Reactions of Co-ordinated Ligands. Part V.[1] The Addition of Tetrafluoroethylene to Tricarbonyl(diene)iron, Tricarbonyl(*trans*-cinnamaldehyde)iron, and Tricarbonyl(*o*-styryldiphenylphosphine)iron Complexes †

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Tetrafluoroethylene reacts with tricarbonyl(buta-1,3-diene, *trans*-penta-1,3-diene, isoprene, or 2,3-dimethylbuta-1,3-diene)iron on u.v. irradiation to afford 1 : 1 adducts formulated as π-allylic iron(II) complexes, in which the C_2F_4 links the metal and diene, the linking reaction occurring preferentially at the least-substituted end of the diene. Similar reactions are observed with tricarbonyl(cyclohexa-1,3-diene or bicyclo[4.2.0]octa-1,3-diene)iron to give π-allylic adducts. The corresponding reaction with tricarbonyl(cyclo-octa-1,3-diene)iron affords two complexes, a π-allylic adduct and a tetracarbonylferracyclopentane. Tetra- and tri-carbonyl(*trans*-cinnamaldehyde)iron react with C_2F_4 to give tetracarbonylferracyclopentanes, in which the aldehyde and phenyl groups have a relative *cis*-configuration. Tricarbonyl(norbornadiene)iron and tricarbonyl(*o*-styryldiphenylphosphine)iron also form adducts with C_2F_4, the former giving a nortricyclene tetracarbonyl species. The n.m.r. spectra of these complexes and possible modes of formation are discussed.

In previous papers in this series the reaction of neutral electrophilic molecules with tricarbonyl(cyclobutadiene and tetramethylcyclobutadiene)iron,[2] tricarbonyl(cycloheptatriene)iron,[3] tricarbonyl(*N*-methoxycarbonylazepine)iron,[4] and tricarbonyl(cyclo-octatetraene)iron [3] have been described. In the photochemical reaction of fluoro-olefins with, for example, $[Fe(\pi\text{-}C_4Me_4)(CO)_3]$ a π-tetramethylcyclobutenyl complex is formed, in which the fluoro-olefin links the C_4 ring and iron atom, a reaction which involves a formal *endo*-attack and a change in the oxidation state of the iron from (0) to (2+). In contrast, tetracyanoethylene and related molecules such as hexafluoroacetone react thermally with $[Fe(C_7H_8)(CO)_3]$, $[Fe\{C_6(NCO_2Me)H_6\}(CO)_3]$, and $[Fe(C_8H_8)(CO)_3]$ to form 1 : 1 adducts, in which the electrophile adds *exo*-1,3- to the co-ordinated olefinic species. In an effort to understand the factors controlling these reactions, related processes have been examined, and in this paper the photochemical reaction of tetrafluoroethylene with tricarbonyl(1,3-diene)iron, tricarbonyl(norbornadiene)iron, tetracarbonyl(cinnamaldehyde)iron, and tricarbonyl(*o*-styryldiphenylphosphine)iron are reported. The complexes obtained have been characterised by elemental analysis, mass spectroscopy, and i.r. and n.m.r. spectroscopy.

RESULTS

U.v. irradiation of hexane solutions of an excess of tetrafluoroethylene and the compounds tricarbonyl(1,3-diene)iron (diene = buta-1,3-diene, *trans*-penta-1,3-diene, isoprene, or 2,3-dimethylbuta-1,3-diene) affords moderate yields of the air-stable crystalline adducts (I), (II), (III), and (IV), respectively. The adducts are assigned the illustrated structures, in which a formal *endo*-oxidative linking reaction occurs resulting in the hydrocarbon fragment being bonded to the metal in the 1,2,3-η mode with one end of the fluorocarbon being attached to the iron *via* an Fe–C σ bond. Both isoprene and *trans*-penta-1,3-diene are unsymmetrical dienes and it has been firmly established, on the basis of the n.m.r. data, that the linkage reaction of tricarbonyl(*trans*-penta-1,3-diene)iron with C_2F_4 proceeds specifically at the unsubstituted end of the co-ordinated diene affording (II) as the only product. The reaction of tricarbonyl(isoprene)iron is not as specific but attack at the unsubstituted end of the diene, affording (IIIa), occurs approximately five times as readily as does reaction to give (IIIb) (see below).

The i.r. spectra of (I)—(IV) each show three sharp bands assignable to terminal carbonyl groups, one band appearing in the range 2083—2086 cm^{-1} and the other two in the range 2009—2032 cm^{-1}. This is consistent with an $Fe(CO)_3$ group, and the presence of this structural feature was confirmed by the mass spectra.

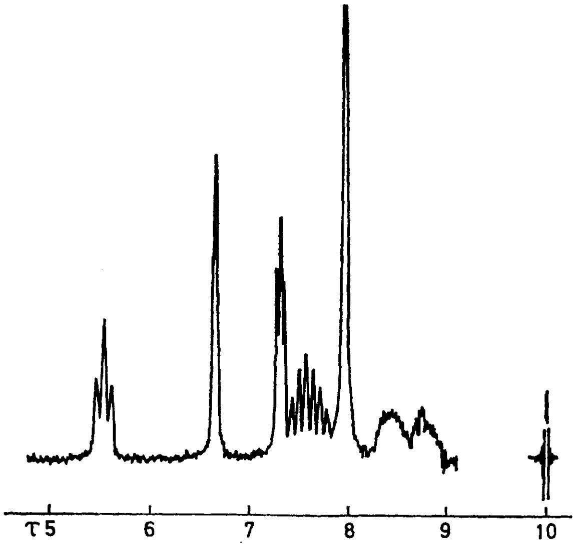

FIGURE 1 ^1H N.m.r. spectrum of complex (IIIa) in $CDCl_3$

The ^1H and ^{19}F n.m.r. spectra of the four adducts show very similar features, and therefore a detailed discussion is restricted to the tricarbonyl(isoprene)iron adduct. In the ^1H spectrum of (IIIa) (Figure 1), H^1 appears as a doublet of doublets at τ 7·31 and H^2 as an apparent triplet centred at τ 6·66; ^1H–^1H decoupling established a value for $J_{1,2}$ of 2·5 Hz, leaving a coupling of 4·0 Hz on H^1 to be assigned, which further decoupling revealed was not due to a proton.

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† No reprints available.

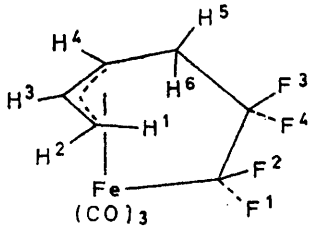
[1] Part IV, P. K. Maples, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 2069.

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

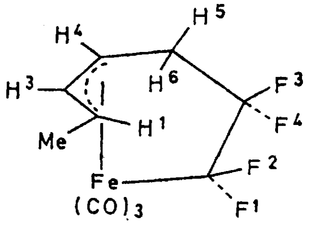
[3] M. Green, S. M. Heathcock, and D. C. Wood, *J.C.S. Dalton*, 1973, 1564.

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

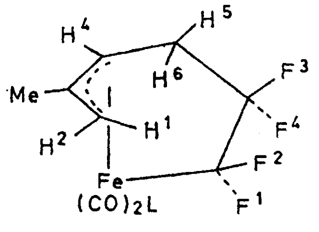
The resonance due to H^4 appears as an apparent triplet at τ 5·54 and irradiation of this signal showed coupling to H^2, H^5, and H^6; $J_{2,4}$ is small (2·5 Hz) but $J_{4,5}$ (7·5 Hz) and $J_{4,6}$ (8·0 Hz) are larger and almost equal. The signal due to H^5 appears as seven equally spaced lines of relative intensity 1 : 2 : 3 : 4 : 3 : 2 : 1 centred at τ 7·58; the H^6 resonance signal takes the form of a double triplet of doublets with a coupling of 35·0, 15·0, 14·0, and 3·0 Hz; the large coupling is clearly $J(F^3H^6)$. The resonances at 76·6 and 88·7 p.p.m. are assigned to F^1 and F^2 respectively, where $J_{1,2}$ is 236 Hz and each half of F^1 appears as a doublet of triplets, while F^2 correspondingly takes the form of multiplets.



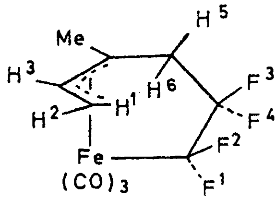
(I)



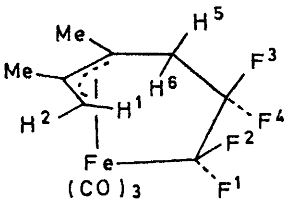
(II)



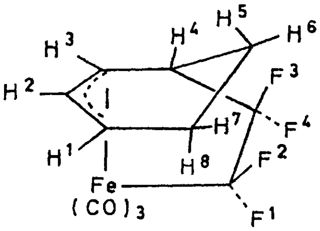
(IIIa) L = CO
(XI) L = P(OMe)3



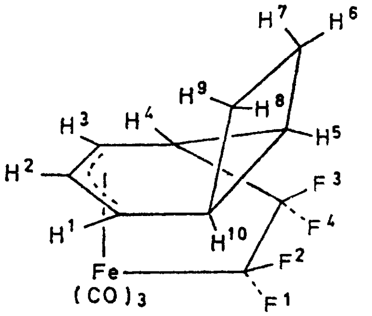
(IIIb)



(IV)



(V)



(VI)

appears as a complex doublet at τ 8·95. It was only possible to make firm assignments for the H^5 and H^6 resonances by examination of a molecular model. The H^5 resonance structure arises from four doublet couplings of 14·0, 14·0, 7·5, and 7·0 Hz. One of these (7·5 Hz) was assigned to $J_{4,5}$ and irradiation of H^5 showed that another is due to $J_{5,6}$; H^5 is coupled to no other proton. At this stage in the analysis no precise value could be assigned to $J_{5,6}$. The only coupling constant immediately apparent from the H^6 resonance is a large (35·0 Hz) coupling, clearly due to $^1H-^{19}F$ coupling.

