Insertion Reactions of Hexafluorobut-2-yne, Tetrafluoroethylene, and Hexafluoroacetone with η^5-Cyclopentadienyl-iron, -ruthenium, -palladium, and -molybdenum Complexes; Molecular and Crystal Structures of $[Fe_2(CO)\{C_4(CF_3)_4CO\}(\eta^5\text{-}C_5H_5)_2]$ and $[Fe\{COCF_2C_5H_5\}(\eta^5\text{-}C_5H_5)]$

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Reaction (u.v. irradiation) of $[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ with hexafluorobut-2-yne (hfb) gives $[Fe_2(CO)\{C_8F_{12}CO\}(\eta^5\text{-}C_5H_5)_2]$, structurally identified by *X*-ray crystallography as a ferracyclohexadienone complex. The ruthenium compound $[\{Ru(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ reacts with hfb to give $[Ru\{trans\text{-}C(CF_3){:}C(CF_3)H\}(CO)_2(\eta^5\text{-}C_5H_5)]$, which subsequently affords the bis-insertion product $[Ru\{cis\text{-}trans\text{-}C(CF_3){:}C(CF_3)C(CF_3){:}C(CF_3)H\}(CO)(\eta^5\text{-}C_5H_5)]$. Irradiation of $[FeMe(CO)_2(\eta^5\text{-}C_5H_5)]$ and hfb affords $[FeC(CF_3){:}C(CF_3)C(CF_3){:}C(CF_3)COMe(\eta^5\text{-}C_5H_5)]$, which exists in solution as two interconverting conformers. Treatment of $[MnMe(CO)_5]$ with hfb gives the insertion product $[Mn\{cis\text{-}C(CF_3){:}C(CF_3)Me\}(CO)_5]$. Reaction of $[Fe(\eta^1\text{-}C_3H_5)(CO)_2(\eta^5\text{-}C_5H_5)]$ with hfb gives only the *cis* mono-insertion product, whereas, the corresponding molybdenum system $[Mo(\eta^1\text{-}C_3H_5)(CO)_3(\eta^5\text{-}C_5H_5)]$ affords a bis-insertion product; the first step probably involves a *trans*-insertion. A second product is $[Mo_2(CO)_4(CF_3C_2CF_3)(\eta^5\text{-}C_5H_5)_2]$. The photolytic reaction of $[Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)]$ and hfb, in contrast with the Fe and Mo systems, gives a dinuclear complex $[Pd_2C_4(CF_3)_4(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)]$. Irradiation of hfb and $[Fe(\eta^1\text{-}C_5H_5)(CO)_2(\eta^5\text{-}C_5H_5)]$ gives a product corresponding to a formal $(2 + 4)\pi$ addition to an unco-ordinated substituted cyclopentadiene, followed by a carbonyl insertion reaction. Tetrafluoroethylene undergoes an unusual carbon–carbon double bond cleavage on reaction with $[Fe(\eta^1\text{-}C_5H_5)(CO)_2(\eta^5\text{-}C_5H_5)]$ to give $[Fe(COCF_2C_5H_5)(\eta^5\text{-}C_5H_5)]$, structurally characterised by *X*-ray crystallography. Hexafluoroacetone (hfa) readily reacts at low temperature with $[Fe(\eta^1\text{-}C_5H_5)(CO)_2(\eta^5\text{-}C_5H_5)]$ to give products, in which the hfa has formally inserted into a C–H bond on the σ-bonded C_5 ring.

PREVIOUSLY [1] it was shown that reactions of hexafluorobut-2-yne (hfb) and the compounds $[MCl(CO)_3(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) afford sixteen-electron complexes $[MCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$. With the intention of extending the scope of these reactions, particularly with respect to whether CO ligand displacement occurred in other cases, the interaction of hfb with several η^5-cyclopentadienyl carbonylmetal complexes was investigated. However, as detailed herein, cyclisation and insertion reactions involving the carbonyl groups often occurred.

RESULTS AND DISCUSSION

U.v. irradiation of $[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ with hfb in methylene chloride solution gave a black crystalline complex (I). A molecular formula of $[Fe_2(CO)\{C_8F_{12}CO\}(C_5H_5)_2]$ was indicated for (I) by elemental analyses, and by the appearance in the mass spectrum of peaks corresponding to $[P]^+$, $[P - CO]^+$, and $[P - 2CO]^+$. In addition, the mass spectrum showed peaks corresponding to the fragmentation of a cyclopentadienone ring $[C_4(CF_3)_4CO]$. The i.r. spectrum showed terminal and ketonic carbonyl bands at 1 945 and 1 670 cm^{-1}, respectively. However, although the ^1H n.m.r. spectrum had two singlets of equal intensity corresponding to the presence of inequivalent η^5-C_5H_5 ligands, the presence in the ^{19}F spectrum of two distinct quartets, rather than two multiplets, was not consistent with a co-ordinated tetrakis(trifluoromethyl)cyclopentadienone. A single-

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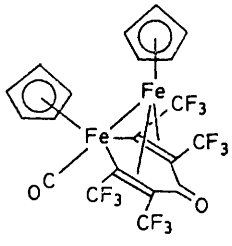
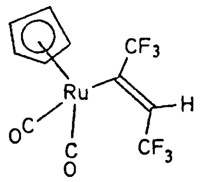
[1] J. L. Davidson, M. Green, D. W. A. Sharp, F. G. A. Stone, and A. J. Welch, *J.C.S. Chem. Comm.*, 1974, 706; J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J.C.S. Dalton*, 1976, 738.

crystal *X*-ray diffraction study was therefore undertaken.[2] A perspective view of a single molecule, demonstrating the atomic numbering scheme adopted, is given in Figure 1.



(I)



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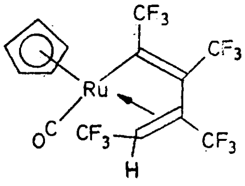

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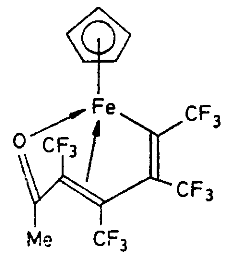
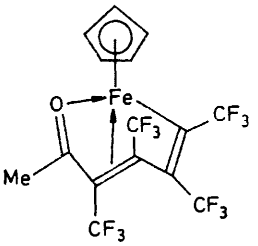
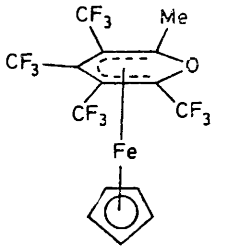


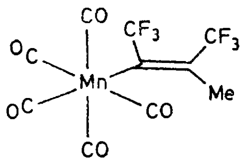
(IVa)



(IVb)



(IVc)



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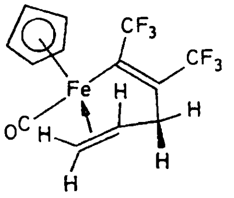
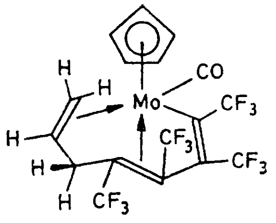


(VI)



(VII)

The results establish (I) as a ferracyclohexadienone which has effective C_s symmetry about a plane containing Fe(1), Fe(2), C(1), C(4), O(1), and O(4). Important bond lengths are listed in Table 1. Metal atom Fe(1) is formally σ-bonded to C(2) and C(6) (mean 1.951 Å) as part of the heterocyclic system. It also carries a terminal carbonyl group [Fe(1)–C(1) 1 768(8), C(1)–O(1) 1.148(11) Å] and an η^5-cyclopentadienyl ligand which, in the crystal phase, is disordered over two sets of positions [C(11)—(15), 71% population, and C(101)—(105),* 29% population].

The six-atom condensed ring, which is completed by C(4) of the bridging carbonyl function C(4)O(4) and two hfb ligands, now formally 1,2-bis(trifluoro)alkenes, is of envelope conformation [Fe(1) and C(4) apical] with acute folding angles across C(3) · · · C(5) and C(2) · · · C(6) of 41.4 and 40.2°, respectively.

