Reactions of Tricarbonyltetramethylcyclobutadieneiron with Fluoro-ketones, -olefins, and -acetylenes

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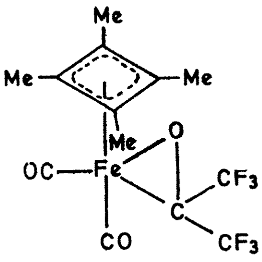
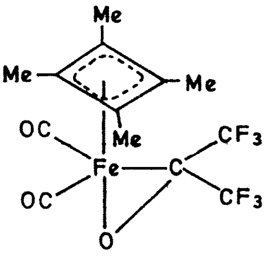
Summary Irradiation of [Fe(CO)$_3$π-C$_4$Me$_4$] with hexafluoroacetone gives [FeC(CF$_3$)$_2$O(CO)$_2$π-C$_4$Me$_4$], whereas, tetrafluoroethylene and hexafluoropropene afford novel π-allylic complexes, in which the fluoro-olefin links the C$_4$ ring to the metal atom.

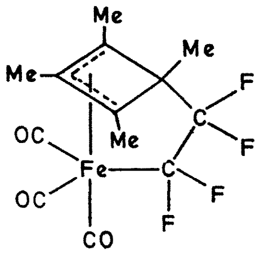
THE synthesis[1] of tricarbonylcyclobutadieneiron led to important advances in cyclobutadiene chemistry. It was found[2] that the co-ordinated cyclobutadiene readily underwent electrophilic substitution reactions such as acylation, mercuration, chloromethylation, formylation, and deuteriation; the reactions being considered to proceed *via* cationic π-allylic intermediates. In addition it was observed[3] that oxidative decomposition of the iron complex in the presence of dienophiles or dienes afforded adducts corresponding to the Diels–Alder addition of singlet cyclobutadiene.



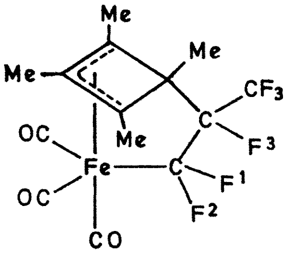
(Ia)



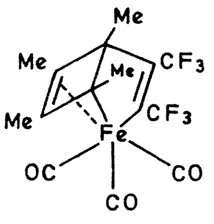
(Ib)



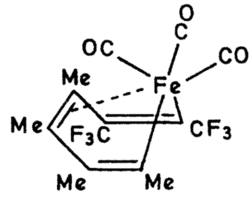
(II)



(III)



(IVa)



(IVb)

We have previously[4] found that a wide variety of d^{10} and d^8 transition-metal complexes undergo oxidative-addition or elimination reactions with electronegatively substituted unsaturated systems. However, similar reactions with the d^8 complexes C$_8$H$_8$M(CO)$_3$ (M = Fe or Ru) afforded products, in which the unsaturated system had added to the C$_8$ ring.[5] Clearly, reactions of the latter type with the d^8 system tricarbonylcyclobutadieneiron would be of interest. We report here some preliminary studies with tricarbonyltetramethylcyclobutadieneiron; it being thought that the methyl groups would effectively increase the reactivity of the iron.

U.v. irradiation of a hexane solution of hexafluoroacetone and tricarbonyltetramethylcyclobutadieneiron afforded red crystals of (I) [m.p. 61°, ν (hexane) 2041s and 1999s cm^{-1}, singlet ^{1}H n.m.r. resonances at τ8·4 and 8·8 (relative intensity 3 : 2), ^{19}F n.m.r. resonance at 80·0 p.p.m. (s, 6F) and 82·8 (overlapping multiplets, 6F)], which is formulated as an isomeric mixture of the complexes (Ia), (Ib), and (Ic), the last being identical with (Ib) but with the oxygen and C(CF$_3$)$_2$ groups interposed.

In contrast, the corresponding reaction with fluoro-olefins affords novel π-allylic complexes in which the fluoro-olefin links the C$_4$ ring and metal atom. For example, irradiation of [Fe(CO)$_3$π-C$_4$Me$_4$] with an excess of tetrafluoroethylene affords pale yellow crystals of (II), m.p. 148—150°; ν (hexane) 2076m, 2011s, and 1999m cm^{-1}; singlet ^{1}H n.m.r. resonances at τ7·80 (s, 3H), 8·34 (s, 6H), and 8·90 (s, 3H); ^{19}F n.m.r. resonances 70·8 p.p.m. (m, 2F) and 120·8 (m, 2F) (double irradiation collapsing the other multiplet to a singlet); an excess of hexafluoropropene giving pale yellow crystals of (III) m.p. 123°; ν (hexane) 2076m, 2063w, 2023s, and 1996s cm^{-1}; singlet ^{1}H n.m.r. resonances at τ7·80 (s, 3H), 8·21 (s, 3H), 8·38 (s, 3H), and 8·88 (s, 3H); ^{19}F n.m.r. resonances at 69·3 p.p.m. {m, 3F, J (3-F–CF$_3$) 12·0 Hz, J (2-F–CF$_3$) 17·0 Hz, J (1-F–CF$_3$) 3·0 Hz, 107·5 [d of m, 1F$_1$, J (1-F–2-F) 240 Hz, J (1-F–3-F) 12·0 Hz, J (1-F–CF$_3$) 3·0 Hz], 112·3 [d of m, 1F$_2$, J (1-F–2-F) 240 Hz, J (2-F–CF$_3$) 17·0 Hz, J (2-F–3-F) 6·0 Hz], and 155·0 [m, 1F$_3$, J (3-F–CF$_3$) 12·0 Hz, J (1-F–3-F) 12·0 Hz, J (2-F–3-F) 6·0 Hz]}.

These observations are compatible with the illustrated structures (II) and (III); the ^{1}H n.m.r. spectrum of (II) showing three chemical shifts with relative intensities of 1 : 2 : 1 as required by a π-allylic structure. In agreement with this, the ^{1}H n.m.r. spectrum of the hexafluoropropene complex, which is formed stereospecifically, shows an additional peak due to the absence of the plane of symmetry present in (II).

Whereas the formation of the hexafluoroacetone complex (I) parallels the report[6] that tricarbonylcyclobutadieneiron reacts on irradiation with dimethyl fumarate or dimethyl maleate to form the corresponding complexes [Fe(CO)$_2$-π-C$_4$H$_4$ MeO$_2$C·CH : CH·CO$_2$Me], the reaction with fluoro-olefins is without precedent, and represents a new class of reaction of co-ordinated cyclobutadiene.

The reaction on irradiation of [Fe(CO)$_3$π-C$_4$Me$_4$] with hexafluorobut-2-yne was also investigated and found to give orange crystals of (IV), m.p. 62°; ν (hexane) 2069s, 2013s, and 1991m; ^{1}H n.m.r. resonances at τ7·4 (s, 3H), 7·58 (s, 3H), 8·28 (q, 3H, J_{HF} 3·0 Hz), and 8·44 (s, 3H);

^{19}F n.m.r. resonances at 55·2 p.p.m. (q, 3F, J_{FF} 18·0 Hz) and 55·4 (q of q, 3F, J_{FF} 18·0 Hz, J_{HF} 3·0 Hz).

These observations suggest the structure (IVa), where the C_4 ring is bonded to the iron atom by a σ-π system rather than a π-system as (II) and (III). However, on the present evidence an alternative structure for this complex is (IVb), which could be formed *via* a metal-promoted[7] disrotatory ring-opening reaction.

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