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Olefin complexes of tetracarbonyliron

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In our earlier work[1,2] on mono(fluoro–olefin) complexes derived from iron carbonyls the complexes were prepared by UV irradiation of the olefin with either pentacarbonyliron or, in two cases, with nonacarbonyldiiron. We now report the formation of complexes from a number of olefins by reaction with nonacarbonyldiiron under much milder conditions. Thus trifluoroethylene and 1,1-dichloro-2,2-difluoroethylene form complexes of the type olefin·$Fe(CO)_4$ when kept in the dark at room temperature with $Fe_2(CO)_9$, and other olefins (see Table 1) do so under irradiation from a tungsten filament lamp; tetrakis(trifluoromethyl)ethylene was inert under these conditions but formed a stable complex under irradiation from a medium pressure mercury arc lamp.

The yields in these reactions are typically 1–57% based on $Fe_2(CO)_9$ and the equation:

$$\text{olefin} + Fe_2(CO)_9 \rightarrow \text{olefin} \cdot Fe(CO)_4 + Fe(CO)_5$$

although the yield from C_2Cl_4 was only 0.1%. The optimum reaction conditions are often closely defined for a particular olefin and with all olefins except $(CF_3)_2C{=}C(CF_3)_2$, which forms a very stable complex, too long a reaction time or over-vigorous irradiation leads to decomposition of the olefin complex and the formation of carbon monoxide and/or iron carbonyls, and a residue whose solution in acid contains fluoride ion (except for olefin = C_2Cl_4). The complexes, which range in stability from the highly stable $[(CF_3)_2C{=}C(CF_3)_2]Fe(CO)_4$ and $(CF_2{=}CHF)Fe(CO)_4$ to $(CH_2{=}CF_2)Fe(CO)_4$, which decomposes in minutes at room temperature, have been characterised by elemental analysis, and their IR, NMR, and, in most cases, their mass spectra. In none of the reactions did we find any trace of compounds analogous to the five-membered heterocycle formed in analogous reactions[3,4,5] of tetrafluoroethylene.

The IR absorptions in the CO stretching region, together with the next highest frequency band, are shown for the complexes in Table 1. The carbonyl bands are consistent with either a trigonal bipyramid structure, with the olefin considered as occupying one position, or with an octahedral structure in which the two carbon atoms of the olefin are each considered to be σ-bonded to the iron (*cf.* ref.2). The band at next