TABLE 1

Compound (I) $C_{20}H_{10}O_2F_{12}Fe_2$: important bond lengths (Å)

Fe(1)–C(1)	1.768(8)	Fe(1)–Fe(2)	2.5876(14)
Fe(1)–C(2)	1.949(7)	Fe(2)–C(2)	1.987(7)
Fe(1)–C(6)	1.953(7)	Fe(2)–C(3)	2.114(7)
Fe(1)–C(11)	2.129(13)	Fe(2)–C(5)	2.111(7)
Fe(1)–C(12)	2.148(10)	Fe(2)–C(6)	1.990(7)
Fe(1)–C(13)	2.187(10)	Fe(2)–C(21)	2.082(8)
Fe(1)–C(14)	2.115(12)	Fe(2)–C(22)	2.089(8)
Fe(1)–C(15)	2.113(13)	Fe(2)–C(23)	2.080(9)
Fe(1)–C(101)	2.13(2)	Fe(2)–C(24)	2.089(9)
Fe(1)–C(102)	2.11(2)	Fe(2)–C(25)	2.098(9)
Fe(1)–C(103)	2.11(2)	C(1)–O(1)	1.148(11)
Fe(1)–C(104)	2.09(2)	C(2)–C(3)	1.422(10)
Fe(1)–C(105)	2.28(2)	C(5)–C(6)	1.423(10)

The function of the alkene units C(2),C(3) and C(5),C(6) as two-electron donors to the second metal atom, Fe(2), is supported by both the long co-ordinated C–C distances [1.422(10) Å] and the significant degree of rehybridisation observed. Thus C(2) and C(6) are displaced 0.23 Å,

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* C(105) is poorly defined under full-matrix least-squares refinement, with unrealistic bond lengths of 2.28(2), 1.11(3), and 1.69(3) Å to Fe(1), C(101), and C(104) respectively. Since, however, this fractional atom effectively represents less than two electrons, no attempt was made to idealise its position.

[2] J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J C.S. Chem. Comm.*, 1975, 286.

and C(3) and C(5) 0.16 Å, out of the respective Fe(1),C(211),C(311),C(4) and Fe(1),C(611),C(511),C(4) planes, towards Fe(2).

Atom Fe(2) is formally six-co-ordinate iron and carries a well defined η^5-cyclopentadienyl ring C(21)—(25) at a mean Fe–C distance of 2.088 Å. Stable eighteen-electron configurations of both metal atoms are completed by an Fe–Fe bond of unexceptional length [2.5876(14) Å].

Bond lengths and interbond angles involving the bridging carbonyl group, C(4)O(4), and each of the CF_3 groups are all as expected.

Metallacyclohexadienone ring systems of the kind found in (I) have been postulated as being present in a number of iron and osmium[3] complexes, which have resulted from similar reactions of carbonyl complexes with acetylenes. However, complex (I) is the first such system to be structurally characterised, and it is noteworthy that in several of the other known examples alternative structures are equally plausible. Such ring systems are considered to be intermediates in the formation of quinones from metal carbonyls and acetylenes;[4] however, a detailed understanding of the reaction paths involved in such ring-forming reactions is lacking.

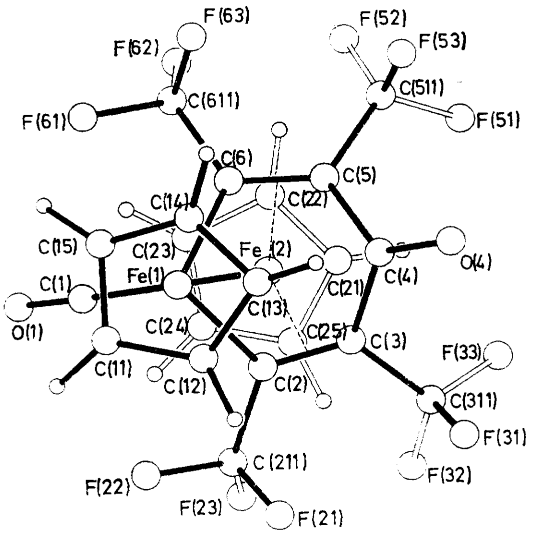

FIGURE 1 Complex (I) viewed normal to the ferracyclohexadienone ring. The 29% occupancy C_5 ring C(101)—(105), omitted for clarity, is related to C(11)—(15) by a rotation through *ca.* $2\pi/10°$ about an axis from Fe(1) to its centre. Cyclopentadienyl H-atoms are numbered according to the carbon to which they are bound

In contrast to the iron system, the corresponding reaction of hfb with $[\{Ru(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ in diethyl ether as solvent affords the mononuclear complexes (II) and (III). When the reaction was monitored by i.r. spectroscopy it was observed that the dicarbonyl species (II) is the precursor of (III). Moreover, the thermal reaction of $[RuH(CO)_2(\eta^5\text{-}C_5H_5)]$ with hfb gave (II), which only on u.v. irradiation in the presence of hfb was transformed into (III).

These insertion reactions are closely related to the formation of $[Ru\{cis\text{-}C(CF_3){:}C(CF_3)H\}(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ and $[Ru\{cis,cis\text{-}C(CF_3){:}C(CF_3)C(CF_3){:}C(CF_3)H\}(PPh_3)(\eta^5\text{-}C_5H_5)]$ in reactions of $[RuH(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ with hfb.[5] However, the magnitude of the ^{19}F–^{19}F coupling constants in the ^{19}F n.m.r. spectra of (II) and (III) suggest that in (II) [$J(CF_3\text{–}CF_3)$ 2.3 Hz] the trifluoromethyl groups have a relative *trans* configuration. In the case of (III) the ^{19}F spectrum contains a doublet [J(HF) 8.0 Hz], two quartets [$J(CF_3\text{–}CF_3)$ 8.4 Hz and 5.5 Hz] and a complex multiplet, which is consistent with the illustrated structure where the $[C(CF_3){:}CH(CF_3)]$ group retains the *trans* stereochemistry.

This change in stereochemistry on replacement of triphenylphosphine ligands by carbon monoxide is interesting, and implies a change in mechanism, possibly to a concerted $\sigma^2s + \pi^2a$ process[6] leading to the *trans* inserted product directly.

In extending the investigation, the corresponding reaction of $[FeMe(CO)_2(\eta^5\text{-}C_5H_5)]$ was examined. Ultraviolet irradiation of a hexane solution of hfb and the methyliron species gave a complex mixture, from which (IV) was isolated by column chromatography. The i.r. spectrum of the reaction mixture during the course of the reaction suggested the initial formation of a mono-insertion product; however, the concentration of this species did not increase on further irradiation, and attempts to isolate this intermediate were not successful.

The spectroscopic features of (IV) are consistent with the illustrated structure, *i.e.* a bis-insertion product, in which carbonyl insertion to give an acetyl group has taken place. A medium intensity band at 1 518 cm^{-1} in the i.r. spectrum is attributed to the ν_{CO} mode of a co-ordinated ketonic carbonyl group. An alternative structure for this complex is structure (IVc), which is related to that proposed[7] for the product of the reaction of phenylacetylene with $[MnMe(CO)_5]$. However, the ^{19}F n.m.r. spectrum of the complex is temperature dependent, a feature which is not consistent with the rigid ring system present in (IVc). The spectrum at room temperature shows a peak at 57.85 p.p.m. exhibiting fine structure due to two CF_3 groups, and singlets at 58.23 and 67.55 p.p.m. each due to one CF_3 group. On cooling to −90 °C the high-field signal broadens considerably with only a slight change in the appearance of the other two signals. Such changes can, however, be rationalised in terms of rapid interconversion of the two conformers (IVa) and (IVb). Attempts to obtain the limiting spectrum at lower tem-

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[3] W. C. Jackson, B. F. G. Johnson, J. W. Kelland, J. Lewis, and K. T. Schorpp, *J. Organometallic Chem.*, 1975, **88**, C17, and refs. therein.

[4] W. Hübel in I. Wender and P. Pino, ' Organic Syntheses via Metal Carbonyls,' Interscience, New York, 1968, pp. 285—331.

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

[6] A. Nakamura and S. Otsuka, ' Prospects in Organotransition Metal Chemistry,' ed. M. Tsutsui, Plenum Press, New York, 1975.

[7] B. L. Booth and R. G. Hargreaves, *J. Chem. Soc.* (*A*), 1970, 308.

peratures have so far been unsuccessful. The gross structure of the $\overline{\mathrm{FeC_5O}}$ ring is in some respects similar to that established[8] in the solid state by *X*-ray crystallography for the nickelacyclohepta-*cis*,*trans*,*cis*-triene $[\overline{\mathrm{NiC(CF_3)\!:\!C(CF_3)C(CF_3)\!:\!C(CF_3)C(CF_3)\!:\!C}}\mathrm{(CF_3)(PEt_3)_2}]$.

