Perfluorobutadieneiron Tetracarbonyl

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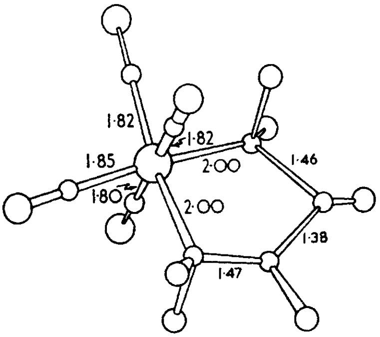
THE mode of attachment of butadiene or butadiene fragments of cyclic unsaturated ligands to transition-metal ions has been examined by a number of structural analyses which have been completed recently.[1] The controversy, relating to the question as to whether butadiene forms a 'π' or a 'σ—π' complex, has been resolved by a molecular orbital view of the bonding in these molecules.[2]

It was clear that the electronegative substituents in the butadiene fragment of such ligands as tetrakistrifluoromethylcyclopentadienone, hexakistrifluoromethylbenzene, and octafluorocyclohexadiene encouraged, in valence bond terms, the formation of localised metal–carbon bonds. This tendency is also demonstrated by the fact that whereas the reaction of butadiene with iron pentacarbonyl gives the well-known butadieneiron tricarbonyl, the reaction of perfluorobutadiene with iron pentacarbonyl yields perfluorobutadieneiron tetracarbonyl;[3] the molecular structure of C_4F_6-$Fe(CO)_4$ is shown in the Figure.

The C_4Fe ring is planar ($\pm 0{\cdot}02$ Å) so that there is no evidence of 'sandwich' bonding. In addition to the σ-bonds formed between the metal and the 1,4 carbon atoms there is presumably some interaction, albeit small, between the 2-3 ethylenic-type bond and unfilled metal orbitals such as the 4*p*. The co-ordination symmetry of the iron is closely octahedral, the difference of 0·18 Å between the mean Fe–$C(F_2)$ bond length (2·00 Å) and the Fe-C(O) length (1·82 Å) reflecting the difference in metal–carbon π-bond character (the corrected difference, allowing for the dependence of the covalent radius of carbon on formal hybridisation state, is *ca.* 0·12 Å).

The formation of the iron tetracarbonyl species with perfluorobutadiene raises the question as to whether it may be possible to form butadieneiron tetracarbonyl and perfluorobutadieneiron tricarbonyl. A study of the reactions of, say, 1,1′,2-trifluorobutadiene and other halogenobutadienes with iron pentacarbonyl would be of considerable interest. With other metal carbonyls, one may envisage the formation of allylic species[4] which represent the intermediate situation between the extreme π- and σ–π formalisms of metal to butadiene bonding.



FIGURE

The *X*-ray analysis of $C_4F_6Fe(CO)_4$ has been completed using Patterson, Fourier, and least-squares analysis of 950 independent reflexions. The mean standard deviations of the bond lengths, obtained by inversion of the block-diagonal least-squares matrix, are presently Fe–C 0·02 Å, C–C, C–O, and C–F 0·025 Å and correspond to a discrepancy index of 0·094.

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[1] M. R. Churchill and R. Mason, *Adv. Organometallic Chem.*, in the press.

[2] S. F. A. Kettle and R. Mason, *J. Organometallic Chem.*, **1966**, **5**, 97.

[3] R. L. Hunt, M. Roundhill, and G. Wilkinson, private communication.

[4] P. B. Hitchcock and R. Mason, *Chem. Comm.*, 1966, 503.