Tetracarbonylallyliron Cations. Proton Exchange Reactions

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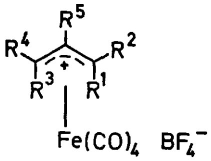
Summary Two types of exchange reactions have been observed which involve tetracarbonylallyliron cations bearing *anti*-substituents: intramolecular 1,4 hydrogen migration and equilibration with solvent media(CF_3CO_2D).

IN the course of our study of the disproportionations of tricarbonyldieneiron complexes in strong acid solution which yield tetracarbonylallyliron cations,[1] we observed that dissolution of either cation (I) [2] or (II) in trifluoroacetic acid solution would eventually lead to a mixture of the two in the ratio 45:55 (after 1 h at ambient temperature). Examination of these in CF_3CO_2D showed that deuterium was not incorporated, even after several days, although an equilibrium mixture of (I) and (II) (35:65) was again obtained. Although the interconversions also occur in sulphuric and fluorosulphonic acids, the presence of an acid is not required. Compound (I) is quite soluble in CH_2Cl_2 and the n.m.r. spectrum of a freshly prepared solution reveals none of (II); if the sample is set aside, the amount of (II) increases until it reaches a maximum (*ca.* 40%) at which point precipitation begins. Interconversions of these cations are thus 1,4 sigmatropic rearrangements involving hydrogen migrations in carbonium ions, a process which is not allowed to proceed suprafacially by orbital symmetry considerations.[3] The exact role of the metal in these reactions is not yet known but may be related to the allyl alcohol isomerizations by $Fe(CO)_5$ which were studied by von Rosenberg and Cowherd[4] and to hydrogen migrations in cycloheptatriene–metal carbonyl complexes studied by Grimme [5] and Pauson.[6]



	R^1	R^2	R^3	R^4	R^5
(I)	Me	Me	Me	Me	H
(II)	Me_2CH	H	H	H	Me
(III)	Me	Me	H	H	H
(IV)	Me	H	H	H	Me
(V)	Me	H	H	H	H
(VI)	Me	H	Me	H	H
(VII)	H	Et	H	H	H

Solutions of cation (III) in CF_3CO_2H contain a small amount of a second compound (*ca.* 10%) whose n.m.r. spectral properties are consistent with its formulation as (IV), the proton tautomer of (III). Solutions of these in CF_3CO_2D lead to cations in which complete deuteriation at the *anti* methyl substituent and positions R^3 and R^4 of (III) has occurred and complete deuteriation at R^1 of (IV) has also apparently occurred (disappearance of the *anti*-methyl doublet at τ 8·23). Deuterium incorporation into (III) is very slow in comparison to that of the diene–metal systems recently studied by Whitesides[7] and Lewis;[8] incorporation at the methyl group occurs to the extent of *ca.* 20% after 1 h in CF_3CO_2D. Cation (V) also incorporates deuterium at positions R^3 and R^4 as well as in the *anti* methyl substituent R^1. Our preliminary data indicate that the rate of deuterium incorporation into the methyl groups is about the same in cations (III) and (V).

Cation (VI)† was prepared by disproportionation of tricarbonyl-*cis*-penta-1,3-dieneiron as described previously.[1] It shows no tautomerism of the type shown by (I) in CF_3CO_2H but slowly incorporates deuterium exclusively at the methyl groups when left for a long period in CF_3CO_2D (*ca.* 14% after 2 weeks). Cation (VII),† which has a *syn*-ethyl group, is easily obtained by direct protonation of tetracarbonyl-*cis*-penta-1,3-dieneiron with HBF_4–Ac_2O followed by precipitation in ether. No rearrangement is observed and deuterium incorporation into this cation in CF_3CO_2D solution cannot be detected even after two weeks.

None of the solutions of the above cations in CF_3CO_2H show n.m.r. signals (up to τ 18·0) which might be attributable to a metal-hydride species such as observed for (cyclohexadiene)(cyclopentadienyl)rhodium(I).[8] It is also not possible to observe i.r. or n.m.r. spectra) deprotonated olefin complexes; indeed if such a complex were intermediate, it seems likely that cation (VI) would be converted into the *syn*-1-ethyl cation since (VII) was found to be the exclusive product of direct protonation of the tetracarbonyldiene complex.

The observed exchanges in (III) and (V) may be accounted for by either of the following: (a) exchange between CF_3CO_2D and *anti* methyl followed by 1,4 hydrogen (deuterium) migration; (b) a concerted process in which a solvent molecule interacts with the *anti*-methyl and the terminal carbon of the allyl ligand, functioning as proton (deuteron) donor and acceptor. We presently favour (a) since deuterium incorporation is observed to be faster at the *anti* methyl groups than at R^3 and R^4 in these ions.

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† N.m.r. and i.r. spectral properties of the ion are consistent with this formulation.

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