Similarities in the chemistry of the species $[\mathrm{FeX(CO)_2(\eta^5\text{-}C_5H_5)}]$ and $[\mathrm{MnX(CO)_5}]$ have been observed previously, and consequently the reaction of hfb with $[\mathrm{MnMe(CO)_5}]$ was studied. On photolysis high yields of a complex (V) were obtained. There was no evidence for the formation of bis-insertion products analogous to (IV). The ^{19}F spectrum of (V) showed two quartets $[J(\mathrm{CF_3\text{-}CF_3})$ 18.9 Hz], which clearly identified the product as a *cis* insertion adduct.[9] This contrasts with the thermal reaction of $[\mathrm{MnH(CO)_5}]$ with hfb which affords a *trans* insertion product.[10] The terminal carbonyl-stretching modes in the i.r. spectrum of (V) are similar in intensity but to higher wavelengths than those of $[\mathrm{MnMe(CO)_5}]$, confirming that no substantial change in the geometry of the molecule had occurred. However, the appearance of an extra weak band at 2 064 cm^{-1} and broadening of the strongest band indicates the loss of the four-fold axis of symmetry due to the geometry of the olefin ligand.[11]

The difference in the reactivity of $[\mathrm{MnMe(CO)_5}]$ and $[\mathrm{FeMe(CO)_2(\eta^5\text{-}C_5H_5)}]$ towards hfb contrasts with that of $[\mathrm{Mn(SC_6F_5)(CO)_5}]$ and $[\mathrm{Fe(SC_6F_5)(CO)_2(\eta^5\text{-}C_5H_5)}]$ where the manganese complex readily (60 °C) undergoes a double insertion reaction, although the iron compound requires prolonged irradiation.[12] In further contrast, a double insertion of $\mathrm{PhC{\equiv}CH}$ readily occurs with $[\mathrm{MnMe(CO)_5}]$[7], whereas $\mathrm{C_2(CO_2Me)_2}$ forms the cyclic carbonyl-inserted product $[\overline{\mathrm{MnC(CO_2Me)\text{=}C(CO_2Me)CO}}\mathrm{Me(CO)_4}]$.[7] Bis-insertion of hfb into the cobalt–allyl bond of $[\mathrm{Co(CO)_3(\eta^3\text{-}C_3H_5)}]$ has previously been observed,[13] but on extending this study to the reaction of $[\mathrm{Fe(\eta^1\text{-}C_3H_5)(CO)_2(\eta^5\text{-}C_5H_5)}]$ only the mono-insertion product (VI) was isolated in a photolytic reaction, which also gave ferrocene and traces of two other products which were not identified.

The appearance of two quartets $[J(\mathrm{CF_3\text{-}CF_3})$ 13.8 Hz] in the ^{19}F n.m.r. spectrum of (VI) confirms that *cis* insertion into the iron–carbon bond has occurred. The low-field quartet exhibits further coupling to two equivalent hydrogen atoms of the hydrocarbon residue.

In contrast, insertion of two molecules of hfb into the molybdenum–carbon bond of $[\mathrm{Mo(\eta^1\text{-}C_3H_5)(CO)_3(\eta^5\text{-}C_5H_5)}]$ was observed in a photolytic reaction, which affords complex (VII) in addition to a binuclear compound (VIII). The ^{19}F n.m.r. spectrum of (VII) resembles that of the ruthenium species (III) giving four peaks but the fine structure is different indicating that the insertion process involving the second molecule of hfb has occurred in a different manner to that found in (III). It is suggested that (VII) has the illustrated structure. In agreement, the ^{1}H n.m.r. spectrum shows a singlet at τ 4.55 (η^5-$\mathrm{C_5H_5}$) and resonances corresponding to a co-ordinated allyl system. The i.r. spectrum showed the expected single terminal carbonyl band, there being no evidence for a band due to an unco-ordinated double bond.

Elemental analyses and mass spectroscopy suggested that the second product of the reaction of $[\mathrm{Mo(\eta^1\text{-}C_3H_5)(CO)_3(\eta^5\text{-}C_5H_5)}]$ with hfb, the complex (VIII), had the molecular formula $[\mathrm{Mo_2(CO)_4(CF_3C_2CF_3)(\eta^5\text{-}C_5H_5)_2}]$. The presence in the ^{1}H and ^{19}F n.m.r. spectra of only singlet signals, and the observation of only terminal carbonyl bands in the i.r. spectrum together with the band at 1 495 cm^{-1} ($\mathrm{C{\equiv}C}$), suggested that (VIII) has the illustrated structure, in which one hfb molecule bridges two molybdenums. Structures of this type have been previously suggested[14] for complexes obtained in the reactions of $[\mathrm{MoR(CO)_3(\eta^5\text{-}C_5H_5)}]$ (R = Me, Et) with acetylenes $\mathrm{RC_2R'}$ (R = Ph, R′ = H, Ph). In a subsequent reaction, involving photolysis of $[\{\mathrm{Mo(CO)_3(\eta^5\text{-}C_5H_5)}\}_2]$ and hfb in methylene chloride solution, complex (VIII) was isolated in moderate yield (45%). This suggests that formation of (VIII) in reaction of the allyl complex involves a subsequent reaction of the metal–metal bonded species formed in a decomposition reaction.

The photolytic reaction of $[\mathrm{Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)}]$ and hfb, in contrast to the Fe and Mo systems, affords a dinuclear complex (IX), in which an η^3-$\mathrm{C_3H_5}$ ligand remains intact, and has not reacted with the acetylene. This is suggested by the appearance of the ^{1}H n.m.r. spectrum which is almost identical with that of the starting material, and by the ^{19}F n.m.r. spectrum which showed two complex multiplets with fine structure characteristic of a tetrakis(trifluoromethyl)metallacyclopentadiene. The complex $[\{\mathrm{Ni_2[C_4(CF_3)_4](C_5H_5)_2}\}_2]$ has a similar structure confirmed[15] by *X*-ray crystallography. An interesting feature of complex (IX) is the ability of a metallacyclopentadiene to act as an apparent five-electron donor analogous to the η^5-$\mathrm{C_5H_5}$ system.

These observations suggest that hfb has a significantly lower tendency to react with η^3-allyl groups when these are co-ordinated to an η^5-$\mathrm{C_5H_5Pd}$ system. However, insertion of hfb into the Pd–allyl linkage of $[\mathrm{PdCl(PMe_2Ph)(\eta^3\text{-}2\text{-}MeC_3H_4)}]$ has proved to be quite facile,[16]

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[8] J. Browning and B. R. Penfold, *J. Cryst. Mol. Struct.*, 1974, **4**, 347; J. Browning, M. Green, B. R. Penfold, J. L. Spencer, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1973, 31.

[9] P. K. Maples, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 2069; and refs. 18 and 23—25 cited therein.

[10] P. M. Treichel, E. Pitcher, and F. G. A. Stone, *Inorg. Chem.*, 1962, **1**, 511.

[11] J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, 1965, **4**, 389.

[12] J. L. Davidson and D. W. A. Sharp, *J.C.S. Dalton*, 1975, 2283.

[13] A. Greco, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 3476.

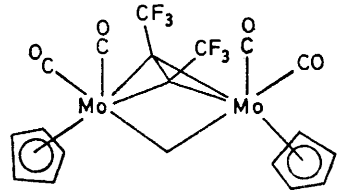
[14] A. Nakamura and N. Hagihara, *Nippon Kagaka Zasshi*, 1963, 344; see also R. J. Klinger, W. Butler, and M. D. Curtis, *J. Amer. Chem. Soc.*, 1975, **97**, 3535.

[15] J. L. Davidson, R. Herak, L. J. Manojlović-Muir, K. W. Muir, and D. W. A. Sharp, *J.C.S. Chem. Comm.*, 1973, 865.

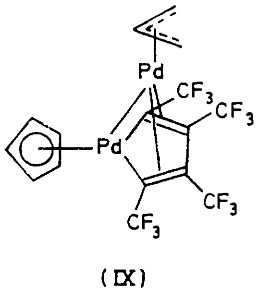
[16] T. G. Appleton, H. C. Clark, R. C. Poller, and R. J. Puddephatt, *J. Organometallic Chem.*, 1972, **39**, C13.

implying that other factors besides the metal can influence the reaction path followed.

