Insertion Reactions of Hexafluoroacetone with Tricarbonyl(diene)iron and π-Cyclopentadienyl(diene)rhodium Complexes

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Summary The reaction of hexafluoroacetone (HFA) with various tricarbonyl-(1,3-diene)iron complexes affords adducts containing one or two molecules of HFA, the latter adducts being transformed on heating into products, in which HFA has formally inserted into carbon–hydrogen bonds; analogous reactions with cyclopentadienylrhodium complexes lead to insertion of one or two HFA molecules into cyclopentadienyl carbon–hydrogen bonds.

WHEREAS, hexafluoroacetone behaves like tetracyanoethylene and adds *exo*-1,3 to tricarbonylcycloheptatrieneiron,[1] tetrafluoroethylene and hexafluoropropene add *endo* to tricarbonyl-(1,3-diene)iron complexes[2] and tricarbonylcycloheptatrieneiron[3] to form π-allylic species, in which the fluoro-olefin formally links the iron and the organic ligand.

Hexafluoroacetone reacts on u.v. irradiation with tricarbonyl-(2,3-dimethylbuta-1,3-diene)iron or thermally (60 °C) with π-cyclopentadienyl(isoprene)rhodium to form, respectively, the crystalline 1:1 adducts (I) [m.p. 108—110°, ν_{CO} (hexane) 2096s, 2051s and 2001s cm^{-1}] and (II) [m.p. 109—111°, a mixture (2·5:1) of the isomers (IIa) and (IIb)]. Examination of the n.m.r. spectra† of the adducts showed that in both reactions the hexafluoroacetone had added formally *endo* to the co-ordinated diene with the formation of a π-allylic system as observed in the reactions of tetrafluoroethylene.

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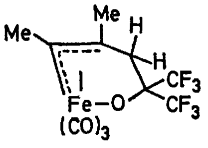
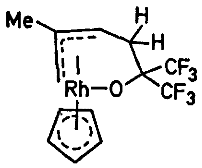
† All compounds described were fully characterised by elemental analysis and n.m.r. spectroscopy.

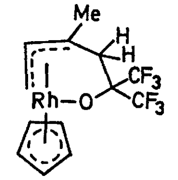
In contrast, a room temperature reaction of hexafluoroacetone with tricarbonyl(isoprene)iron resulted in a hitherto unobserved kind of reaction to form a yellow 2:1 adduct (III) [m.p. 105—107°, ν_{CO} (hexane) 2905w, 2022s, and 1992s cm^{-1}; ^{1}H n.m.r. τ 5·57 ($J_{1,3}$ 13·0, $J_{2,3}$ 8·0 Hz, 3-H), 6·07 ($J_{5,6}$ 15·0 Hz, 5-H), 6·92 ($J_{5,6}$ 15·0 Hz, 6-H), 6·95 ($J_{1,3}$ 13·0, $J_{1,2}$ 2·5 Hz, 1-H), 7·31 ($J_{2,3}$ 8·0, $J_{1,2}$ 2·5 Hz, 2-H), and 7·92 (s, Me); ^{19}F n.m.r. 75·0 (3F, m), 75·5 (3F, m), 76·2 (3F, m) and 76·9 (3F, m)], which is assigned the illustrated π-allylic structure where two hexafluoroacetone molecules have linked head to tail *endo* onto the co-ordinated isoprene. When (III) is heated (80°, 24 h) in hexane two products are formed; an isomeric complex (IV) [m.p. 49—51°, ν_{CO} (hexane) 2073s, 2012s, and 1999s, ν_{OH} (Nujol) 3340br cm^{-1}] which on the basis of the spectroscopic data is formulated as a π-allylic complex, but which in contrast with the parent compound no longer contains a methyl group, this being replaced by a $CH_2C(CF_3)_2OH$ group arising *via* a formal insertion of hexafluoroacetone into a carbon–hydrogen bond. The second product of this reaction (m.p. 85—89°) proved to be an organic compound for which the structure (V) was established. Separate experiments showed that (V) is formed from (IV) on heating; a reaction which involves cleavage of an iron–oxygen bond and a hydrogen shift.



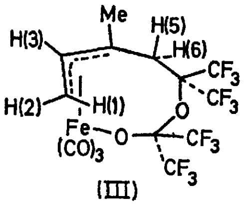
(I)



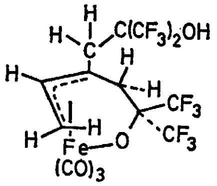
(IIa)



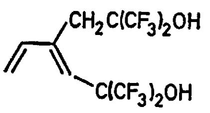
(IIb)



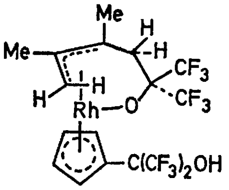
(III)



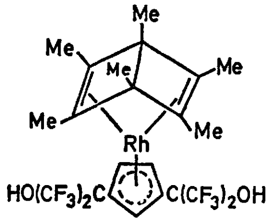
(IV)



(V)



(VI)



(VII)

Possibly related insertions into the carbon–hydrogen bonds of co-ordinated cyclopentadienyl ligands were observed on studying the thermal reaction of π-cyclopentadienyl(2,3-dimethylbuta-1,3-diene)rhodium and π-cyclopentadienylhexamethyl(Dewar)benzenerhodium with hexafluoroacetone. The former reaction lead to the formation of the 1:2 adduct (VI) (m.p. 128—130°). Examination of the n.m.r. spectra showed that one hexafluoroacetone molecule had linked the diene and the rhodium as found with the iron system (I), but that a second hexafluoroacetone had inserted into a cyclopentadienyl ring C–H bond. In the reaction of the hexamethyl(Dewar)benzene complex attack only occurred on the C_5 ring to give (VII) (m.p. 128—130°), a 1,3-disubstituted diol.

Electrophilic substitution reactions of this type have not been previously observed, but it is possible that intermediate complexes analogous to (III) are involved in the formation of the rhodium C_5 substituted systems.

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[1] M. Green, S. Tolson, J. Weaver, D. C. Wood, and P. Woodward, *Chem. Comm.*, 1971, 222.
[2] A. Bond, M. Green, B. Lewis, and S. F. W. Lowrie, *Chem. Comm.*, 1971, 1230.
[3] M. Green and S. Tolson, unpublished observations.