The ^{19}F n.m.r. spectrum of (IIIa) shows that all four fluorine nuclei are chemically inequivalent and that each CF_2 group forms an AB system. One CF_2 group has resonances at 76·6 and 88·7 p.p.m. while the other two resonances occur at higher field, 113·6 and 116·9 p.p.m. The higher field signals are assigned to the CF_2 group β to the iron atom.[5] This assignment is supported by the ^{19}F spectrum of the corresponding adduct of tricarbonyl(isoprene)iron and hexafluoropropene, whose structure has been established by *X*-ray crystallography, which showed resonances at 101·2 p.p.m. and 117·0 assignable to $FeCF(CF_3)\mathit{CF}_2$.[6] In both (IIIa) and the hexafluoropropene adduct the higher field resonance of the β-CF_2 group displays a large J(HF) coupling (36·0 Hz) to the adjacent methylene group. Examination of a molecular model of (IIIa) suggests that the signal at 116·9 p.p.m. be assigned to F^3, and therefore the resonance at 113·6 p.p.m. to F^4; regarding F^3, the large $J_{3,4}$ coupling (222 Hz) is readily assigned and each ' half ' of the

Heteronuclear $^1H-^{19}F$ decoupling experiments (Figures 2 and 3) facilitated firm allocation of the remaining coupling constants. In Figure 3 the decoupling results concerning F^3 and F^4 are detailed. Simultaneous irradiation of H^5 and H^6 collapses each half of F^3 to a doublet of doublets. The 35·0 and 14·0 Hz couplings are removed, giving $J(F^3H^5)$ as 14·0 Hz, and leaving vicinal FF couplings of 15·0 and 3·0 Hz. At the same time each half of F^4 is reduced to show only the vicinal FF couplings 7·0 and 4·0 Hz. Irradiation of H^6 only removes the 35·0 Hz coupling from F^3, providing confirmation of the $J(F^3H^6)$ assignment; this also reduced each ' half ' of F^4 to a doublet of doublets. Irradiation of H^5 only reduced each ' half ' of the F^3 resonance to three doublet coupling, and also caused F^4 to revert to its original complexity, demonstrating that $J(F^4H^6)$ is 3·0 Hz.

Similarly, in Figure 2 the decoupling experiments concerned with F^1 and F^2 are illustrated. Simultaneous irradiation of H^5 and H^6 collapsed each ' half ' of the F^1 resonance to a doublet of doublets by removal of a 7·0 Hz coupling, which irradiation of H^5 only confirms is due to $J(F^1H^5)$. Thus, three of the four couplings to H^5 have been allocated: $J_{4,5}$ 7·5, $J(F^1H^5)$ 7·0, and $J(F^3H^5)$ 14·0 Hz giving $J_{5,6}$ as 14·0 Hz, by elimination. Vicinal FF couplings of 15·0 and 7·0 Hz remain on F^1, and clearly $J_{1,3} = 15·0$ and $J_{1,4} = 7·0$ Hz. Thus, the two outstanding vicinal FF couplings may be assigned as $J_{2,4}$ 4·0 and $J_{2,3}$ 3·0 Hz. Simultaneous irradiation of both H^5 and H^6 does not, however, affect the F^2 resonance, suggesting that this fluorine is the one coupled to H^1 by 4·0 Hz. A model of the complex

[5] E. Pitcher, A. D. Buckingham, and F. G. A. Stone, *J. Chem. Phys.*, 1962, **36**, 124.

[6] M. Green, B. Lewis, J. J. Daly, and F. Sanz, following paper.

demonstrates the close proximity of H^1 and F^2 suggesting a through-space coupling.

Further support for these assignments was provided by a study of the reaction of (IIIa) with trimethyl phosphite. The thermal reaction afforded the crystalline complex (XI), which showed two strong bands in the i.r. spectrum suggesting the reaction involves displacement of carbon monoxide by phosphite. Although the ^1H and ^{19}F n.m.r. spectra of (XI) closely resemble those of (IIIa) significant changes occur in both the chemical shifts and resonance widths of the low-field pair of ^{19}F resonances, thus providing support for the suggestion that these are due to the FeCF_2 group.

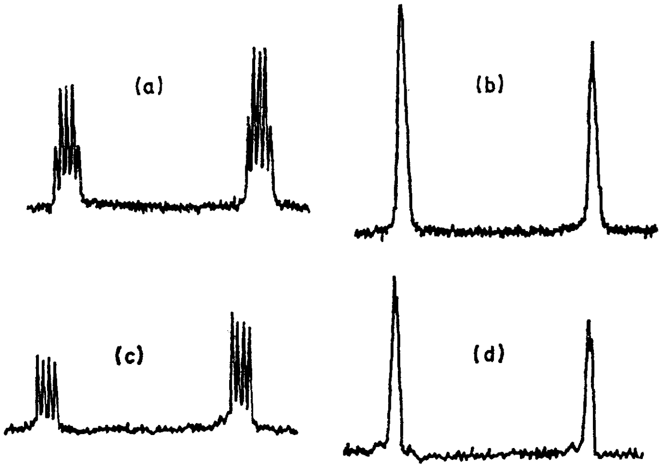


FIGURE 2 F^1 (a) and F^2 (b) resonances of complex (IIIa) in $CDCl_3$; (c) shows F^1 with H^5 and H^6 decoupled; (d) shows F^2 with H^5 and H^6 decoupled

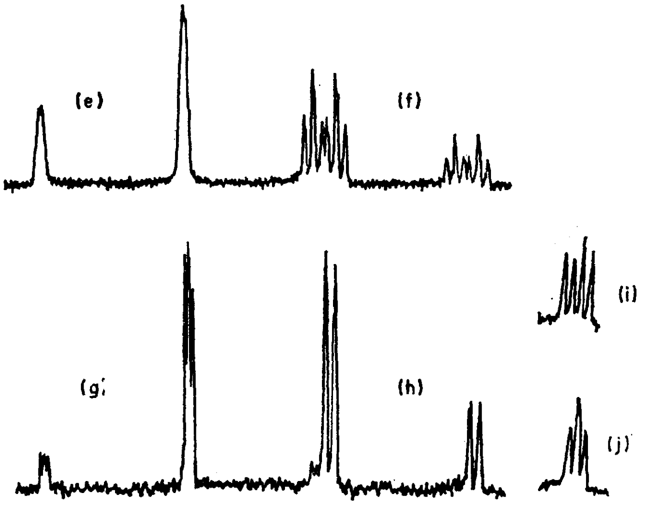


FIGURE 3 F^3 (f) and F^4 (e) resonances of (IIIa) ($CDCl_3$); (g) shows F^4 with H^5 and H^6 decoupled; (h) shows F^3 under the same conditions; (i) shows one half of F^3 with H^5 decoupled; (j) shows F^3 with H^6 decoupled

As required by the illustrated structure of (II), in which the C_2F_4 links to the unsubstituted end of the pentadiene, comparison of the ^1H spectra of (I) and (II) show only small variation in both the chemical shifts and splitting patterns of the H^5 and H^6 resonances. The $^1H-^1H$ couplings within the allylic group also indicate the presence of a *syn*-methyl substituent at the terminal carbon atom. In agreement, the resonance assigned to H^1, which differs in chemical shift from its counterpart in (I) and (IIIa) has a coupling to F^2 (6·0 Hz) associated with it. Interestingly, the H^3 resonance of (II) displays, in addition to the typical allylic couplings to H^1 and H^4, two equal couplings (3·5 Hz), which $^1H-^1H$ decoupling experiments showed did not arise from coupling with any other protons. This is supported by the fact [7] that the H^3 signal of the corresponding adduct of $CF_3C_2CF_3$ and buta-1,3-diene(tricarbonyl)iron, where HF coupling is restricted to the methylene protons, shows only three couplings, all of the expected allylic type. Since the splitting patterns of the F^1 and F^3 signals of (II) are identical with their counterparts in (I), whereas those of F^2 and F^4 are not, it is concluded that the latter nuclei must be coupled to H^3. These unusual couplings are also a feature of the central allylic proton of (I) and the adduct from C_2F_4 and $[Fe(\pi\text{-}C_4H_4)(CO)_3]$.[2]

It was demonstrated that the fluoro-olefin oxidative linking reaction is not restricted to open-chain diene complexes of $Fe(CO)_3$ by studying the reaction of C_2F_4 with tricarbonyl-(cyclohexa-1,3-diene, bicyclo[4.2.0]octa-2,4-diene, or cycloocta-1,3-diene)iron.

U.v. irradiation of a hexane solution of C_2F_4 and tricarbonyl(cyclohexa-1,3-diene)iron afforded the crystalline 1 : 1 adduct (V), which showed the expected i.r. and mass spectra. Examination of the n.m.r. spectra with the aid of $^1H-^1H$ decoupling experiments and reference to a molecular model led to the assignment of resonances due to a π-allylic group and a C_2F_4 linked system.