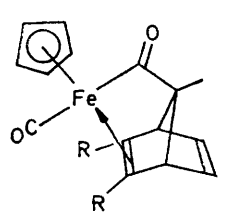
In view of the formation of (VI), the reaction of hfb with $[Fe(\eta^{1}-C_{5}H_{5})(CO)_{2}(\eta^{5}-C_{5}H_{5})]$ was examined. Ultraviolet irradiation of a hexane solution gave traces of ferrocene, but the major product was an orange air-sensitive complex which analysed as a 1 : 1 adduct (X). The i.r. spectrum showed bands at 1 980 and 1 668 cm^{-1}, indicating the presence of a ketonic carbonyl group in addition to a terminal carbonyl ligand. Comparison of the n.m.r. data for (X) with that of the adduct of hfb with nickelocene[17] suggests a close structural correspondence, and on this basis the illustrated structure for (X) is proposed. It is likely that a carbonyl insertion reaction of a σ-bonded Fe–C$_5$ system would readily occur under the reaction conditions, thus leading to the formation of an acyl complex.



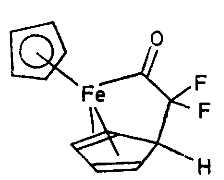
(VIII)



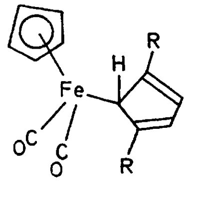
(IX)



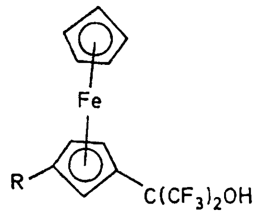
(X) R=CF$_3$
(XI) R=CO$_2$Me



(XII)



(XIII) R=C(CF$_3$)$_2$OH



(XIV) R=C(CF$_3$)$_2$OH
(XV) R=H

The reaction of $[Fe(\eta^{1}-C_{5}H_{5})(CO)_{2}(\eta^{5}-C_{5}H_{5})]$ with dimethyl acetylenedicarboxylate proceeds similarly to give the crystalline complex (XI) with spectroscopic features comparable to those of the hfb adduct.

Although a far more detailed investigation of some of these reactions is required before a mechanistic discussion is warranted, it is worth commenting briefly at this stage that formation of (X) and (XI) probably proceeds by a very different reaction path to that involved in the formation of (IV), (VI), and (VII). The reaction is probably an example of a Diels–Alder $(2 + 4)\pi$ addition reaction, in which the acetylene does not enter the co-ordination sphere in the initial stages of the reaction, the system $[Fe(\eta^{1}-C_{5}H_{5})(CO)_{2}(\eta^{5}-C_{5}H_{5})]$ functioning as a substituted cyclopentadiene.[18]

Although tetrafluoroethylene reacts very readily with $[Co(CO)_{3}(\eta^{3}-C_{3}H_{5})]$ to give an insertion product,[13] no analogous reactions were observed with the iron and molybdenum allyl systems. However, the photolytic reaction of C_2F_4 with $[Fe(\eta^{1}-C_{5}H_{5})(CO)_{2}(\eta^{5}-C_{5}H_{5})]$ gave, in addition to ferrocene, small quantities of a red crystalline complex (XII). Elemental analyses, mass spectroscopy, and the n.m.r. spectra of this complex suggested a molecular formula $[Fe\{COCF_{2}C_{5}H_{5}\}(\eta^{5}-C_{5}H_{5})]$. Such a reaction would require the unusual cleavage of the carbon–carbon double bond of tetrafluoroethylene, and, therefore, confirmation of this structure was sought by *X*-ray crystallography.[2]

A perspective view of a single molecule is shown in

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[17] D. W. McBride, E. Dudek, and F. G. A. Stone, *J. Chem. Soc.*, 1964, 1752.

[18] H. C. Clark, D. G. Ibbott, N. C. Payne, and A. Shaver, *J. Amer. Chem. Soc.*, **1975**, **97**, 3555.

Figure 2. The analysis confirms the nature of the complex, which crystallises as well-separated, neutral,

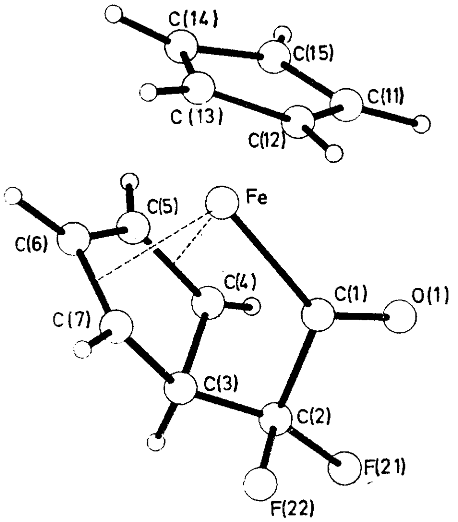


FIGURE 2 A perspective view of the complex (XII). The number assigned to the hydrogen atoms is the same as that of their parent carbon

monomeric molecules with effective, though not crystallographically required, C_s symmetry about a plane containing Fe,C(1)—(3). Interatomic distances (uncorrected for thermal motion) appear in Table 2.

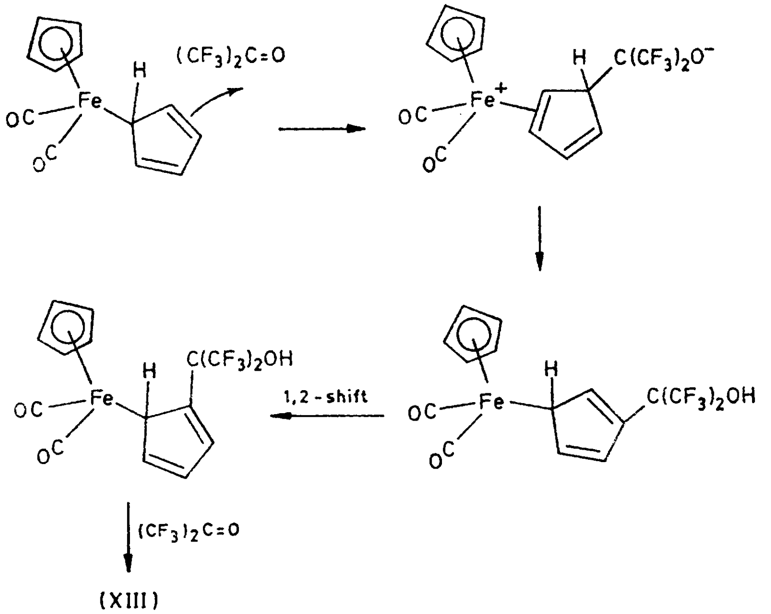
We again emphasise the effectiveness of co-ordination of the diene fragment by citing the C(4)–C(5) and C(6)–C(7) lengths, statistically comparable to, and even, in the latter case, slightly longer than, the accepted $C(sp^2)$–$C(sp^2)$ single-bond separation (1.42 Å). Unspecified internuclear distances and all interbond angles for this complex are as expected.

TABLE 2

Compound (XII) $C_{12}H_{10}OF_2Fe$: bond lengths (Å)

Fe–C(11)	2.087(9)	C(1)–O(1)	1.213(12)
Fe–C(12)	2.102(11)	C(1)–C(2)	1.543(14)
Fe–C(13)	2.122(10)	C(2)–F(21)	1.374(9)
Fe–C(14)	2.124(11)	C(2)–F(22)	1.383(12)
Fe–C(15)	2.112(12)	C(2)–C(3)	1.491(16)
Fe–C(1)	1.990(10)	C(3)–C(4)	1.514(14)
Fe–C(4)	2.143(11)	C(4)–C(5)	1.396(12)
Fe–C(5)	2.035(13)	C(5)–C(6)	1.423(13)
Fe–C(6)	2.027(10)	C(6)–C(7)	1.432(15)
Fe–C(7)	2.139(8)	C(7)–C(3)	1.513(12)
C(11)–C(12)	1.434(12)	C(3)–H(3)	0.83(14)
C(12)–C(13)	1.388(12)	C(4)–H(4)	0.90(11)
C(13)–C(14)	1.411(20)	C(5)–H(5)	0.91(10)
C(14)–C(15)	1.447(14)	C(6)–H(6)	1.02(8)
C(15)–C(11)	1.413(19)	C(7)–H(7)	1.04(10)

The molecules hfb and C_2F_4, although electronegatively substituted, are symmetrical, and it was speculated that the highly polar molecule hexafluoroacetone would readily react with $[Fe(\eta^1\text{-}C_5H_5)(CO)_2(\eta^5\text{-}C_5H_5)_7]$. This was confirmed. At low temperatures a facile reaction occurred without irradiation



SCHEME

The iron atom is bonded to an essentially planar η^5-C_5 ring at 2.087(9)—2.124(11) Å, a bridging carbonyl function C(1)O(1), with Fe–C(1) 1.990(10) Å, and an η^4-C_5H_5 group at two separations of *ca.* 2.03 Å [Fe–C(5),Fe–C(6)] and two of *ca.* 2.14 Å [Fe–C(4),Fe–C(7)]. This latter ring is linked to the carbonyl through a single CF_2 moiety.

to give the 1 : 2 adduct (XIII). The i.r. spectrum of the adduct showed a strong hydroxyl band suggesting the presence of the group $C(CF_3)_2OH$. Insertion of hexafluoroacetone into C–H bonds of cyclopentadienyl groups has been observed before,[5,19-21] and this, together with the nature of the ^1H and ^{19}F n.m.r.

