Reaction of Fluoro-olefins with Tricarbonyl(buta-1,3-diene, trimethylenemethane, or cinnamaldehyde)iron

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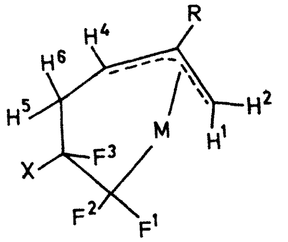
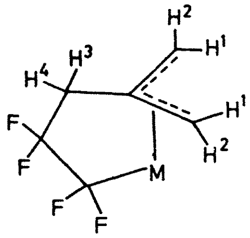
Summary Tetrafluoroethylene and hexafluoropropene react with $Fe(CO)_3$(diene) (diene = buta-1,3-diene, isoprene, or cinnamaldehyde) or tricarbonyl(trimethylenemethane)-iron to form π-allylic complexes, in which the iron atom and the allyl group are linked by a fluorocarbon chain; treatment of $[\mathrm{FeC(CF_3)_2O(CO)_2}\pi\text{-}\mathrm{C_4Me_4}]$ with trimethyl phosphite leads to a similar linking reaction.

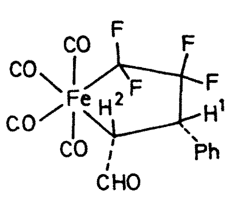
THE recent report[1] that the three-membered ring complex $\mathrm{(Ph_3P)_2NiCF_2CF_2}$ reacts with C_2F_4 to form the octafluoronickelacyclopentane, $\mathrm{(Ph_3P)_2NiCF_2CF_2CF_2CF_2}$, and that the complexes $\mathrm{L_2NiC(CF_3)_2X}$ (X = O or NH, L = $\mathrm{Bu^tNC}$) react with $\mathrm{(CF_3)_2C{=}X}$ to form analogous five-membered heterocyclic compounds $\mathrm{L_2NiC(CF_3)_2XC(CF_3)_2X}$, suggested the possible general importance of 3- to 5-membered metallo-ring transformations. Moreover, the observation[2] that tetrafluoroethylene and hexafluoropropene react with tricarbonyl(tetramethylcyclobutadiene)iron to form π-allylic complexes in which the C_4 ring is linked to the metal by a C_2 fluorocarbon chain indicated that a wide range of unsaturated hydrocarbon compounds may be activated towards carbon–carbon bond formation by co-ordination to a metal with a d^8 configuration. Herein, we report some new reactions† which support this concept.



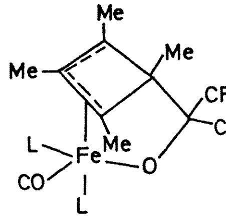
[Ia ; R = H, X = F, M = Fe(CO)₃]
[Ib ; R = Me, X = CF₃, M = Fe(CO)₃]



[II; M = Fe(CO)₃]



(III)



[IV L = P(OMe)₃]

U.v. irradiation of a hexane solution of a fluoro-olefin and a tricarbonyl-(1,3-diene)iron complex affords high yields of crystalline 1:1 adducts. *E.g.*, tetrafluoroethylene and buta-1,3-dienetricarbonyliron afforded pale yellow crystals of (Ia), m.p. 83°, ν_{CO} (hexane) 2085s, 2035m, and 2019scm^{-1}; ^{1}H, τ 4·90 (1H, H^3, J_{13} 13, $J_{23} = J_{34}$ 7, J_{HF} 3·5 Hz), 5·32 (1H, H^4, $J_{34} = J_{45} = J_{46}$ 7·0 Hz), 6·54 (1H, H^2, J_{12} 3·0, J_{23} 7·0 Hz), 7·32 (1H, H^1, J_{12} 3·0, J_{13} 13·0, J_{HF} 5·0 Hz), 7·58 (1H, H^6, $J_{56} = J_{HF}$ 14·0, J_{46} 7·0 Hz), and 8·60 (1H, H^5, J_{56} 14·0, J_{45} 7·0, J_{HF} 38·0 Hz); ^{19}F, 108·5 [1F, F^1, J_{12} 222, J_{13} 2·0, $J_{14} = J(F^1H^6)$ 14·0, $J(F^2H^5)$ 38·0 Hz], 104·5 (1F, F^2, J_{12} 222 Hz), 76·8 [1F, F^4, J_{34} 236, J_{24} 1, J_{14} 14·0, $J(F^4H)$ 6·0, $J(F^4H)$ 5·0 Hz], and 87·3 p.p.m. (1F, F^3, J_{34} 236, J_{13} 2·0, J_{23} 8·0 Hz). Double-irradiation experiments confirmed these assignments.