In the ^1H n.m.r. spectrum of (V), H^2 appears at τ 4·52 as an apparent doublet of triplets, with coupling constants of 6·5, 6·5, and 4·0 Hz, and H^3 resonates as a triplet of doublets centred at τ 5·03 with associated couplings of 6·5, 6·5, and 2·0 Hz. The remaining allylic proton, H^1, occurs as a complex multiplet centred at τ 5·58. Double irradiation of H^2 removed a doublet coupling of 6·5 Hz from both H^1 and H^3; this irradiation has no affect on the other protons, leaving H^2 with a 4·0 Hz $^1H-^{19}F$ coupling. When H^1 was irradiated the H^3 signal collapsed to a triplet giving $J_{1,3}$ 2·0 Hz. Thus, H^1 can be allocated $J_{1,2}$ 6·5 and $J_{1,3}$ 2·0 Hz, and further double-irradiation experiments showed that H^1 is also coupled equally (5·0 Hz) to the adjacent methylene protons H^7 and H^8. The H^4 resonance appeared as a six-line multiplet at τ 7·26; irradiation of this signal affects three resonances, H^3 and the methylene signals, leading to the assignments $J_{4,5} = J_{4,6}$ 7·0, and $J_{3,4}$ 6·5 Hz. This suggested that the remaining coupling (15·0 Hz) on H^4 must be due to $^1H-^{19}F$ coupling.

The ^{19}F spectrum of (V) shows two AB systems; signals due to the α-CF_2 group appear at 63·0 and 97·2 p.p.m. Both these signals are well resolved and one of them (97·2 p.p.m.) exhibits, in addition to a large geminal FF coupling (247 Hz), only one other vicinal FF coupling (7·5 Hz). In contrast, the resonance at 63·0 p.p.m. exhibits couplings of 247, 12·0, and two of 7·5 Hz; of these, two (12·0 and 7·5 Hz) are vicinal FF couplings while the remaining (7·5 Hz) coupling must arise from a through-space interaction with a nearby methylenic proton, implying that this fluorine resonance corresponds to F^2. Examination of a molecular model supports this interpretation and suggests that the proton involved is H^8. Therefore, it appears that in (V), F^2 resonates at higher field than F^1, a reversal of the trend found with the related acyclic system. The signals due to F^3 and F^4 occur at above 100 p.p.m., in line with the shifts observed with (I)—(IV). Allocation of the vicinal FF couplings, with the exception of $J_{1,4}$, was possible; the latter must be $<0·5$

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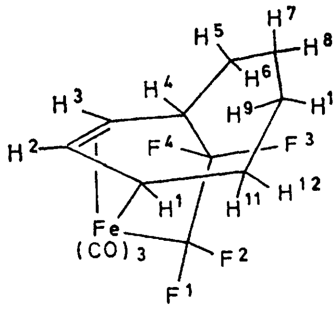
[7] M. Green and B. Lewis, unpublished observations.

Hz. In addition, the ^1H–^{19}F couplings $J(F^3H^4)$ 15·0 and $J(F^4H^2)$ 4·0 Hz were established, the latter comparing favourably with the corresponding couplings in (I) and (II).

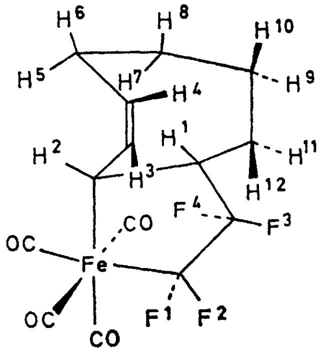
The corresponding reaction between C_2F_4 and tricarbonyl(bicyclo[4.2.0]octa-2,4-diene)iron afforded the 1 : 1 adduct (VI), which was assigned the illustrated structure on the basis of the analytical and spectroscopic data. The n.m.r. data closely corresponded to that found for (V). There was no evidence for the formation of a C_8 ring-opened adduct.

Reaction of C_2F_4 and tricarbonyl(cyclo-octa-1,3-diene)iron occurred on irradiation to give a mixture (3 : 1) of two crystalline compounds (VII) and (VIII) which were separated by fractional crystallisation. The i.r. spectrum of (VII) shows three strong terminal bands in agreement with the illustrated π-allylic structure containing an $Fe(CO)_3$ group.

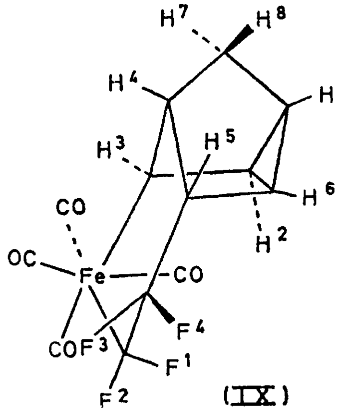
The ^1H n.m.r. spectrum of (VII) shows low-field resonances at τ 5·00 (2H) and 5·82 (1H), which, although not typical of a π-allyl group contained in an acyclic system, may be assigned to an allylic group bonded in the σ,π-mode. Decoupling experiments confirm this interpretation, and determination of *cis* $J(H^2H^2)$ gave a typical value of 7·5 Hz.



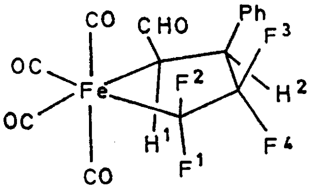
(VII)



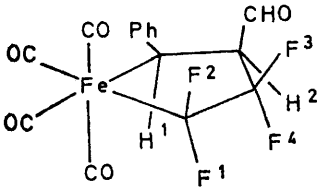
(VIII)



(IX)



(Xa)



(Xb)

Two of the methylene proton resonances occur at lower field than the others, and from examination of a molecular model it is assumed that these are due to H^{11} and H^{12}, the low-field shift arising due to close proximity of the α-CF_2 group. Further study of the model demonstrated that several other methylene protons are quite close to the $FeCF_2CF_2$ chain suggesting the possibility of widespread through-space ^1H–^{19}F coupling. In agreement, the ^{19}F n.m.r. spectrum, although exhibiting typical chemical shifts, shows complex multiplets unlike the other adducts.

The i.r. spectrum of the other product (VIII) showed, in addition to a weak band at 1624 cm^{-1} assigned to $\nu_{C=C}$, four terminal carbonyl bands, suggesting the presence of an $Fe(CO)_4$ group. This was supported by the mass spectrum.

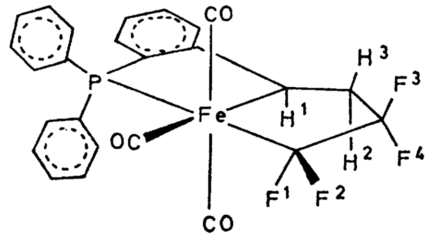
In the ^1H n.m.r. spectrum of (VIII) the unco-ordinated double-bond protons, H^3 and H^4, appear at low field (τ 4·02—4·40) as overlapping multiplets with a *cis*-coupling of 7·5 Hz. Apart from a complex resonance (9H) in the methylenic region the only other signal in the spectrum is a multiplet (1H) at τ 6·48. The latter cannot be due to H^1, because one of the β-CF_2 fluorines bears a J(HF) coupling of 37·0 Hz (clearly to H^1) which is present in this signal, therefore, by elimination this signal must correspond to H^2. This is supported by the fact that irradiation of the $H^{3,4}$ signal removes a 10·5 Hz splitting from the resonance at τ 6·48, which also allows the allocation of the unco-ordinated double-bond position.

Thus, the complex (VIII) is a ferracyclopentane, formed from (VII) by displacement by carbon monoxide of the co-ordinated double bond. An alternative conformation for the C_8 ring in (VIII), in which the ring is bent towards the $FeCF_2CF_2$ group, is considered unlikely due to the presence in a model of considerable non-bonding interactions. The ^{19}F n.m.r. spectrum, which exhibited typical chemical shifts and coupling constants, showed no evidence of through-space ^1H–^{19}F coupling, which might be expected if this was the preferred conformation in solution.

Irradiation of a solution of tricarbonyl(norbornadiene)iron and tetrafluoroethylene leads to the formation of an $Fe(CO)_4$ species (IX), which is assigned a nortricyclene structure. The i.r. and mass spectra show the expected features for such a structure.

In the ^1H n.m.r. spectrum of (IX) all the resonances occur in the range τ 7·5—8·7, there being no evidence for resonances corresponding to protons attached to either a co-ordinated or unco-ordinated double bond. Comparison of chemical shifts with those reported for other nortricyclenes and decoupling experiments allowed the assignments to be made, which are listed in the Experimental section.

It has been observed [8] that in nortricyclene systems bearing electronegative groups at C^3 and at C^5 noticeable paramagnetic shifts are experienced by all protons, especially the bridgehead hydrogen, H^4. Accordingly, the slightly broad singlet (1H) at τ 7·53 is assigned to this proton and a sharper singlet (1H) at τ 7·96 is attributed to H^1. The corresponding resonance in nortricyclene itself occurs [8] at τ 8·09. The broad multiplet (1H) at τ 7·79 is assigned to H^5, the signal showing HF coupling. The methylene protons H^7 and H^8 resonate as a sharp multiplet (2H) at τ 8·55 with only a small coupling to the bridgehead protons. The multiplet (1H) at τ 8·68 is assigned to H^3, the high-field position being attributed to shielding by the metal.[9] Finally, the multiplet (2H) at τ 8·41 is assigned to H^2 and H^6; the chemical shifts being similar to those observed [10] in related electronegatively substituted nortricyclenes.