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[19] N. V. Raghavan and R. E. Davis, *J. Cryst. Mol. Struct.*, 1975, **5**, 163.

[20] M. Green and B. Lewis, *J.C.S. Chem. Comm.*, 1973, 114.

[21] M. I. Bruce, F. G. A. Stone, and B. J. Thomson, *J. Organometallic Chem.*, 1974, **77**, 77.

spectra and the presence in the i.r. of two terminal carbonyl bands, suggested the illustrated structure (XIII) containing a 1,3-disubstituted C_5 ring. U.v. irradiation of (XIII) led to loss of carbon monoxide and formation of (XIV), a ferrocene derivative closely related to (XV).[21] It is suggested that (XIII) is formed by the sequence of reactions illustrated in the Scheme, in which initial electrophilic attack (*exo* or *endo*) occurs by hexafluoroacetone on an unco-ordinated double bond. Proton transfer, followed by a 1,2-shift of the $Fe(CO)_2(\eta\text{-}C_5H_5)$ group, and further reaction with hexafluoroacetone leads to the observed product.

EXPERIMENTAL

^1H and ^{19}F n.m.r. spectra were recorded on a Varian Associates HA 100 spectrometer at 100 and 94.1 MHz, respectively. ^{19}F shifts are relative to CCl_3F (0.00 p.p.m.), positive values indicating a shift to high field. I.r. spectra were measured with a Perkin-Elmer 457 instrument using carbon tetrachloride or hexane solutions. Solvents were dried and distilled under nitrogen, and all operations were conducted in an atmosphere of dry, oxygen-free nitrogen. Analytical data are given in Table 3.

TABLE 3

Analytical [a] and physical data for the complexes

Complex	Colour	M.p.(θc/°C)	C	H	F	*M* [b]
(I)	Black	161—162	38.4(38.6)	1.9(1.6)		622(622)
(II)	White	42				375(375)
(III)	White	103—105	33.1(33.3)	1.3(1.2)		519(519)
(IV)	Brown	124—125	37.9(36.9)	2.1(1.6)	47.9(47.7)	488(488)
(V)	White	93—94	32.1(32.3)	0.7(0.8)		372(372)
(VI)	Yellow	87	44.3(44.3)	3.0(2.8)	32.5(32.4)	352(352)
(VII)	Yellow	173—176	36.5(36.8)	1.9(1.8)	41.6(41.2)	554(554)
(VIII)	Red-brown	>250 [c]	36.3(36.2)	1.8(1.7)	19.4(19.1)	596(596)
(IX)	Dark red	119—120 [c]	29.0(29.7)	1.6(1.6)	36.1(35.5)	642(642)
(X)	Orange-red	148—151	46.8(47.5)	2.6(2.5)	27.7(28.2)	404(404)
(XI)	Red	161—163	55.5(56.2)	4.2(4.2)		384(384)
(XII)	Dark red	170 [c]	54.8(54.6)	3.7(3.8)	14.2(14.4)	264(264)
(XIII)	Orange-brown	97—99	37.8(37.6)	2.1(1.8)	41.1(39.7)	
(XIV)	Yellow	97.5 [c]	36.9(37.0)	2.0(1.9)		518(518)

[a] Calc. values in parentheses. [b] Mass spectrometry. [c] Decomp.

Reaction of Hexafluorobut-2-yne with (a) *Dicarbonyl(cyclopentadienyl)iron Dimer.*—A solution of $[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ (0.28 g, 0.79 mmol) in dichloromethane (25 cm³) was placed in a thick glass tube (80 cm³ fitted with a Westef Stopcock), and the solution degassed. Hexafluorobut-2-yne (2.0 g, 12.4 mmol) was condensed (−196 °C) into the tube, which was then irradiated (20 cm from a 250 watt Hanovia u.v. lamp) for 180 h. The volatile material was removed *in vacuo*, and the residue dissolved in dichloromethane. Addition of hexane and cooling (−20 °C) gave black *crystals* of (I) (98 mg, 20%), $\nu(CCl_4)$ 1 985s (CO), 1 670m (CO), 1 268m and 1 212s (CF) cm⁻¹; ^1H n.m.r. resonances ($CDCl_3$) at τ 5.7 (s, 5 H, C_5H_5) and 6.14 (s, 5 H, C_5H_5); ^{19}F n.m.r. resonances (CH_2Cl_2) at 44.52 (q, 6 F, J_{FF} 14.0) and 57.13 p.p.m. (q, 6 F, J_{FF} 14 00 Hz).

Chromatography of the residue on a Florisil packed column, using hexane as eluant, gave three weak bands, which could not be identified due to decomposition.

(b) *Dicarbonyl(cyclopentadienyl)ruthenium Dimer.*—In a similar manner a solution of $[\{Ru(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ (0.15 g, 0.34 mmol) and hexafluorobut-2-yne (2.0 g, 12.4 mmol) in diethyl ether (20 cm³) was irradiated (60 h), the reaction being followed by i.r. spectroscopy. Formation of (II) was observed, followed by further reaction to give complex (III). Filtration of the reaction mixture followed by partial removal of the solvent *in vacuo*, and addition of hexane, gave on cooling (−20 °C) white *crystals* of (III) (0.15 g, 58%), $\nu(CCl_4)$ 2 043s (CO), 1 671w (C=C), 1 290m, 1 272m, 1 265m, 1 256s, 1 195m, 1 180m, 1 166m, 1 160m, and 1 144m (CF) cm⁻¹; ^1H n.m.r. resonances ($CDCl_3$) at τ 5.45 (s, 5 H, C_5H_5) and 6.35 [q, 1 H, $CH(CF_3)$, J_{HF} 8.0 Hz]; ^{19}F n.m.r. resonances (CH_2Cl_2) at 57.88 [d, 3 F, $CH(CF_3)$, J_{HF} 8.0], 59.02 (q, 3 F, CF_3, J_{FF} 8.4), 61.22 (q, 3 F, CF_3, J_{FF} 5.45 Hz), and 64.63 p.p.m. (m, 3 F, CF_3).

Reaction of Dicarbonyl(cyclopentadienyl)hydridoruthenium with Hexafluorobut-2-yne.—A solution of the unstable complex $[RuH(CO)_2(\eta^5\text{-}C_5H_5)]$ (*ca.* 1.0 mmol) and hexafluorobut-2-yne (1.0 g, 6.2 mmol) in octane (20 cm³) was allowed to react (4 d, 20 °C). The reaction mixture was filtered through a Florisil column, followed by removal of the solvent *in vacuo*. Sublimation (35 °C on to −78 °C probe) *in vacuo* gave white *crystals* of (II), m.p. 42 °C, ν(hexane) 2 050s, 2 000s (CO), 1 615w (C=C), 1 240ms, 1 142ms, and 1 136ms (CF) cm⁻¹; ^1H n.m.r. resonances τ 5.50 (s, 5 H, C_5H_5) and 4.30 (qq, 1 H, J_{HF} 2.3 and 8.2 Hz); ^{19}F n.m.r. resonances (CH_2Cl_2) at 56.67 (dq, 3 F, J_{FF} 2.3, J_{HF} 8.15) and 60.48 p.p.m. (q, 3 F, J_{FF} 2.3 Hz).

The above reaction was repeated, but the reaction mixture was also irradiated. The formation of (II) was observed (i.r. spectroscopy), which rapidly transformed into (III).