The observations are fully consistent with the illustrated π-allylic structure.[3] The related reaction of hexafluoropropene with tricarbonyl(isoprene)iron gave pale yellow crystals of (Ib), m.p. 97°, ν_{CO} (hexane) 2088s, 2035m, and 2014s cm^{-1}. The ^{1}H and ^{19}F n.m.r. spectra of this compound show that the reaction is stereospecific, and, as illustrated involves the attachment of the trifluoromethyl-substituted carbon atom to the unsubstituted double bond of the co-ordinated diene.

Tricarbonyl(trimethylenemethane)iron[4] and tetrafluoroethylene react on u.v. irradiation to give the 1:1 adduct (II), m.p. 73°, ν_{CO} (hexane) 2090s, 2033m, and 2026s cm^{-1}; ^{1}H, τ 6·62 (2H, H^2, J_{12} 2·0 Hz), 7·30 (1H, H^3, J_{HF} 3·0 Hz), 7·44 (1H, H^4, $J_{\ F}$ 3·0 Hz), and 7·58 (2H, H^1, J_{12} 2·0 Hz). Examination of molecular models indicates that the inequivalence of H^3 and H^4 arises from a twisting of the fluorocarbon chain. The ^{19}F n.m.r. spectrum showed resonances at 75·8 (2F, m) and 106·2 p.p.m. (2F, m). This suggests the illustrated π-allylic structure for (II). It is interesting that protonation and bromination of tricarbonyl(trimethylenemethane)iron are reported[4] to give π-allylic iron complexes, suggesting that if it is assumed that C_2F_4 is an electrophilic reagent there is a formal relationship to the formation of (II). Tricarbonyl(phenyltrimethylenemethane)iron reacts in a similar way with C_2F_4 to give a π-allylic complex, in which the fluorocarbon chain becomes attached to the carbon atom carrying the phenyl group.

Both tetra- and tri-carbonyl(cinnamaldehyde)iron[5] react with tetrafluoroethylene to give pale yellow crystals of (III), m.p. 151°, ν (hexane) 2154m, 2094m, 2080s, 2062s, and 1667s (CHO) cm^{-1}. The ^{1}H and ^{19}F n.m.r. and i.r. spectra showed that (III), which is formed stereospecifically, does not contain a $-CF_2OCH-$ or π-oxapropenyl system, but is a ferracyclopentane containing a functional group, *i.e.* CHO, formed by the linking of the cinnamaldehyde and tetrafluoroethylene within the co-ordination sphere. In (III) the CHO and the Ph groups have a relative *cis*-configuration.

An insight into the mechanism of these reactions was obtained from a study of the reaction of the previously described[2] complex $\mathrm{FeC(CF_3)_2O(CO)_2}\pi\text{-}\mathrm{C_4Me_4}$ with phosphorus ligands. Trimethyl phosphite afforded orange crystals of (IV), m.p. 124°, ^{1}H, τ 6·65 (d, 18H, MeOP, $|J|_{POCH}$ 10·0 Hz), 8·16 (s, 3H), 8·21 (s, 3H), 8·27 (s, 3H), and 8·88 (s, 3H); ^{19}F, 71·4 p.p.m. (s, 6F). Thus, reaction with

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† The new compounds described have been characterised by elemental analysis, and mass, i.r., and ^{1}H and ^{19}F n.m.r. spectroscopy

phosphite leads to a linking of the carbon of the co-ordinated hexafluoroacetone to the C_4 ring; this arrangement being indicated by the absence of $^{31}P-^{19}F$ coupling. It is likely that a similar oxidative (d^8 to d^6) two-step process is involved in the formation of (I), (II), and (III).

Preliminary results indicate that tricarbonyl(cycloheptatriene)iron reacts with fluoro-olefins in a similar manner, which provides an interesting contrast with our previous[6] finding that strongly electrophilic molecules like tetracyanoethylene add *exo*-1,3 to $C_7H_8Fe(CO)_3$.

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[1] A. Greco, M. Green, S. K. Shakshooki, and F. G. A. Stone, *Chem. Comm.*, 1970, 1374.
[2] A. Bond and M. Green, *Chem. Comm.*, 1971, 12.
[3] L. A. Fedovov, *Russ. Chem. Rev.*, 1970, **39**, 655.
[4] K. Erlich and G. F. Emerson, *Chem. Comm.*, 1969, 59.
[5] K. Stark, J. E. Lancaster, H. D. Murdoch, and E. Weiss, *Z. Naturforsch.*, 1964, **19b**, 284.
[6] M. Green, S. Tolson, J. Weaver, D. C. Wood, and P. Woodward, *Chem. Comm.*, 1971, 222.