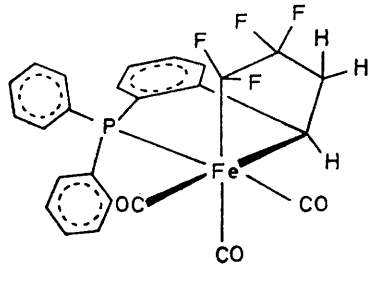


(XIIIa)

The ^{19}F n.m.r. chemical shifts are not the same as those found in the other complexes described, the α-CF_2 fluorines having very similar (within 3 p.p.m.) chemical shifts at rather low field. The β-CF_2 shifts are more typical. Examination of molecular models shows that this complex can exist in either a boat or a chair conformation, however, it is not possible on the present evidence to distinguish firmly between these two alternatives. It may be noted that F^2 is equally coupled (5·5 Hz) to F^3 and F^4, an observation which is more readily accommodated by the chair form.

Both tetra- and tri-carbonyl(*trans*-cinnamaldehyde) iron [11,12] react with tetrafluoroethylene on irradiation to afford a pale yellow crystalline material which is formulated as a mixture (4 : 5) of the tetracarbonyl species (Xa) and (Xb). The presence in the i.r. spectrum of a band at 1667s cm^{-1} (CHO) in addition to four terminal carbonyl bands suggested that in the reaction leading to the formation of the isomeric ferracyclopentanes the co-ordinated cinnamaldehyde behaves as a mono-olefin. This is supported by both the ^1H and ^{19}F n.m.r. spectra.

Proton–proton decoupling experiments enable the C*H*(CHO) resonance, which is coupled (3·0 Hz) to the aldehydic proton, to be distinguished for both isomers in a spectrum of the mixture. This allowed C*H*Ph to be assigned for each isomer. It is clear that the isomerism in (Xa) and (Xb) arises from formal attack by C_2F_4 at opposite ends of the co-ordinated olefinic bond of unidentate cinnamaldehyde. Such isomerism also accounts for the complex nature of the F^3 and F^4 resonance in the ^{19}F spectrum of the mixture. Although the ^1H–^1H coupling ($J_{1,2}$) constant cannot be accurately extracted from the spectrum, an approximate value of 4·0 Hz can be assigned for both isomers, suggesting that in both (Xa) and (Xb) the phenyl and *CHO* group have a relative *cis*-configuration.



(XIIIb)

Since in a previous investigation it was found that the zerovalent species $[M(CO)_3L_2]$ (L = phosphine or phosphite; M = Fe,[13] Ru,[13] or Os [14]) react on u.v. irradiation with tetrafluoroethylene to form the complexes $[\overline{MCF_2CF_2}(CO)_2L_2]$, and in contrast a variety of zerovalent tricarbonyl(olefin)iron complexes undergo an oxidative linking reaction with C_2F_4, it was clearly important to examine the reaction of C_2F_4 with tricarbonyl(*o*-styryldiphenylphosphine)iron, *i.e.* $[Fe(sp)(CO)_3]$.[15,16]

Irradiation of a solution of $[Fe(sp)(CO)_3]$ in the presence of an excess of tetrafluoroethylene gave the yellow crystalline 1 : 1 adduct (XII), which showed, in the i.r. spectrum, three terminal carbonyl bands with similar frequencies to those observed in the complexes discussed above. However, the relative intensities of the bands are not the same. In (XII) the highest band is weak, whereas in the other complexes this band is strong.

The ^1H n.m.r. spectrum of (XII) shows three resonances in addition to a broad complex multiplet at low field due to the aromatic protons of the Ph_2P group. A signal at τ 6·11 is assigned to H^1 of the illustrated structure, and appears as a doublet of doublets due to ^1H–^1H couplings, which are easily measured (12·0 and 6·0 Hz) and assigned, with the aid of decoupling experiments, to $J_{1,3}$ and $J_{1,2}$ respectively. In agreement with this assignment this signal does not display HF coupling. The two remaining resonances (τ 7·10 and 7·40), due to the methylene protons H^2 and H^3, are more complex. However, decoupling experiments showed that the signal at τ 7·10 is coupled to H^1 by 12·0 Hz, and this finding, in conjunction with examination of dihedral angles in a molecular model, permits its allocation to proton H^3.

The ^{19}F n.m.r. spectrum shows four AB type resonances with chemical shifts typical of a ferracyclopentane. Significantly, both F^1 and F^2 show a PF coupling (16·5 and 18·0 Hz respectively); in addition, F^1 is coupled (5·5 Hz) to H^3.

These observations are comparable with either of the two

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illustrated ferracyclopentane structures (XIIa) and (XIIb). However, the relative intensity of the terminal carbonyl bands is more easily understood in terms of structure (XIIa). In addition, the presence of PF coupling to the α-CF_2 nuclei is more consistent with the CF_2 group being *trans* to the phosphorus ligand in an essentially octahedral structure.

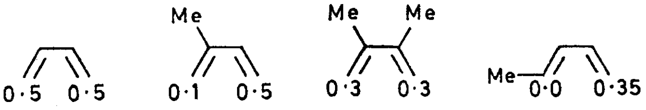
DISCUSSION

In considering possible reaction paths for the formation of the C_2F_4 adducts the reaction of tetra- and tri-carbonyl(*trans*-cinnamaldehyde)iron with C_2F_4 to give (Xa) and (Xb) is first considered. The formation of a ferracyclopentane, in which the phenyl and CHO groups have a relative *cis*-configuration, from a *trans*-cinnamaldehyde suggests that at some point in the reaction *trans*- to *cis*-isomerisation occurs *via* C–C bond rotation. Because both the tetra- and tri-carbonyl complexes require u.v. irradiation to react with C_2F_4, it is suggested that the reaction involves electrophilic attack by C_2F_4 on a tricarbonyl(*cis*-cinnamaldehyde)iron complex formed *in situ*; the *cis–trans* isomerisation being promoted by u.v. irradiation. Such a reaction would be facilitated by increased population of the π^* antibonding orbital of the olefin, which is the highest occupied m.o., and would be expected to be the point of attack by an electrophile. Since it has been suggested [17] that the electron density in the π-orbitals of a complexed olefinic ligand will be greatest in the bonding region between the metal and the co-ordinated olefin, attack by C_2F_4 on the *endo*-face might be expected. Such an approach by an electrophile has been established in the protonation of tricarbonyl(cyclohexa-1,3-diene)iron [18] and (cyclohexa-1,3-diene)(η-cyclopentadienyl)rhodium,[19] and for the acetylation of tricarbonyl(*trans,trans*-hexa-1,4-diene)iron.[20] In those cases where *exo*-protonation or acetylation has been observed both co-ordinated and unco-ordinated olefinic bonds have been available within the same molecule for possible reaction. Moreover, in the case of both protonation and acylation, reaction at an unco-ordinated olefin is a readily available reaction even in the absence of a metal. Thus it is suggested that *exo*-attack is only observed when reaction occurs at an unco-ordinated olefin. A similar rationale can be applied to the reactions of tetracyanoethylene with tricarbonyl(cycloheptatriene or cyclo-octatetraene)iron where *exo*-attack has been demonstrated.[3]

Thus, in the reaction of C_2F_4 with co-ordinated *cis*-cinnamaldehyde *endo*-attack to give a dipolar species is probably preferred. Although the observed *cis–trans* isomerisation could also be explained by *exo*-attack followed by C–C bond rotation, this is thought to be less likely.

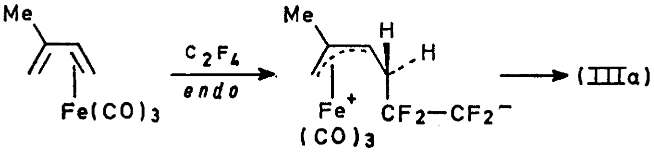
A similar *endo*-attack by C_2F_4 on the tricarbonyl(1,3-diene)iron complexes would lead to the formation of an intermediate cationic π-allylic species, a process closely resembling the acylation of tricarbonyl(1,3-diene)iron complexes with acetyl chloride–$AlCl_3$.[21] Recently,[22] Graf and Lillya have determined the relative reactivities of several substituted tricarbonyl(1,3-diene)iron complexes toward acylation, by allowing each to compete with *m*-xylene for a limited amount of acetyl chloride–$AlCl_3$ in methylene chloride. Examination of the partial rate factors showed that substituent effects are relatively small, and that the steric effect of substituents outweighs possible electronic stabilising influences. This is illustrated by the low reactivity of tricarbonyl(cyclohexa-1,3-diene)iron.

In order to examine the possible relationship between the acylation and C_2F_4 reaction, selected pairs of tricarbonyl(1,3-diene)iron complexes were allowed to compete for a limited amount of tetrafluoroethylene.



SCHEME 1 The overall reactivity of C_4H_6 is set at unity

Analysis of the resultant reaction mixture by n.m.r. spectroscopy allowed the relative reactivities shown in Scheme 1 to be established, suggesting a close parallel between the two reactions. Thus, it is suggested that the formation of (I)—(IV) involves *endo*-attack by C_2F_4 on a co-ordinated double bond of a *cisoid* † 1,2-η bonded species formed by u.v. irradiation; the $Fe(CO)_3$ group migrating to stabilise the generated change (Scheme 2).