The Reaction of Dicarbonyl(cyclopentadienyl)methyliron with Hexafluorobut-2-yne.—A solution of $[FeMe(CO)_2(\eta^5\text{-}C_5H_5)]$ (0.15 g, 0.8 mmol) and hexafluorobut-2-yne (1.0 g, 6.2 mmol) in hexane (25 cm³) was irradiated (9 d) at room temperature. Volatile material was removed *in vacuo*, and the residue chromatographed on a Florisil packed column. Elution with light petroleum (b.p. 40—60 °C) gave unreacted iron complex followed by a red-brown fraction. Removal of the solvent, followed by sublimation (−78 °C probe) and recrystallisation (−78 °C) from hexane gave brown *crystals* of (IV) (45 mg, 11%), ν(hexane) 1 610w (C=C), 1 518m (C=O), 1 226s, 1 210sh, 1 202s, 1 180s, 1 160s, 1 152sh, and 1 140m (CF) cm⁻¹. ^1H n.m.r. resonances ($CDCl_3$) at τ 5.10 (s, 5 H, C_5H_5) and 7.91 (s, 3 H, $COCH_3$); ^{19}F n.m.r. resonances (CH_2Cl_2) at 57.85 (m, 6 F), 58.23 (s, 3 F), and 67.55 p.p.m. (s, 3 F).

Reaction of Pentacarbonylmethylmanganese with Hexafluorobut-2-yne.—Irradiation (20 h) of a solution of $[MnMe(CO)_5]$ (0.3 g, 0.14 mmol) and hexafluorobut-2-yne (2.0 g, 12.4 mmol) in hexane (40 cm^3) gave on partial removal of the solvent, followed by cooling (−20 °C), white *crystals* of (V) (0.42 g, 82%), ν(hexane) 2 120m, 2 064wm, 2 036vs, 1 999s (CO), 1 270m, 1 230m, 1 174wm, 1 155m, and 1 135m (CF) cm^{-1}; ^{1}H n.m.r. resonance (CDCl$_3$) at τ 7.72 (s, 3 H, CH_3); ^{19}F n.m.r. resonances (CH$_2$Cl$_2$) at 44.76 (q, 3 F, CF$_3$, J_{FF} 18.8) and 58.29 p.p.m. (q, 3 F, CF$_3$, J_{FF} 18.9 Hz).

Reaction of Allyldicarbonyl(cyclopentadienyl)iron with Hexafluorobut-2-yne.—Similarly, irradiation (24 h, room temperature) of a solution of [Fe(η^1-C$_3$H$_5$)(CO)$_2$(η^5-C$_5$H$_5$)] (0.25 g, 1.1 mmol) and hexafluorobut-2-yne (2.0 g, 12.4 mmol) in hexane (25 cm^3) was followed by removal of volatile material and chromatography of the residue. Elution with light petroleum gave ferrocene. Elution with diethyl ether gave orange *crystals* of (VI) (0.034 g, 8%), ν(CCl$_4$) 1 992s (CO), 1 285m, 1 262w, 1 240m, 1 158m, and 1 135wm (CF) cm^{-1}; ^{1}H n.m.r. resonances (CDCl$_3$) at τ 5.05 (m, 1 H), 5.30 (s, 5 H, C$_5$H$_5$), 6.40 (m, 1 H), 6.85 (m, 1 H), 6.95 (d, 1 H, J_{HH} 9.0), and 7.80 (d, 1 H, J_{HH} 13.0 Hz); ^{19}F n.m.r. resonances (CH$_2$Cl$_2$) at 51.23 (qt, 3 F, J_{FF} 13 8, J_{HF} 3.65) and 59.92 p.p.m. (q, 3 F, J_{FF} 13.8 Hz).

Reaction of Allyltricarbonyl(cyclopentadienyl)molybdenum with Hexafluorobut-2-yne.—Ultraviolet irradiation (18 h, room temperature) of a solution of [Mo(η^1-C$_3$H$_5$)(CO)$_3$-(η^5-C$_5$H$_5$)] (0.30 g, 1.1 mmol) and hexafluorobut-2-yne (2.0 g, 12.4 mmol) in hexane (25 cm^3) gave, on column chromatography of the hexane-soluble part of the reaction mixture and elution with diethyl ether–hexane (50 : 50), a yellow band. Removal of the solvent and recrystallisation (−20 °C) from dichloromethane–hexane gave yellow *crystals* of (VII) (70 mg, 12%), ν(hexane) 2 030s (CO), 1 292w, 1 270m, 1 248m, 1 205wm, 1 185w, 1 158m, 1 139wm, 1 130m, and 1 117wm (CF) cm^{-1}; ^{1}H n.m.r. resonances (CDCl$_3$) at τ 3.48 (m, 1 H), 4.32 (d, 1 H, J_{HH} 17.0), 4.55 (s, 5 H, C$_5$H$_5$), 4.60 (d, 1 H, J_{HH} 14.0), 7.06 (q, 1 H, J 9.9), and 7.40 (q, 1 H, J 9.75 Hz); ^{19}F n.m.r. resonances (CH$_2$Cl$_2$) at 49.91 (d, CF$_3$, J_{HF} 9.75), 52.13 (q, 3 F, J_{FF} 11.6), 53.09 (q, 3 F, J 12.2 Hz), and 54.27 p.p.m. (s, 3 F).

A red band on the chromatography column was eluted with diethyl ether–dichloromethane (50 : 50). Addition of hexane, followed by partial removal of solvent and cooling (−20 °C), gave orange-red *crystals* of (VIII) (75 mg, 21%), ν(CCl$_4$) 2 030s, 2 000m, 1 989vs, 1 970msh, 1 870m (CO), 1 495w (C=C), 1 270wm, 1 182m, 1 132m, and 1 138m (CF) cm^{-1}; ^{1}H n.m.r. resonances (CDCl$_3$) at τ 4.60 (s, 10 H, C$_5$H$_5$); ^{19}F n.m.r. resonance (CH$_2$Cl$_2$) at 46.30 p.p.m. (s, 6 F, CF$_3$). Extraction with dichloromethane of the non-hexane-soluble part of the original reaction product gave on crystallisation low yields of [{Mo(CO)$_3$(η^5-C$_5$H$_5$)}$_2$].

Reaction of Tricarbonyl(cyclopentadienyl)molybdenum Dimer with Hexafluorobut-2-yne.—A solution of [{Mo(CO)$_3$-(η^5-C$_5$H$_5$)}$_2$] (0.20 g, 0.4 mmol) and hexafluorobut-2-yne (2.0 g, 12.4 mmol) in dichloromethane (20 cm^3) was irradiated (3 d). Recrystallisation of the product from dichloromethane–hexane gave (VIII) (0.11 g, 45%).

Reaction of η^3-Allyl(η^5-cyclopentadienyl)palladium with Hexafluorobut-2-yne.—A solution of [Pd(η^3-C$_3$H$_5$)(η^5-C$_5$H$_5$)] (0.30 g, 1.4 mmol) and hexafluorobut-2-yne (2.0 g, 12.4 mmol) in hexane (20 cm^3) was irradiated (60 h, room temperature). Recrystallisation of the product from dichloromethane–hexane gave black *crystals* of (IX) (0.29 g, 64%), ν(CCl$_4$) 1 219m, 1 197m, and 1 177m (CF) cm^{-1}; ^{1}H n.m.r. resonances (CDCl$_3$) at τ 4.15 (s, 5 H, C$_5$H$_5$), 4.50 (m, 1 H), 5.66 (d, 2 H, J_{HH} 6.25), and 6.60 (d, 2 H, J_{HH} 11.3 Hz); ^{19}F n.m.r. resonances 48.54 (m, 6 F, α-CF$_3$) and 54.94 p.p.m. (m, 6 F, β-CF$_3$).

Reaction of Dicarbonyl(η^1-cyclopentadienyl)(η^5-cyclopentadienyl)iron with (a) *Hexafluorobut-2-yne.*—Irradiation (30 h, room temperature) of a solution of [Fe(η^1-C$_5$H$_5$)(CO)$_2$-(η^5-C$_5$H$_5$)] (0.30 g, 1.2 mmol) and hexafluorobut-2-yne (1.0 g, 6.2 mmol) in hexane (20 cm^3) gave orange crystals. These were collected and recrystallised (−20 °C) from dichloromethane–hexane to give *crystals* of (X) (0.40 g, 78%), ν(CHCl$_3$) 1 980s, 1 668s (CO), 1 305s, 1 276m, 1 240w, and 1 189s (CF) cm^{-1}; ^{1}H n.m.r. resonances (CDCl$_3$) at τ 4.50 (s, 5 H, C$_5$H$_5$), 4.50 (m, 1 H), 6.22 (m, 1 H), 6.40 (m, 1 H), and 7.75 (m, 1 H); ^{19}F n.m.r. resonances (CH$_2$Cl$_2$) at 61.1 (m, 3 F, CF$_3$) and 61.7 p.p.m. (m, 3 F, CF$_3$).

