), 528 (*P* − 2CO − F, 14%), 519 (*P* − 3CO, 95%), 500 (*P* − 3CO − F, 48%), and 499 (*P* − 3CO − HF, 30%). The ^1H n.m.r. spectrum ([$^2H_6$]acetone) showed resonances at τ 3.87 (d, 1 H, H^4, J_{45} 6.0 Hz), 6.06 (m, 1 H, H^2), 6.50 (m, 1 H, H^1, J_{17} 6.0 Hz), 7.32 (m, 2 H, H^7 and H^8, J_{17} 6.0 Hz), 7.46 (s, 3 H, CH_3), and 8.06 (m, 2 H, H^5 and H^6, J_{45} 6.0 Hz). The ^{19}F n.m.r. spectrum ([$^2H_6$]acetone) showed resonances at 46.6 (q, 3 F, αCF_3, $J_{\alpha\beta}$ 17.5 Hz), 52.6 (q, 3 F, γCF_3, $J_{\gamma\delta}$ 14.5 Hz), 58.7 (q, 3 F, δCF_3, $J_{\gamma\delta}$ 14.5 Hz), and 58.9 (q, 3 F, βCF_3, $J_{\alpha\beta}$ 17.5 Hz).

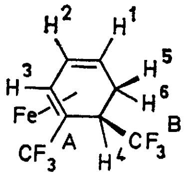
Reaction of Complex (7) *with* 4-*Methyl*-2,6,7-*trioxa*-1-*phosphabicyclo*[2.2.2]*octane.*—A solution of (7) (0.10 g, 0.17 mmol) and $P(OCH_2)_3CMe$ (0.03 g, 0.20 mmol) in hexane (20 cm^3) was refluxed (1 h). The solvent was removed *in vacuo* and the residue recrystallised from methylene chloride–hexane to give *crystals* of (9) (0.09 g, 70%) (Found: C, 35.5; H, 2.1. $C_{21}H_{17}F_{12}O_5PRu$ requires C, 35.5; H, 2.4%). The ^{19}F n.m.r. spectrum ([$^2H_6$]acetone) showed resonances at 46.6 p.p.m. (qd, 3 F, CF_3, J_{PF} 3.0 Hz, J_{FF} 18.0 Hz), 53.2 (q, 3 F, CF_3, J_{FF} 14.0 Hz), 58.5 (q, 3 F, CF_3, J_{FF} 14.0 Hz), and 58.9 (q, 3 F, CF_3, J_{FF} 18.0 Hz).

Reaction of Carbon Monoxide with Complex (2).—A solution of (2) (0.40 g, 1.1 mmol) in hexane (12 cm^3) contained in a 100 cm^3 stainless-steel autoclave (glass-liner) was maintained at 80 °C under 50 atm of carbon monoxide for 4 days. The reaction mixture was cooled to 0 °C giving yellow *crystals* of (10) (0.13 g, 30%), m.p. 114—116 °C (Found: C, 40.6; H, 2.4; F, 28.8. $C_{14}H_{10}F_6FeO_4$ requires C, 40.7; H, 2.4; F, 27.17%), ν_{CO} (hexane) 2 068s, 2 007s, 1 994s, and 1 704s (CO) cm^{-1}; $\nu_{C=C}$ (Nujol) 1 534m cm^{-1}. The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 6.62 (s, 1 H, H), 7.08 (s, 1 H, H), 8.25 (s, 3 H, CH_3), 8.32 (d, 1 H, H, *J* 14.0 Hz), 8.70 (s, 3 H, CH_3), and 8.90 (d, 1 H, H, *J* 14.0 Hz). The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at 54.3 p.p.m. (q, 3 F, α-CF_3, $J_{\alpha\beta}$ 9.0 Hz) and 58.2 (q, 3 F, β-CF_3, $J_{\alpha\beta}$ 9.0 Hz).

Thermolysis of Complex (2). A solution of (2) (0.90 g, 2.34 mmol) in hexane (100 cm^3) was heated under reflux for 4 days, the progress of the reaction being monitored by i.r. spectroscopy. The solution was filtered through kieselguhr, volatile material was removed *in vacuo*, and the residue chromatographed on an alumina-packed column. Elution with hexane gave first a minor product [ν_{CO} (hexane) 2 069s, 2 013s, and 1 998s cm^{-1}] which was not isolated, followed by a yellow band. Removal of solvent and re-crystallisation (−78 °C) from hexane gave yellow *crystals* of (11) (0.42 g, 47%), m.p. 63 °C (Found: C, 40.5; H, 2.6. $C_{13}H_{10}F_6FeO_3$ requires C, 40.6; H, 2.6%), ν_{CO} (hexane) 2 063s, 2 004s, and 1 991s cm^{-1}. The mass spectrum (base peak *m/e* 225) showed peaks at *m/e* 384 (*P*, 4%), 356 (*P* − CO, 29%), 328 (*P* − 2CO, 3%), 300 (*P* − 3CO, 36%), and 225 (*P* − 3CO − Fe − F, 100%). The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 4.33 (s, 1 H, H^3), 7.04 (ddq, 1 H, H^4, J_{45} 3.0 Hz, J_{46} 11.0 Hz, J_{FH} 8.5 Hz), 7.56 (dd, 1 H, H^6, J_{46} 11.0 Hz, J_{56} 16.0 Hz), 7.83 (s, 3 H, $CH_3{}^2$), 8.11 (dd, 1 H, H^5, J_{45} 3.0 Hz, J_{56} 16.0 Hz), and 8.37 (s, 3 H, $CH_3{}^1$). The ^{19}F n.m.r. spectrum ($CDCl_3$) showed resonances at 56.56 p.p.m. (q, 3 F, $CF_3{}^A$, J_{FF} 11.5 Hz) and 66.88 (dq, 3 F, $CF_3{}^B$, J_{FH} 8.5 Hz, J_{FF} 11.5 Hz).



