Mono(fluoro-olefin) Complexes of Pentacarbonyliron

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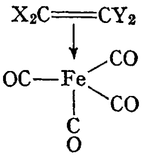
SEVERAL complexes of fluoro-olefins with transition metals have been described recently.[1] We now report the first mono-(fluoro-olefin) complexes obtained from pentacarbonyliron.

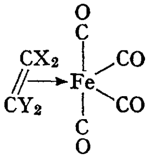
Ultraviolet irradiation (2—14 days) of pentacarbonyliron with the liquid olefins chlorotrifluoroethylene, hexafluoropropene, perfluorocyclopentene, perfluorocyclohexene, or 1,1-dichlorodifluoroethylene gives analytically pure complexes of the type olefin,$Fe(CO)_4$ in 70—80% yield with the first two olefins, and 1—20% yield with the others. The complexes from the first two olefins are liquids which decompose slowly in air; the others are crystalline solids, m.p. 53°, 34°, and 30° respectively, which are stable in air. The olefin is readily displaced from the complex. For example, the chlorotrifluoroethylene complex, a yellow liquid, b.p. 25°/5 mm., obtained in 70% yield, liberates chlorotrifluoroethylene and carbon monoxide quantitatively in ratio 1 : 4 on treatment with iodine; the hexafluoropropene complex $C_3F_6Fe(CO)_4$ liberates carbon monoxide, the olefin, or both on treatment with triphenylphosphine to give axial-$Ph_3PFe(CO)_4$ (19%), $C_3F_6,Fe(CO)_3$-(PPh_3) (17%), and *trans*-$(Ph_3P)_2Fe(CO)_3$ (11%), where the stereochemistry[2] follows from the infrared spectra.

Irradiation of pentacarbonyliron with tetrafluoroethylene gives a liquid mixture of pentacarbonyliron (85%) and the complex $C_2F_4,Fe(CO)_4$ (C–F bands at 6·97, 8·60 and 9·45 μ; ^{19}F n.m.r., singlet, 13·8 p.p.m. to high field of external trifluoroacetic acid), but the pure complex has not yet been isolated. The olefin in the complex is completely displaced as tetrafluoroethylene by reaction with iodine; this and the singlet n.m.r. spectrum excludes the possibility of an unsymmetrical complex containing two carbons, and makes complexes containing three or four carbons unlikely. Prolonged irradiation of pentacarbonyliron with tetrafluoroethylene leads only to the formation of the known[3,4] cyclic compound $(CF_2)_4Fe(CO)_4$.

Tetrafluoroethylene partially displaces chlorotrifluoroethylene from the complex $C_2ClF_3,Fe(CO)_4$ when the latter is irradiated in the presence of tetrafluoroethylene. Treatment with iodine of the mixture of liquid complexes liberates tetrafluoroethylene and chlorotrifluoroethylene in a 1 : 3 ratio.

The bonding in these new mono-(fluoro-olefin) complexes may be visualised as involving either (i) donation of the olefin π-electrons to iron, and back-donation into π^*-antibonding orbitals by filled *d*-orbitals (I or II), or (ii) two carbon–iron σ-bonds (III). The ready liberation of the olefin on pyrolysis of the complexes or on treatment with iodine tends to favour (I) or (II), but the ^{19}F n.m.r. coupling constants are widely different from those of the unco-ordinated olefins, [*e.g.*, C_2ClF_3,-$Fe(CO)_4$ shows an ABX pattern with coupling constants 131, 62, and 2 c./sec., compared with 78, 58, and 115 c./sec.[5] in the pure olefin], and suggest an approach to sp^3 hybridisation. Detailed discussion of physical data and structure is deferred to full publication.


(I)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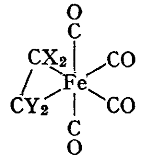
(III)

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[1] G. W. Parshall and F. N. Jones, *J. Amer. Chem. Soc.*, 1965, **87**, 5356; M. J. Mays and G. Wilkinson, *J. Chem. Soc.*, 1965, 6629.

[2] F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1960, 1440.

[3] H. H. Hoehn, L. Pratt, K. F. Watterson, and G. Wilkinson, *J. Chem. Soc.*, 1961, 2738.

[4] T. A. Manuel, S. L. Stafford, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1961, **83**, 249.

[5] H. M. McConnell, C. A. Reilly, and A. D. McLean, *J. Chem. Phys.*, 1956, **24**, 479.