The hexane-soluble fraction was sublimed after solvent removal to give ferrocene (15 mg).

(b) *Dimethyl Acetylenedicarboxylate.*—A similar reaction (20 h irradiation) of [Fe(η^1-C$_5$H$_5$)(CO)$_2$(η^5-C$_5$H$_5$)] (0.3 g, 1.2 mmol) and C$_2$(CO$_2$Me)$_2$ (0.5 g, 3.5 mmol) gave *crystals* of (XI) (0.18 g, 39%), ν(CHCl$_3$) 1 970vs, 1 720s, 1 640s (CO) cm^{-1}; ^{1}H n.m.r. resonances (CDCl$_3$) at τ 4.50 (m, 1 H), 5.15 (m, 1 H), 5.25 (s, 5 H, C$_5$H$_5$), 6.10 (s, 3 H, *Me*), 6.20 (s, 3 H, *Me*), and 6.30 (m, 1 H).

(c) *Tetrafluoroethylene.*—A solution of [Fe(η^1-C$_5$H$_5$)(CO)$_2$-(η^5-C$_5$H$_5$)] (0.16 g, 0.7 mmol) and tetrafluoroethylene (1.0 g, 10.0 mmol) in hexane (25 cm^3) was irradiated (50 h, room temperature). The red crystals which had deposited on the walls of the reaction vessel were collected and recrystallised (−20 °C) from dichloromethane–hexane to give dark red *crystals* of (XII) (10 mg, 8%), ν(CCl$_4$) 1 640s, 1 623s (CO), 1 124m, 1 074m, and 1 055 (CF) cm^{-1}; ^{1}H n.m.r. resonances (CDCl$_3$) at τ 3 35 (m, 2 H), 5.38 (s, 5 H, C$_5$H$_5$), 6.90 (m, 2 H), and 7.15 (m, 1 H); ^{19}F n.m.r. resonances (CH$_2$Cl$_2$) at 149.10 p.p.m. (apparent t).

(d) *Hexafluoroacetone.*—An excess of hexafluoroacetone (1.0 g, 6.0 mmol) was condensed (−196 °C) into a tube (80 cm^3) containing a solution of [Fe(η^1-C$_5$H$_5$)(CO)$_2$(η^5-C$_5$H$_5$)] (0.30 g, 1.4 mmol) in hexane (20 cm^3). The tube and contents were allowed to warm to room temperature, when a rapid reaction occurred. Volatile material was removed *in vacuo*, and the residue recrystallised from dichloromethane–hexane to give orange *crystals* of (XIII) (0.33 g, 46%), ν(CCl$_4$) 3 551m (OH), 2 026s, 1 973s (CO), 1 270m, 1 235m, 1 214m, and 1 150m (CF) cm^{-1}; ^{1}H n.m.r. resonances (CDCl$_3$) at τ 3.04 (s, 1 H), 4.50 (s, 2 H), 5.62 (s, 5 H, C$_5$H$_5$), and 6.75 (s, 2 H); ^{19}F n.m.r. resonances (CH$_2$Cl$_2$) at 75.30 (q, 6 F, CF$_3$, J_{FF} 9.8) and 76.89 p.p.m. (q, 6 F, CF$_3$, J_{FF} 9.8 Hz).

(e) *Hexafluoroacetone (photochemical).*—Irradiation (6 h, room temperature) of a solution of (XIII) (0.10 g, 0.24 mmol) in diethyl ether (30 cm^3) gave a pale yellow solution. Partial removal of solvent followed by addition of hexane and cooling (−20 °C) gave *crystals* of (XIV) (63 mg, 63%), ν(CCl$_4$) 3 532m (OH), 1 271s, 1 240vs, 1 221vs, 1 209s, 1 163s, 1 121m, and 1 104m (CF) cm^{-1}; ^{1}H n.m.r. resonances (CDCl$_3$) at τ 5.25 (m, 1 H), 5.30 (m, 2 H), 5.52 (s, 5 H, C$_5$H$_5$), and 6.74 (s, 2 H); ^{19}F n.m.r. resonance (CH$_2$Cl$_2$) 74.33 p.p.m. (s, 12 F, CF$_3$).

Molecular Structure Determinations.—The single-crystal analyses of both compounds followed similar lines and will therefore be described for (I) only, data in square brackets representing differences in respect of compound (XII).

The species was recrystallised from dichloromethane–n-hexane as black [dark red] transparent needles elongated along [100] [irregular blocks]. A single crystal, *ca.* 0.01 × 0.01 × 0.03 [0.02 × 0.02 × 0.03] cm was selected for analysis, and approximate unit-cell parameters determined from oscillation and equi-inclination Weissenberg photographs.

The specimen was then transferred to a computer-controlled Syntex $P2_1$ four-circle diffractometer and accurate unit cell and intensity data recorded following a well-established procedure.[22] Details applicable to the present experiment were as follows: 15 reflections, $27° > 2\theta > 11°$ [$19° > 2\theta > 6°$] were used in the centring program; for data collection Mo-K_α radiation ($\lambda_{\alpha1} = 0.709\,26$, $\lambda_{\alpha2} = 0.713\,54$ Å) and a θ—2θ scan in 96 steps were used; the scan rate was determined from an initial 2 s peak count and varied from 0.0337° s^{-1} (for counts $\leqslant$150) to 0.4993° s^{-1} (counts $\geqslant$1 500 [2 000]). Data were limited by the criteria $50.0° \geqslant 2\theta \geqslant 2.9°$ and $0 \leqslant h \leqslant 9$, $0 \leqslant k \leqslant 13$, $0 \leqslant l \leqslant 20$ [$0 \leqslant h \leqslant 12$, $0 \leqslant k \leqslant 8$, $\bar{1}\bar{1} \leqslant l \leqslant 11$ with equivalent $0kl$ and $0kl$ reflection intensities afterwards merged]; three check reflections were monitored once every 23. Subsequent analysis of their net counts as individual functions of time revealed that whilst (I) remained intact in the *X*-ray beam, (XII) had decomposed by *ca.* 22% over the *ca.* 33 h exposure. An exponential 22% decay correction was therefore applied;[23] of the 1 824 [773] independent reflections collected, 1 630 [740] were deemed significantly intense having $I \geqslant 2.5\sigma(I)$, and were used to solve and refine the structure; no absorption correction was applied.

TABLE 4

Compound (I) $C_{20}H_{10}O_2F_{12}Fe_2$: final positional parameters (fractional, × 10^4, Fe × 10^5) for the $O_2F_{12}Fe_2$ fraction, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Fe(1)	15 015(10)	−4 221(7)	−5 752(7)
Fe(2)	−11 352(9)	840(7)	−5 047(6)
O(1)	485(8)	−2 359(5)	−1 032(5)
O(4)	533(7)	2 407(5)	85(4)
F(21)	1 128(6)	885(4)	−2 702(3)
F(22)	1 128(7)	−654(4)	−2 470(3)
F(23)	−817(6)	86(5)	−2 682(3)
F(31)	399(7)	2 731(5)	−1 767(5)
F(32)	−1 313(7)	1 862(4)	−2 234(3)
F(33)	−1 579(7)	2 659(4)	−1 096(4)
F(51)	−1 630(7)	1 982(5)	1 137(4)
F(52)	−1 469(8)	637(5)	1 775(4)
F(53)	277(8)	1 619(7)	1 805(4)
F(61)	735(9)	−1 790(5)	878(4)
F(62)	−1 100(6)	−1 147(5)	1 393(4)
F(63)	908(7)	−632(6)	1 787(3)

Crystal Data.—(I), $C_{20}H_{10}F_{12}Fe_2O_2$, $M = 613.0$, Orthorhombic, $a = 9.446(3)$, $b = 13.708(6)$, $c = 15.748(6)$ Å, $U = 2\,039(1)$ Å^3, $D_m = 2.00$ (flotation), $Z = 4$, $D_c = 2.025$, $F(000) = 1\,224$. Mo-K_α radiation, $\bar{\lambda} = 0.710\,69$ Å; μ(Mo-K_α) = 16.2 cm^{-1}. Space group $P2_12_12_1$.