Thermolysis of Complex (1). A solution of (1) (0.65 g, 1.83 mmol) in heptane (100 cm^3) was refluxed (24 h). The solution was filtered, the solvent removed *in vacuo*, and the residue chromatographed on an alumina-packed column. Elution with hexane gave a trace of a minor product followed by a yellow band. Removal of solvent and recrystallisation (−78 °C) from hexane gave yellow *crystals* of (12) (0.09 g, 14%), m.p. 28—30 °C (Found: C, 37.0; H, 1.8. $C_{11}H_6F_6FeO_3$ requires C, 37.1; H, 1.7%), ν_{CO} (hexane) 2 071s, 2 010s, and 2 001s cm^{-1}. The mass spectrum (base peak *m/e* 127) showed peaks at *m/e* 356 (*P*, 12%), 328 (*P* − CO, 34%), 300 (*P* − 2CO, 5%), 272 (*P* − 3CO, 51%), 216 (*P* − 3CO − Fe, 11%), and 197 (*P* − 3CO − Fe − F, 41%). The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 4.07 (d, 1 H, H^3, J_{23} 5 Hz), 4.63 (dd, 1 H, H^2, J_{12} 5.0 Hz, J_{23} 5.0 Hz), 6.91 (ddd, 1 H, H^1, J_{12} 5.0 Hz, $J_{15} = J_{16} =$ 3.0 Hz), 7.03 (ddq, 1 H, H^4, J_{45} 3.0 Hz, J_{46} 11.0 Hz, J_{FH} 8.5 Hz), 7.61 (ddd, 1 H, H^6, J_{16} 3.0 Hz, J_{46} 11.0 Hz, J_{56} 16.0 Hz), and 8.00 (ddd, 1 H, H^5, J_{15} 3.0 Hz, J_{45} 3.0 Hz, J_{56} 16.0 Hz). The ^{19}F n.m.r. spectrum ($CDCl_3$) showed resonances at 56.64 (q, 3 F, CF_3^A, J_{FF} 11.5 Hz) and 66.46 (dq, 3 F, CF_3^B, J_{FH} 8.5 Hz, J_{FF} 11.5 Hz).



Reaction of 1,2-*Bis(trifluoromethyl)cyclohexa*-1,4-*diene with Enneacarbonyldi-iron*.—A suspension of $[Fe_2(CO)_9]$ (10.0 g, 27.5 mmol) and $C_6H_6(CF_3)_2$ (1.0 g, 4.63 mmol) in hexane (100 cm^3) was refluxed (8 h). Removal of the solvent *in vacuo* and chromatography gave (12) (0.13 g, 10%).

Crystal Structure Determination of Complex (9).—Crystals of the complex grow as colourless plates. The crystal chosen for data collection was of dimensions 0.25 × 0.09 × 0.21 mm, and diffracted intensities were recorded for $2.9° < 2\theta < 50°$ on a Syntex $P2_1$ four-circle diffractometer. Of the total 4 710 recorded independent intensities 2 418 had $I \geqslant 2.5\sigma(I)$, where $\sigma(I)$ is the standard deviation based on counting statistics, and were used in the solution and refinement of the structure. All computations were carried out with the '*X*-Ray' System of programmes [20] available for CDC 7600 at the London Computing Centre.

Crystal Data.—$C_{21}H_{17}F_{12}O_5PRu$, $M = 709.4$, Monoclinic, $a = 8.875(5)$, $b = 17.841(9)$, $c = 16.517(5)$ Å, $\beta = 94.51(3)°$, $U = 2\,607(2)$ Å^3, $D_m = 1.80$ (flotation), $Z = 4$, $D_c = 1.81$ g cm^{-3}, $F(000) = 1\,400$. Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å; μ(Mo-K_α) = 7.78 cm^{-1}. Space group $P2_1/c$ (No. 14).

Structure Solution and Refinement.—The ruthenium and phosphorus atoms were located from a Patterson synthesis, and all the remaining atoms (excluding hydrogen) by successive electron-density difference syntheses. The structure was refined by blocked-matrix least squares, with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were incorporated at calculated positions (C–H 0.98 Å); positional and thermal parameters for these atoms ($U_H = 1.10U_C$) were fixed during refinement. Refinement converged at $R = 0.078$ ($R' = 0.080$) with a mean shift-to-error ratio in the last cycle of 0.02. A weighting scheme of the form $w = 1.0/(6.29 - 0.199|F| + 0.0024|F|^2)$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks >0.6 or <-0.4 eÅ^{-3}. Scattering factors were from ref. 21 for carbon, oxygen, and phosphorus, ref. 22 for hydrogen, and ref. 23 for ruthenium including corrections for the effects of anomalous dispersion. Atomic positional parameters are in Table 1, interatomic distances and angles in Table 2. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 21980 (14 pp., 1 microfiche).*

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

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