SCHEME 2

Although in a 1,2-η bonded diene–$Fe(CO)_3$ species both co-ordinated and unco-ordinated double bonds are available for electrophilic attack it is suggested that with C_2F_4 the activation energy for reaction at the two sites is very different unlike the reactions with protons, acylium ions, or tetracyanoethylene. This is because reaction of unco-ordinated olefins with C_2F_4 *via* an ionic pathway is not normally observed, the alternative radical path ‡ being followed. Thus, it is considered that the reactions occur as shown in Scheme 2. A similar mechanism can be postulated for the reaction of tricarbonyl(*o*-styryldiphenylphosphine)iron with C_2F_4 if it is assumed that

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† A reaction in the *transoid* form would afford adducts with the wrong stereochemistry.

‡ The addition of radial inhibitors has no effect on the reactions described in this paper.

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u.v. irradiation leads to dissociation of the phosphine ligand, and that *endo*-attack occurs on the co-ordinated olefin. The direction of addition of C_2F_4 parallels that observed[23] for addition of HX (X = Cl or Br) to [Fe(sp)(CO)$_3$], although it is interesting that the direction of protonation of a co-ordinated mono-olefin has not so far been established.

When tricarbonyl(cyclohexa-1,3-diene)iron was allowed to compete with the other 1,3-diene complexes for a limited amount of tetrafluoroethylene it was found (see Experimental section) that the parallel with the acylation reaction was no longer observed, the cyclohexa-1,3-diene complex showing a reactivity comparable to tricarbonyl(buta-1,3-diene)iron. This suggested the possible availability of an alternative reaction path involving initial attack by C_2F_4 on the metal. Clearly, information about such processes could come from a study of the related reaction with unsymmetrical fluoro-olefins, and this is described in the following paper.

EXPERIMENTAL

^{1}H and ^{19}F N.m.r. spectra were recorded on a Varian Associated HA100 spectrometer at 100 and 94·1 MHz respectively. Chemical shifts are relative to Me_4Si (τ 10·00) and CCl_3F (0·00 p.p.m., internal standard). I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer. Mass spectra were obtained on an A.E.I. MS 902 spectrometer at an ionising voltage of 70 eV. All reactions, other than those in Carius tubes, were carried out in an atmosphere of dry oxygen-free nitrogen. Both tetra- and tri-carbonyl(cinnamaldehyde)iron and all other tricarbonyl(diene)iron substitutes were prepared by published methods.

Reactions of Tetrafluoroethylene.—(*a*) *With* (*buta*-1,3-*diene*)*tricarbonyliron*. An excess of tetrafluoroethylene (0·30 g, 3·0 mmol) was condensed (−196 °C) into a Pyrex Carius tube (100 ml) containing (buta-1,3-diene)tricarbonyliron (0·50 g, 2·5 mmol) dissolved in n-hexane (20 ml). The tube contents were irradiated (250 W, Hanovia lamp) for 24 h. The solvent was removed *in vacuo* and the residue chromatographed on an alumina-packed column. Elution with benzene–n-hexane (1 : 9) gave, on recrystallisation (0 °C) from n-hexane, pale yellow *crystals* of (I) (0·30 g, 40%), m.p. 83 °C (Found: C, 36·9; H, 2·0; F, 26·0. $C_9H_6F_4FeO_3$ requires C, 36·8; H, 2·0; F, 25·9%), $\nu_{max.}$ (CO) (n-hexane) 2085s, 2035m, and 2019s cm^{-1}. The mass spectrum (base peak *m*/*e* 266) showed peaks at 294 (*P*, 8%), 266 (*P* − CO, 100%), 247 (*P* − CO − F, 2%), 238 (*P* − 2CO, 23%), 219 (*P* − 2CO − F, 6%), 210 (*P* − 3CO, 48%), and 191 (*P* − 3CO − F, 6%). The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 4·90 [ddddd, 1H, H^3, $J_{1,3}$ 13·0, $J_{2,3}$ = $J_{3,4}$ 7·5, $J(H^3F^4)$ = $J(H^3F^2)$ 3·5 Hz], 5·32 (dddd, 1H, H^4, $J_{3,4}$ = $J_{4,6}$ 7·5, $J_{4,5}$ 7·0, $J_{2,4}$ 1·0 Hz), 6·52 (ddd, 1H, H^2, $J_{2,3}$ 7·5, $J_{1,2}$ 3·0, $J_{2,4}$ 1·0 Hz), 7·32 [ddd, 1H, H^1, $J_{1,3}$ 13·0, $J_{1,2}$ = $J(H^1F^2)$ 3·0 Hz], 7·58 [dddd, 1H, H^5, $J_{5,6}$ = $J(H^5F^3)$ 14·0, $J_{4,5}$ = $J(H^5F^1)$ 7·0 Hz], and 8·60 [m, 1H, H^6, $J_{5,6}$ 14·0, $J_{4,5}$ 7·5, $J(H^6F^3)$ 36·0 Hz]. The ^{19}F n.m.r. spectrum ($CDCl_3$) showed resonances at 108·5 [1F, F^3, $J_{3,4}$ 222, $J_{1,3}$ = $J(F^3H^5)$ 14·0, $J_{2,3}$ 3·0, $J(F^3H^6)$ 36·0 Hz], 104·5 [1F, F^4, $J_{3,4}$ 222, $J_{1,4}$ 7·0, $J_{2,4}$ 3·0, $J(F^4H^3)$ 3·5 Hz], 76·8 [1F, F^1, $J_{1,2}$ 236, $J_{1,3}$ 14·0, $J_{1,4}$ = $J(F^1H^5)$ 7·0 Hz], and 87·3 p.p.m. [1F, F^2, $J_{1,2}$ 236, $J_{2,3}$ = $J_{2,4}$ 3·0, $J(F^2H^3)$ 3·5, $J(F^2H^1)$ 3·0 Hz].

(*b*) *With tricarbonyl*(trans-*penta*-1,3-*diene*)*iron*. U.v. irradiation (65 h) of a solution of tricarbonyl(*trans*-penta-1,3-diene)iron (0·50 g, 2·4 mmol) and tetrafluoroethylene (0·40 g, 4·0 mmol) in n-hexane (12 ml) and removal of volatile material *in vacuo* gave, on recrystallisation (0 °C) of the residue from methylene chloride–n-hexane, pale yellow *crystals* of (II) (0·20 g, 27%), m.p. 55—57 °C (Found: C, 38·8; H, 2·5; F, 24·9. $C_{10}H_8F_4FeO_3$ requires C, 38·9; H, 2·5; F, 24·9%), ν_{CO} (n-hexane) 2086s, 2031s, and 2013s cm^{-1}. The mass spectrum (base peak *m*/*e* 280) showed peaks at *m*/*e* 308 (*P*, 20%), 280 (*P* − CO, 100%), 261 (*P* − CO − F, 4%), 252 (*P* − 2CO, 20%), 233 (*P* − 2CO − F, 4%), 224 (*P* − 3CO, 48%), and 205 (*P* − 3CO − F, 8%). The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 5·06 [dddd, 1H, H^3, $J_{1,3}$ 12·0, $J_{3,4}$ 7·5, $J(H^3F^4)$ = $J(H^3F^2)$ 3·5 Hz], 5·59 (ddd, 1H, H^4, $J_{3,4}$ 7·5, $J_{4,5}$ = $J_{4,6}$ 7·0 Hz), 6·37 [ddq, 1H, H^1, $J_{1,3}$ 12·0, $J(H^1Me)$ = $J(H^1F^2)$ 6·0 Hz], 7·61 [dddd, 1H, H^5, $J_{5,6}$ = $J(H^5F^3)$ 14·0, $J_{4,5}$ = $J(H^5F^1)$ 7·0 Hz], 8·18 [d, 3H, Me, $J(H^1Me)$ 6·0 Hz], and 8·59 [m, 1H, H^6, $J_{5,6}$ 14·0, $J_{4,6}$ 7·0, $J(H^6F^3)$ 36·0 Hz]. The ^{19}F n.m.r. spectrum ($CHCl_3$) showed resonances at 116·9 [1F, F^3, $J_{3,4}$ 222, $J_{1,3}$ = $J(F^3H^5)$ 14·0, $J_{2,3}$ 3·0, $J(F^3H^6)$ 36·0 Hz], 110·6 [1F, F^4, $J_{3,4}$ 222, $J_{1,4}$ 7·0, $J(F^4H^3)$ 3·5 Hz], 76·3 [1F, F^1, $J_{1,2}$ 238, $J_{1,3}$ 14·0, $J_{1,4}$ = $J(F^1H^5)$ 7·0 Hz], and 87·1 p.p.m. [1F, F^2, $J_{1,2}$ 238, $J_{2,3}$ 3·0, $J(F^2H^1)$ 6·0, $J(F^2H^3)$ 3·5 Hz].