(XII), $C_{12}H_{10}F_2FeO$, $M = 264.8$, Monoclinic, $a = 12.204(3)$, $b = 8.386(4)$, $c = 11.262(3)$ Å, $\beta = 120.11(2)°$, $U = 997(1)$ Å^3, $D_m = 1.76$ (flotation), $Z = 4$, $D_c = 1.763$, $F(000) = 936$. Mo-K_α radiation, μ(Mo-K_α) = 15.5 cm^{-1}. Space group *Cc*.

Observed data were corrected for Lorentz and polarisation effects, and the structure solved *via* a three-dimensional Patterson synthesis (Fe atoms), full-matrix least-squares refinement, and electron-density difference Fourier syntheses (F, O, and C atoms). Both compounds crystallise in acentric space groups. Whilst a significant difference in *R* factors was found for refinements of the two possible enantiomorphs of (I) (results presented correspond to the lowest *R*), no such conclusion could be made concerning (XII).

TABLE 5

Compound (I) $C_{20}H_{10}O_2F_{12}Fe_2$: final carbon atom positional (fractional co-ordinate × 10^4) and isotropic thermal * (Å^2 × 10^4) parameters

Atom	*x*	*y*	*z*	U_j
C(1)	846(9)	−1 585(6)	−865(5)	380(19)
C(2)	371(7)	370(5)	−1 350(4)	267(16)
C(3)	−50(8)	1 293(6)	−1 024(4)	266(16)
C(4)	266(8)	1 568(6)	−120(5)	335(18)
C(5)	−121(7)	810(5)	509(5)	286(15)
C(6)	277(7)	−183(5)	403(4)	282(16)
C(211)	415(9)	169(6)	−2 287(5)	385(19)
C(311)	−626(10)	2 134(7)	−1 533(6)	460(21)
C(511)	−717(10)	1 247(7)	1 321(6)	506(23)
C(611)	181(9)	−924(7)	1 100(6)	440(21)
C(11) †	3 532(14)	−782(19)	−1 072(8)	468(30)
C(12) †	3 293(11)	277(9)	−1 155(7)	316(23)
C(13) †	3 135(10)	671(7)	−323(6)	289(22)
C(14) †	3 253(12)	−32(9)	190(7)	445(26)
C(15) †	3 474(13)	−958(9)	−146(8)	460(28)
C(101) ‡	3 328(22)	−658(15)	195(13)	180(43)
C(102) ‡	3 549(19)	−1 026(13)	−667(11)	113(37)
C(103) ‡	3 446(22)	−240(15)	1 216(12)	180(43)
C(104) ‡	3 202(23)	553(17)	−629(15)	305(52)
C(105) ‡	3 139(25)	112(19)	383(15)	329(55)
C(21)	−3 276(8)	443(6)	−468(5)	455(18)
C(22)	−3 019(8)	−320(6)	94(5)	417(18)
C(23)	−2 474(9)	−1 108(6)	−356(5)	472(21)
C(24)	−2 447(9)	−838(7)	−1 209(6)	473(21)
C(25)	−2 932(9)	111(7)	−1 288(5)	481(20)

* Defined as $\exp\{-8\pi^2U_j(\sin^2\theta)/\lambda^2\}$. † These atoms carry 71% occupancy. ‡ These atoms carry 29% occupancy.

TABLE 6

Compound (XII) $C_{12}H_{10}OF_2Fe$: final positional parameters (fractional co-ordinate × 10^4, Fe × 10^5) of non-hydrogen atoms

Atom	*x*	*y*	*z*
Fe	0	−20 492(10)	0
C(1)	1 286(8)	−408(11)	282(9)
O(1)	2 296(5)	−462(8)	318(6)
C(2)	847(8)	1 244(10)	484(8)
F(21)	1 741(5)	1 940(7)	1 688(5)
F(22)	704(7)	2 281(7)	−539(7)
C(3)	−362(8)	888(11)	459(10)
C(4)	−83(8)	−475(11)	1 452(9)
C(5)	−1 074(8)	−1 576(11)	874(10)
C(6)	−1 783(8)	−1 331(12)	−571(10)
C(7)	−1 202(8)	−14(11)	−853(10)
C(11)	1 467(8)	−3 693(11)	586(8)
C(12)	891(8)	−3 384(9)	−857(8)
C(13)	−376(8)	−3 821(11)	−1 502(9)
C(14)	−622(12)	−4 448(13)	−497(13)
C(15)	532(12)	−4 369(15)	821(12)

For both compounds, η^5-cyclopentadienyl hydrogen atoms were introduced in calculated positions with r(C–H) 1.00 Å, U_H 0.05 Å^2, but for (XII) hydrogen atoms of the η^4-C_5 ring were located from a ΔF map, and subsequently refined. Weights were applied according to $w = (xy)^{-1}$ with $x = b/\sin\theta$ if $\sin\theta < b$, $x = 1$ if $\sin\theta \geqslant b$, and $y = F_o/a$ if $F_o > a$, $y = 1$ if $F_o \leqslant a$, in which a and b took values 50.0 and 0.26 [0.27] respectively.

Mixed refinement [(I): Fe, F, and O atoms anisotropic, C isotropic; (XII): Fe, F, O, and C anisotropic, H iso-

[22] A. G. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

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

tropic] of both compounds continued until the mean shift-to-error ratio of refined parameters was <0.02. An ultimate difference Fourier showed a maximum of *ca.* 0.4 [0.2] e$Å^{-3}$. Final unweighted and weighted R values were 0.04 and 0.046 [0.028 and 0.038].

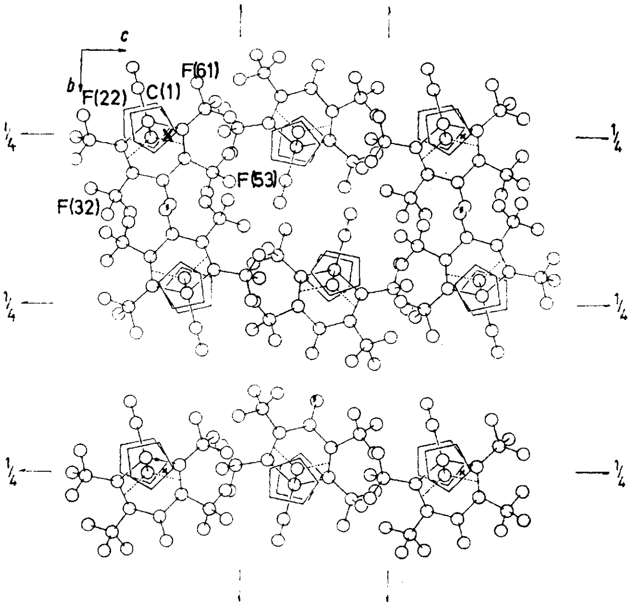

FIGURE 3 View of the crystal packing of (I), looking along the *a* axis, towards the origin (marked ×)

Atomic scattering factors for neutral atoms were taken from ref. 24 for iron and fluorine, ref. 25 for oxygen and carbon (all appropriately corrected for anomalous dispersion [26]), and ref. 27 for hydrogen. Tables 4—6 list the derived non-hydrogen parameters and Figures 3 and 4 demonstrate the crystal packings. Tables of observed and calculated structure factors, hydrogen atom parameters, additional bond lengths for (I), and anisotropic thermal parameters for (I) and (XII) have been deposited as Supplementary Publication No. SUP 21764 (20 pp., 1 microfiche).*

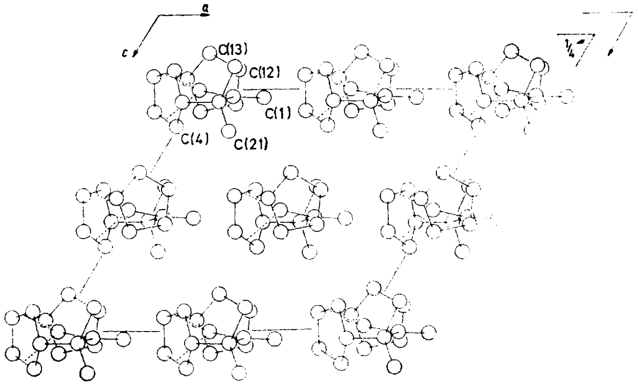

FIGURE 4 Packing diagram of (XII), looking along the *b* axis towards the origin

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index ssue.

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