A Formal Insertion Reaction of Tricarbonyl-π-tetramethylcyclobutadieneiron with 1,1,1-Trifluoroethylidene; Ring-expansion Reactions of π-Cyclobutenyliron Complexes

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Summary U.v. irradiation of $[Fe(CO)_3\pi\text{-}C_4Me_4]$ with C_2F_3H affords as one of the products an adduct (II) containing a bridging $CH(CF_3)$ group; thermolysis of (II) leads to C_4 to C_5 ring-expansion reactions with the formation of $[Fe(CO)_2\pi\text{-}C_5Me_4CF_3]_2$ and a ketonic C_5 π-allylic complex.

TRIFLUOROETHYLENE reacts with tricarbonyltetramethylcyclobutadieneiron in hexane on u.v. irradiation to form two products, which proved† to be isomeric 1:1 adducts. One of these, m.p. 120°, was assigned structure (I) on the basis of i.r. and ^{1}H and ^{19}F n.m.r. spectra. In forming (I) trifluoroethylene has inserted sterespecifically, a reaction which is analogous to the previously observed[1] insertion of tetrafluoroethylene.

The second and more unusual product (20%), complex (II), m.p. 100°, showed ^{1}H n.m.r. resonances at τ 8·12 (3H, s, Me^a), 8·14 (6H, s, Me^b and Me^c), 9·16 (3H, s, Me^d), and 10·2 [1H q, J(H–CF$_3$) 12·0Hz] and a single ^{19}F n.m.r. doublet resonance at 55·7 [d, J(CF$_3$–H) 12·0 Hz] suggesting the presence of a methyl-substituted π-cyclobutenyl system, and also a $CH(CF_3)$ group σ-bonded to the iron atom and C_4 ring. The structure (II) is consistent with preliminary *X*-ray crystallographic studies.[2] The formation of (II), therefore, involves an unusual insertion of 1,1,1-trifluoroethylidene.

When (II) is heated (100°, 6 h) in hexane, red-black needles of a dinuclear complex (III) (28%) are obtained, m.p. 250°, which from the mass spectrum, i.r., ^{1}H n.m.r. [τ 8·13 (6H, s), 8·39 (6H, s)], and ^{19}F n.m.r. [singlet resonance at 52·0] is formulated as a C_5 ring substituted π-cyclopentadienyliron dicarbonyl dimer. There is no precedent for a ring expansion reaction of this kind, in which hydrogen is lost. However, Herberich and his co-workers have demonstrated[3] five- to six-membered ring enlargement reactions in π-cyclopentadienylcobalt chemistry. A plausible reaction path from (II) and (III) would involve migration of hydrogen from the trifluoromethyl substituted carbon on to iron with concomitant ring enlargement *via* a 1,2-shift. The resultant

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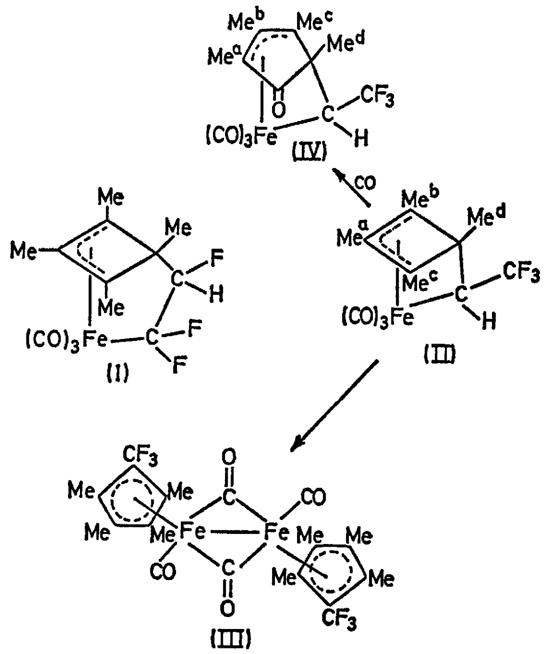
† Satisfactory elemental analyses and mass spectra were obtained for all compounds.



hydride species [FeH(CO)$_2\pi$-C$_5$Me$_4$CF$_3$)] would by analogy with cyclopentadienyliron chemistry[4] be expected to lose hydrogen and dimerise.

A second product of the thermolysis reaction is complex (IV), m.p. 105—106°, which could be obtained in higher (80%) yield by reaction of (II) with carbon monoxide (100 atm, 80 °C). Elemental analysis and mass spectroscopy confirmed the introduction of one mole of carbon monoxide as indicated by the presence in the i.r. of a band at 1731m cm^{-1}. The ^{1}H n.m.r. spectrum showed resonances at τ 7·82 (3H, s, Me^b), 8·01 (3H, s, Me^a), 8·15 (3H, s, Me^c), 9·08 (3H, q, Me^d), and 10·14 [1H, q, J(H–CF$_3$) 13·0 Hz], and the ^{19}F spectrum a resonance at 53·9 [3F, d of q, J(CF$_3$–H) 13·0, J(CF$_3$–Me) 1·5 Hz]. Since complex (IV) is stable to carbon monoxide during its formation this eliminates structures involving a 1,3-diene bonded to Fe(CO)$_3$. On heating, (IV) does not decarbonylate or transform into (III). The formation of (IV) can be understood as involving insertion of carbon monoxide into the π-allylic portion of (II) followed by a ring enlargement; the Fe(CO)$_3$ σ-bonded to the [CH(CF$_3$)] group stabilising the resultant C$_5$ ring.

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