(*c*) *With tricarbonyl*(*isoprene*)*iron*. U.v. irradiation (20 h) of a solution of tricarbonyl(isoprene)iron (0·20 g, 1·0 mmol) and tetrafluoroethylene (0·40 g, 4·0 mmol) in n-hexane (12 ml) and removal of solvent *in vacuo* gave, on recrystallisation (0 °C) of the residue from methylene chloride–n-hexane, light yellow *crystals* of (IIIa) (0·12 g, 38%), m.p. 83—84 °C (Found: C, 39·2; H, 2·6; F, 24·5. $C_{10}H_8F_4FeO_3$ requires C, 38·9; H, 2·6; F, 24·7%), ν_{CO} (n-hexane) 2085s, 2032s, and 2014s cm^{-1}. The mass spectrum (base *m*/*e* 280) showed peaks at *m*/*e* 308 (*P*, 12%), 280 (*P* − CO, 100%), 261 (*P* − CO − F, 6%), 252 (*P* − 2CO, 42%), 233 (*P* − 2CO − F, 9%), 224 (*P* − 3CO, 36%), and 205 (*P* − 3CO − F, 8%). The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 5·54 (ddd, 1H, H^4, $J_{4,6}$ 8·0, $J_{4,5}$ 7·5, $J_{2,4}$ 2·5 Hz), 6·66 (dd, 1H, H^2, $J_{1,2}$ = $J_{2,4}$ 2·5 Hz), 7·31 [dd, 1H, H^1, $J_{1.2}$ 2·5, $J(H^1F^2)$ 4·0 Hz], 7·58 [dddd, 1H, H^5, $J_{5,6}$ = $J(H^5F^3)$ 14·0, $J_{4,5}$ 7·5, $J(H^5F^1)$ 7·0 Hz], 7·95 (s, 3H, Me), and 8·95 [m, 1H, H^6, $J_{5,6}$ 14·0, $J_{4,6}$ 8·0, $J(H^6F^3)$ 35·0, $J(H^6F^4)$ 3·0 Hz]. The ^{19}F n.m.r. spectrum ($CHCl_3$) showed resonances at 76·6 p.p.m. [1F, F^1, $J_{1,2}$ 236, $J_{1,3}$ 15·0, $J_{1,4}$ = $J(F^1H^5)$ 7·0 Hz], 88·7 [1F, F^2, $J_{1,2}$ 236, $J_{2,4}$ = $J(F^2H^1)$ 4·0, $J_{2,3}$ 3·0 Hz], 113·6 [1F, F^4, $J_{3,4}$ 222, $J_{1,4}$ 7·0, $J_{2,4}$ 4·0, $J(F^4H^6)$ 3·0 Hz], and 116·9 [1F, F^3, $J_{3,4}$ 222, $J_{1,3}$ 15·0, $J_{2,3}$ 3·0, $J(F^3H^6)$ 35·0, $J(F^3H^5)$ 14·0 Hz].

(*d*) *With tricarbonyl*(2,3-*dimethylbuta*-1,3-*diene*)*iron*. Similarly, u.v. irradiation (40 h) of a solution of tricarbonyl(2,3-dimethylbuta-1,3-diene)iron (0·40 g, 1·8 mmol) and tetrafluoroethylene (0·40 g, 4·0 mmol) in n-hexane (12 ml) and removal of volatile material *in vacuo* gave, on recrystallisation (0 °C) of the residue from methylene chloride–n-hexane, yellow *needles* of (IV) (0·22 g, 38%), m.p. 116—118 °C (Found: C, 41·3; H, 3·3; F, 23·4. $C_{11}H_{10}F_4FeO_3$ requires C, 40·9; H, 3·1; F, 23·6%), ν_{CO} (n-hexane) 2038s, 2028s, and 2009s cm^{-1}. The mass spectrum (base *m*/*e* 294) showed peaks at *m*/*e* 322 (*P*, 4%), 294 (*P* − CO, 100%), 275 (*P* − CO − F, 4%), 266 (*P* − 2CO, 20%), 247 (*P* − 2CO − F, 4%), 238 (*P* − 3CO, 16%), and 219 (*P* − 3CO − F, 4%). The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 6·83 (d, 1H, H^2, $J_{1,2}$ 3·0 Hz), 7·61 [dd, 1H, H^1, $J_{1,2}$ 3·0, $J(H^1F^2)$ 4·0 Hz], 7·77 [ddd, 1H, H^5, $J_{5,6}$ 13·0, $J(H^5F^3)$ 14·0, $J(H^5F^1)$

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[23] M. A. Bennett, E. B. Robertson, I. B. Tomkins, and P. O. Whimp, *J. Organometallic Chem.*, 1971, **32**, C19.

7·0 Hz], 7·91 [s, 3H, Me$^{(1)}$], 7·99 [s, 3H, Me$^{(2)}$], and 8·43 [m, 1H, H^6, $J_{5,6}$ 13·0, J(H^{6}F^3) 36·0 Hz]. The ^{19}F n.m.r. spectrum (CHCl$_3$) showed resonances at 77·6 p.p.m. [1F, F^1, $J_{1,2}$ 236, $J_{1,3}$ 14·5, $J_{1,4}$ = J(F^{1}H^5) 7·0 Hz], 89·7 [1F, F^2, $J_{1,2}$ 236, $J_{2,3}$ 3·0, J(F$_2$H^1) 4·0 Hz], 110·5 (1F, F^4, $J_{3,4}$ 222, $J_{1,4}$ 7·0 Hz), and 117·9 [1F, F^3, $J_{3,4}$ 222, $J_{1,3}$ 14·5, $J_{2,3}$ 3·0, J(F^{3}H^6) 36·0, J(F^{3}H^5) 14·0 Hz].

(e) *With tricarbonyl(cyclohexa-*1,3*-diene)iron.* U.v. irradiation (60 h) of a solution of tricarbonyl(cyclohexa-1,3-diene)iron (1·0 g, 4·5 mmol) and tetrafluoroethylene (0·40 g, 4·0 mmol) in n-hexane (12 ml) and removal of volatile material *in vacuo* gave, on recrystallisation (0 °C) of the residue from methylene chloride–n-hexane, yellow *needles* of (V) (0·34 g, 26%), m.p. 111—114 °C (Found: C, 41·0; H, 2·4; F, 24·4. $C_{11}H_8F_4FeO_3$ requires C, 41·2; H, 2·5; F, 23·8%), ν_{CO} (n-hexane) 2084s, 2029s, and 2009s cm^{-1}. The mass spectrum (base *m/e* 236) showed peaks at *m/e* 320 (*P*, 4%), 292 (*P* − CO, 27%), 264 (*P* − 2CO, 90%), and 236 (*P* − 3CO, 100%). The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 4·52 [ddd, 1H, H^2, $J_{1,2}$ = $J_{2,3}$ 6·5, J(H^{2}F^3) 3·5 Hz], 5·03 (ddd, 1H, H^3, $J_{3,4}$ 7·0, $J_{2,3}$ 6·5, $J_{1,3}$ 2·0 Hz), 5·58 (dddd, 1H, H^1, $J_{1,2}$ 6·5, $J_{1,7\text{ or }8}$ 5·0, $J_{1,3}$ = $J_{1,7\text{ or }8}$ 2·0 Hz), 7·26 [ddddd, 1H, H^4, $J_{3,4}$ = $J_{4,5}$ = $J_{4,6}$ = J(H^{4}F^1) 7·0, J(H^{4}F^3) 9·0 Hz], 7·84 (m, 2H, H^5 and H^7, $J_{4,5}$ 7·0 Hz), and 8·60 (m, 2H, H^6 and H^8, $J_{4,6}$ 7·0 Hz). The ^{19}F n.m.r. spectrum (CHCl$_3$) showed resonances at 63·0 p.p.m. [1F, F^1, $J_{1,4}$ 247, $J_{1,3}$ 14·0, $J_{1,4}$ = J(F^{1}H^4) 7·0 Hz], 97·2 (1F, F^2, $J_{1,2}$ 247, $J_{2,3}$ 9·0 Hz), 110·5 (1F, F^4, $J_{3,4}$ 226, $J_{1,4}$ 7·0 Hz), and 114·8 [1F, F^3, $J_{3,4}$ 226, $J_{1,3}$ 14·0, $J_{2,3}$ = J(F^{3}H^4) 9·0, J(F^{3}H^2) 3·5 Hz].

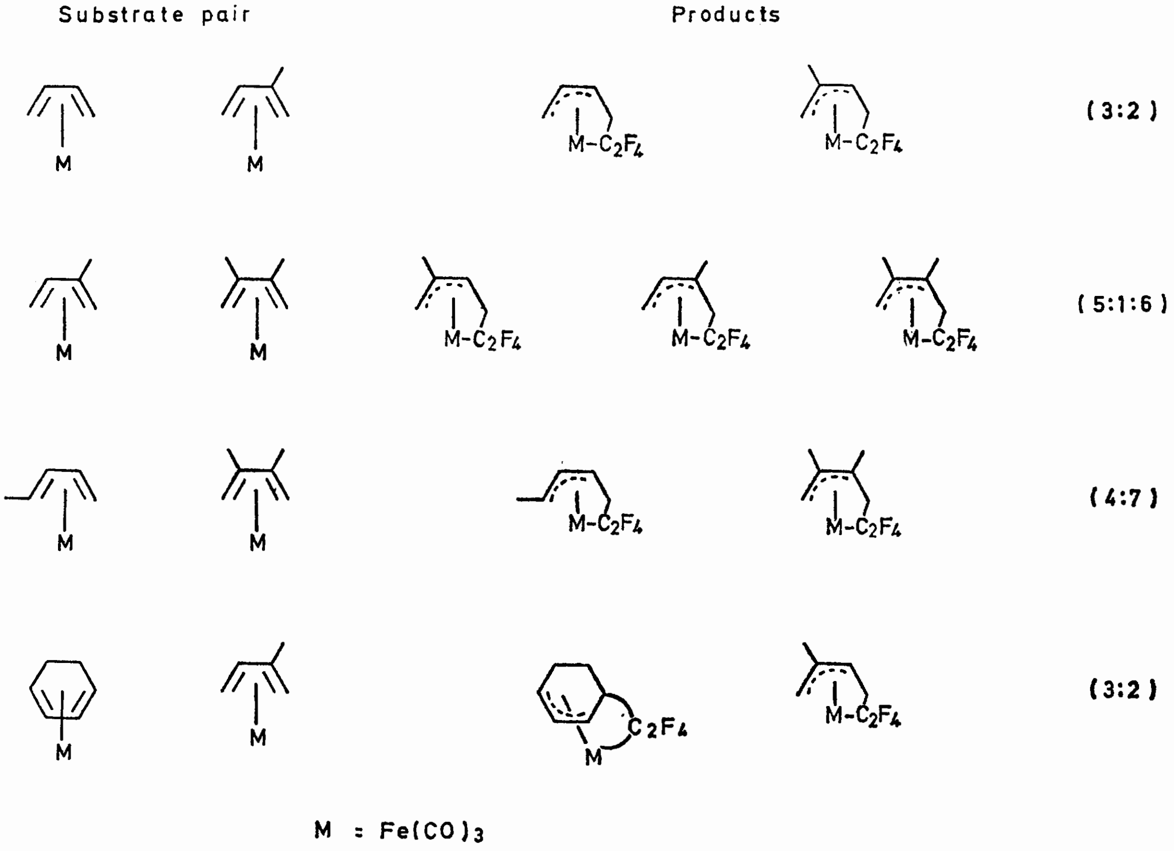
(f) *With (bicyclo*[4.2.0]*octa-*2,4*-diene)tricarbonyliron.* U.v. irradiation (55 h) of a solution of (bicyclo[4.2.0]-octa-2,4-diene)tricarbonyliron (0·50 g, 2·0 mmol) in n-hexane (12 ml) in the presence of an excess of C_2F_4 (0·50 g, 5·0 mmol) produced a large crop of crystals. Recrystallisation (0 °C) from methylene chloride–n-hexane gave yellow *crystals* of (VI) (0·28 g, 40%), m.p. 134—136 °C (Found: C, 45·0; H, 2·9; F, 21·3. $C_{13}H_{10}F_4FeO_3$ requires C, 45·1; H, 3·0; F, 21·9%), ν_{CO} (hexane) 2085s, 2030s, and 2013s cm^{-1}. The mass spectrum (base *m/e* 318) showed peaks at *m/e* 346 (*P*, 10%), 318 (*P* − CO, 100%), 290 (*P* − 2CO, 60%), and 262 (*P* − 3CO, 90%). The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 4·35 [ddd, 1H, H^2, $J_{1,2}$ = $J_{2,3}$ 7·0, J(H^{2}F^4) 3·5 Hz], 5·15 (dd, 1H, H^3, $J_{2,3}$ = $J_{3,4}$ 7·0 Hz), 5·79 (d, 1H, H^1, $J_{1,2}$ 7·0 Hz), 7·22 [m, 1H, H^4, $J_{3,4}$ 7·0, J(H^{4}F^3) 8·5, J(H^{4}F^4) 3·0 Hz], and 7·38—8·55 [complex m, 6H, H$^{5-10}$, J(H^{10}F^2) 7·5 Hz]. The ^{19}F n.m.r. spectrum (acetone) showed resonances at 64·7 p.p.m. [dddd, 1F, F^2, $J_{1,2}$ 248, $J_{2,3}$ 13·0, $J_{2,4}$ = J(F^{2}H^{10}) 7·5 Hz], 91·3 (dm, 1F, F^1, $J_{1,2}$ 248, $J_{1,3}$ 8·5, $J_{1,4}$ 3·0 Hz), 111·4 [ddddd, 1F, F^4, $J_{3,4}$ 222, $J_{2,4}$ 7·5, $J_{1,4}$ = J(F^{4}H^4) 3·0, J(F^{4}H^2) 3·5 Hz], and 114·5 [dddd, 1F, F^3, $J_{3,4}$ 222, $J_{2,3}$ 13·0, $J_{1,3}$ = J(F^{3}H^4) 8·5 Hz].

(g) *With tricarbonyl(cyclo-octa-*1,3*-diene)iron.* A Carius tube containing a solution of tricarbonyl(cyclo-octa-1,3-diene)iron (0·50 g, 2·0 mmol) in hexane (12 ml) and an excess of C_2F_4 (0·50 g, 5·0 mmol) was subjected to u.v. irradiation for 4 days. The resulting solution was filtered and subsequent cooling (0 °C, 3 days) of the filtrate afforded bright yellow *needles* of (VII) (0·20 g, 30%), m.p. 97—100 °C (Found: C, 44·7; H, 3·6; F, 21·3. $C_{13}H_{12}F_4FeO_3$ requires C, 44·8; H, 3·5; F, 21·8%), ν_{CO} (hexane) 2084s, 2030s, and 2014s cm^{-1}. The mass spectrum (base *m/e* 127) showed peaks at *m/e* 348 (*P*, 1%), 320 (*P* − CO, 15%), 292 (*P* − 2CO, 32%), 273 (*P* − 2CO − F, 1%), 264 (*P* − 3CO, 39%), and 245 (*P* − 3CO − F, 4%). The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 5·00 (m, 2H, H^{2,3}, $J_{1,2}$ 7·5, $J_{1,3}$ 3·5 Hz), 5·82 (dddd, 1H, H^1, $J_{1,11}$ = $J_{1,12}$ 9·0, $J_{1,2}$ 7·5, $J_{1,3}$ 3·5 Hz), 6·85 (m, 1H, H^4), 7·91 (m, 2H, $H^{11,12}$, $J_{1,11}$ = $J_{1,12}$ 9·0 Hz), and 8·06—9·04 (complex m, 6H, H$^{5-10}$). The ^{19}F n.m.r. spectrum (C_6H_6) showed resonances at 56·6 p.p.m. (dm, 1F, F^2, $J_{1,2}$ 258 Hz), 89·8 (dm, 1F, F^1, $J_{1,2}$ 258 Hz), 103·8 (dm, 1F, F^4, $J_{3,4}$ 222 Hz), and 107·8 (dm, 1F, F^3, $J_{3,4}$ 222 Hz). Further cooling (−30 °C, 3 days) produced colourless *needles* of (VIII) (0·07 g, 9%), m.p. 113—115 °C (Found: C, 44·0; H, 3·2; F, 20·1. $C_{14}H_{12}F_4FeO_4$ requires C, 44·7; H, 3·2; F, 20·2%), ν_{CO} (hexane) 2124m, 2066m, 2056s, and 2043m cm^{-1}; $\nu_{C=C}$ (Nujol) 1624vw cm^{-1}. The mass spectrum (base *m/e* 127) showed peaks at *m/e* 376 (*P*, 1%), 348 (*P* − CO, 5%), 320 (*P* − 2CO, 26%), 301 (*P* − 2CO − F, 2%), 292 (*P* − 3CO, 40%), 273 (*P* − 3CO − F, 2%), 272 (*P* − 3CO − HF, 2%), 264 (*P* − 4CO, 59%), 245 (*P* − 4CO − F, 2%), and 244 (*P* − 4CO − HF, 2%). The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 4·02—4·40 (complex m, 2H, H^{3,4}, $J_{2,3}$ = $J_{3,4}$ 10·5, $J_{3,5}$ = 4·5, $J_{4,5}$ = $J_{4,6}$ 8·0 Hz), 6·48 [ddd, 1H, H^2, $J_{2,3}$ 10·5, $J_{1,2}$ 7·0, J(H^{2}F^4) 4·5 Hz], and 7·40—8·97 [complex m, 9H, H$^{1,5-12}$, $J_{1,2}$ 7·0, J(H^{1}F^3) 37·0, J(H^{1}F^4) 3·0, J(H^{1}F^2) 2·0, J(H^{1}F^1) 1·5, $J_{4,5}$ = $J_{4,6}$ 8·0, $J_{3,5}$ 4·5 Hz]. The ^{19}F n.m.r. spectrum (acetone) showed resonances at 67·0 p.p.m. [dm, 1F, F^2, $J_{1,2}$ 234, $J_{2,4}$ 4·5, $J_{2,3}$ 2·5, J(F^{2}H^1) 2·0 Hz], 74·2 [dddd, 1F, F^1, $J_{1,2}$ 234, $J_{1,3}$ 11·5, $J_{1,4}$ 7·0, J(F^{1}H^1) 1·5 Hz], 120·7 [ddddd, 1F, F^4, $J_{3,4}$ 225, $J_{1,4}$ 7·0, $J_{2,4}$ = J(F^{4}H^2) 4·5, J(F^{4}H^1) 3·0 Hz], and 128·4 [ddddd, 1F, F^3, $J_{3,4}$ 225, $J_{1,3}$ 11·5, $J_{2,3}$ 2·5, J(F^{3}H^1) 37·0, and J(F^{3}H) 1·5 Hz].

(h) *With tricarbonyl(norbornadiene)iron.* U.v. irradiation (18 g) of a solution of tricarbonyl(norbornadiene)iron (0·30 g, 1·3 mmol) and tetrafluoroethylene (0·40 g, 4·0 mmol) in n-hexane (12 ml) and removal of volatile material *in vacuo* gave, on recrystallisation (−78 °C) of the residue from n-hexane, white *crystals* of (IX) (0·10 g, 24%), m.p. 86—88 °C (Found: C, 42·9; H, 2·4; F, 21·2. $C_{13}H_8F_4FeO_4$ requires C, 43·3; H, 2·2; F, 21·1%), ν_{CO} (n-hexane) 2126m, 2070s, 2058s, and 2042s cm^{-1}. The mass spectrum (base *m/e* 276) showed peaks at *m/e* 360 (*P*, 4%), 332 (*P* − CO, 12%), 304 (*P* − 2CO, 44%), and 276 (*P* − 3CO, 100%). The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 7·53 (bs, 1H, H^4), 7·79 [m, 1H, H^5, $J_{5,6}$ 4·5, J(H^{5}F^3) = J(H^{5}F^4) 10·0 Hz], 7·96 (s, 1H, H^1), 8·41 (m, 2H, H^{2,6}, $J_{2,3}$ = $J_{5,6}$ 4·5 Hz), 8·55 (m, 2H, H^{7,8}), and 8·68 (m, 1H, H^3, $J_{2,3}$ 4·5 Hz). The ^{19}F n.m.r. spectrum (CHCl$_3$) showed resonances at 58·4 [dddd, 1F, F^2, $J_{1,2}$ 252, $J_{2,3}$ = $J_{2,4}$ 5·5, J(F^{2}H) 2·5 Hz], 61·6 [dddd, 1F, F^1, $J_{1,2}$ 252, $J_{1,3}$ = J(F^{1}H) 7·5, $J_{1,4}$ 5·0 Hz], 101·6 [dm, 1F, F^4, $J_{3,4}$ 254, $J_{2,4}$ 5·5, $J_{1,4}$ 5·0, J(F^{4}H^5) 10·0 Hz], and 113·9 [dm, 1F, F^3, $J_{3,4}$ 254, $J_{1,3}$ 7·5, $J_{2,3}$ 5·5, J(F^{3}H^5) 10·0 Hz].

(i) *With tetra- and tri-carbonyl(*trans*-cinnamaldehyde)iron.* U.v. irradiation (2 days) of a solution of (*trans*-cinnamaldehyde)Fe(CO)$_4$ (0·50 g, 1·7 mmol) in benzene (12 ml) in the presence of an excess of C_2F_4 (0·40 g, 4·0 mmol) and removal of volatile material *in vacuo* gave, on recrystallisation (0 °C) of the residue from benzene–octane, light yellow platelets of the inseparable *cis*-isomers (Xa) and (Xb) (4 : 5, by n.m.r.) (0·21 g, 31%), m.p. 151—153 °C (Found: C, 45·1; H, 2·0; F, 19·7. $C_{15}H_8F_4FeO_5$ requires C, 45·0; H, 2·0; F, 19·0%), ν_{CO} (hexane) 2154m, 2094m, 2080s, 2062s, and 1667s (CHO) cm^{-1}. The mass spectrum (base *m/e* 344) showed peaks at *m/e* 400 (*P*, 12%), 372 (*P* − CO, 24%), 344 (*P* − 2CO, 100%), 316 (*P* − 3CO, 72%), and 288 (*P* − 4CO, 24%). The ^{1}H n.m.r. spectrum ([^{2}H$_6$]acetone) of the mixture showed resonances due to (Xa) at τ 0·43 [d, 1H, *CHO*, J(H^{1}C*HO*) 3·0 Hz], 2·49—2·79 (m, 5H, C_6H_5), 5·91 [dd, 1H, H^2, $J_{1,2}$ 2·0, J(H^{2}F) 11·0 Hz], and 5·98 [dd, 1H, H^1, J(H^{1}C*HO*) 3·0, $J_{1,2}$ 2·0 Hz] and due to (Xb) at τ 0·42 [d, 1H, C*HO*, J(H^{2}C*HO*) 3·0 Hz], 2·49—2·79 (m, 5H, C_6H_5), 5·94 (m, 1H, H^1), and 6·31 [dm, 1H, H^2, J(H^{2}C*HO*) 3·0, J(H^{2}F) 12·5 Hz]. The ^{19}F n.m.r. spectrum (acetone) of the mixture showed resonances at 67·0 p.p.m. (dm, 1F, F^2, $J_{1,2}$ 231 Hz), 71·8 (ddd, 1F, F^1, $J_{1,2}$ 231, $J_{1,3}$ 12·5, $J_{1,4}$ 8·5 Hz), 118·2 (dm, 1F, F^4, $J_{3,4}$ 229, $J_{1,4}$ 8·5 Hz), and 125·8 (dm, 1F, F^3, $J_{3,4}$ 229, $J_{1,3}$ 12·5 Hz).

Competitive Reactions of Tricarbonyl(diene)iron Species with a Limited Amount of Tetrafluoroethylene.—Equimolar quantities (2·0 mmol) of a pair of [Fe(diene)(CO)$_3$] substrates in hexane (12 ml) were sealed in a Carius tube (100 ml) along with sufficient C_2F_4 (0·20 g, 2·0 mmol) to react completely with one tricarbonyl complex. The tube and contents were irradiated for 24 h and after removal of volatile material *in vacuo* the residue was chromatographed on alumina to give a mixture of the products. The crystalline mixtures were crushed into fine powders and ^{1}H and ^{19}F n.m.r. spectra recorded of representative amounts (0·05 g) dissolved in $CDCl_3$ (0·5 ml). Careful choice of substrate pairs facilitated reasonable estimates of product ratios. Four pairs of diene substrates were used and the results of each experiment are summarised below.



Reaction of Complex (III) with Trimethyl Phosphite.—Complex (III) (0·20 g, 0·65 mmol) and trimethyl phosphite (1·0 g, 8·0 mmol) were refluxed together in hexane for 0·5 h. Volatile material was removed *in vacuo* and the residue chromatographed on an alumina column. Elution with methylene chloride–hexane gave, on recrystallisation (−78 °C) from hexane, pale yellow *crystals* of (XI) (0·22 g, 84%), m.p. 62—64 °C (Found: C, 35·2; H, 4·2; F, 17·9; P, 8·0. $C_{12}H_{17}F_4FeO_5P$ requires C, 35·6; H, 4·2; F, 18·8; P, 7·7%), ν_{CO} (hexane) 2077s and 2030s cm^{-1}. The mass spectrum (base *m/e* 376) showed peaks at *m/e* 404 (*P*, 15%), 385 (*P* − F, 2%), 376 (*P* − CO, 100%), 357 (*P* − CO − F, 4%), 348 (*P* − 2CO, 80%), 329 (*P* − 2CO − F, 3%), 308 (*P* − C_5H_8 − CO, 15%), 280 (*P* − C_5H_8 − 2CO, 5%), and 252 [*P* − P(OMe)$_3$ − CO, 10%]. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 5·92 (m, 1H, H^4), 6·22 [d, 9H, POMe, J(PH) 11·0 Hz], 6·98 (m, 1H, H^2), 7·60 (m, 1H, H^1), 7·22 [m, 1H, H^5, J(H^{5}P^3) 14·0 Hz], 8·02 (s, 3H, Me), and 8·36 [m, 1H, H^6, J(H^{6}F^3) 37·0 Hz]. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at 83·2 p.p.m. (dm, 1F, F^1, $J_{1,2}$ 242, $J_{1,3}$ 14·0 Hz), 96·1 (dm, 1F, F^2, $J_{1,2}$ 242, $J_{2,3}$ 3·0 Hz), 114·2 (dm, 1F, F^4, $J_{3,4}$ 216 Hz), and 117·3 [ddddd, 1F, F^3, $J_{3,4}$ 216, $J_{1,3}$ 14·0, $J_{2,3}$ 3·0, J(F^{3}H^6) 37·0, J(F^{3}H^5) 14·0 Hz].

*Reaction of Tricarbonyl(*o*-styryldiphenylphosphine)iron with Tetrafluoroethylene.*—U.v. irradiation (1 day) of a solution of tricarbonyl(*o*-styryldiphenylphosphine)iron (0·50 g, 1·2 mmol) and tetrafluoroethylene (0·40 g, 4·0 mmol) in hexane (12 ml) gave large orange cubic crystals, which were recrystallised (0 °C) from methylene chloride–hexane to give pale yellow *crystals* of (XII) (0·36 g, 59%), m.p. 209—212 °C (Found: C, 56·7; H, 3·2; F, 14·1; P, 6·0. $C_{25}H_{17}F_4FeO_3P$ requires C, 56·7; H, 3·2; F, 14·4; P, 5·9), ν_{CO} (hexane) 2087w, 2024s, and 2011s cm^{-1}. The mass spectrum (base *m/e* 350) showed peaks at *m/e* 528 (*P*, 1%), 500 (*P* − CO, 6%), 472 (*P* − 2CO, 7%), 452 (*P* − 2CO − HF, 1%), 444 (*P* − 3CO, 10%), 425 (*P* − 3CO − F, 1%), and 424 (*P* − 3CO − HF, 1%). The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·3—3·1 (complex m, 14H, C_6H_5), 6·15 (dd, 1H, H^1, $J_{1,3}$ 12·0, $J_{1,2}$ 6·0 Hz), 7·10 [m, 1H, H^3, $J_{2,3}$ 13·5, $J_{1,3}$ 12·0, $J(H^3F^3)$ 11·0, $J(H^3F^1)$ 5·5 Hz], and 7·4 [ddd, 1H, H^2, $J_{2,3}$ 13·5, $J_{1,2}$ 6·0, $J(H^2F^3)$ 33·0 Hz]. The ^{19}F n.m.r. spectrum (acetone) showed resonances at 65·9 p.p.m. (dd, 1F, F^2, $J_{1,2}$ 234, J_{PF} 18·0 Hz), 74·4 [ddddd, 1F, F^1, $J_{1,2}$ 234, $J_{1,3}$ 11·0, $J_{1,4}$ = $J(F^1H^3)$ 5·5, J_{PF} 17·5 Hz], 116·4 [dddd, 1F, F^3, $J_{3,4}$ 230, $J_{1,3}$ = $J(F^3H^3)$ 11·0, $J(F^3H^2)$ 33·0 Hz], and 120·5 (dm, 1F, F^4, $J_{3,4}$ 230, $J_{1,4}$ 5·5 Hz).

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