Hydride Reduction of the Cation $[(\eta^5\text{-}C_5H_5)Fe(triphos)]PF_6$: Direct Nucleophilic Attack on the Metal, and Hydrogen Exchange in the Product Hydride $(\eta^5\text{-}C_5H_5)FeH(triphos)$ (triphos = $Ph_2PCH_2CH_2PPhCH_2CH_2PPh_2$)

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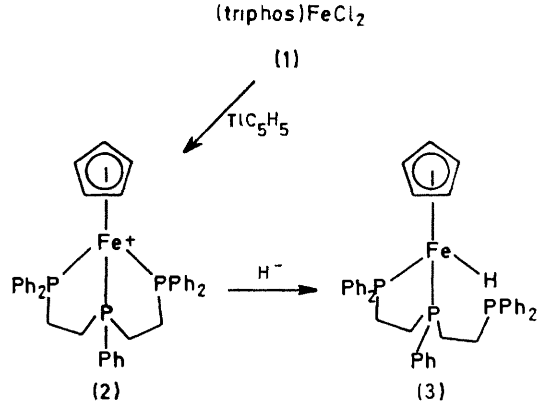
Summary Reduction of the cation $[(\eta^5\text{-}C_5H_5)Fe(triphos)]PF_6$ with lithium aluminium deuteride gives $(\eta^5\text{-}C_5H_5)FeD(triphos)$ which slowly undergoes H–D scrambling at 20 °C (triphos = $Ph_2PCH_2CH_2PPhCH_2CH_2PPh_2$)

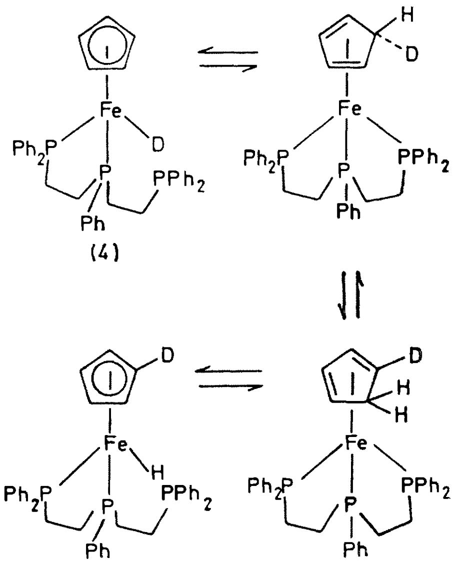
ELECTRON-POOR 18-electron organometallic cations with unsaturated hydrocarbon ligands have been extensively studied[1] They always undergo attack by hydrides on the hydrocarbon ligand (*e g* , cyclopentadienyl) from the *exo* face, rather than directly on the metal

Unlike their electron-poor counterparts, electron-rich cations have received little attention Here we report that the lithium aluminium hydride reduction of the cation (**2**) leads to the hydride (**3**) by direct nucleophilic attack on the metal, and that the corresponding deuteride (**4**) undergoes H–D scrambling at room temperature *via* an unexpected *exo*-hydrogen sigmatropic shift

Treatment of iron(II) chloride dihydrate with the tridentate ligand $(Ph_2PCH_2CH_2)_2PPh$ (triphos) led to the



SCHEME 1



SCHEME 2 Mechanism of H–D scrambling in the deuteride (**4**)

compound (**1**) which, on reaction with thallium cyclopentadienide followed by ammonium hexafluorophosphate, gave the cation (**2**). Brief treatment of (**2**) with lithium aluminium hydride in tetrahydrofuran gave the hydride (**3**) (Scheme 1). The ^{1}H n.m.r. spectrum of (**3**) showed Fe–H as a double doublet at τ 27 (J 65 and 75 Hz), indicating an η^5-cyclopentadienyl structure in which the triphosphine ligand is bidentate with one of the terminal phosphorus atoms not co-ordinated to the metal.

The hydride (**3**) is formed by direct attack on the metal, and not, as might have been expected,[1] *via exo*-attack on the cyclopentadienyl ligand, followed by migration of the *endo*-hydrogen thus produced to the metal.[2] This is demonstrated by the formation of the deuteride (**4**) when (**2**) is reduced under the same conditions using $LiAlD_4$. The Fe–H i.r. absorption at 1875 cm^{-1} for (**3**) was absent from the spectrum of (**4**) immediately after isolation, and the ^{1}H n.m.r. spectrum showed that there was essentially no hydrogen bonded to Fe.

The deuteride (**4**) undergoes smooth interchange of H and D at room temperature. Thus, the ^{1}H n.m.r. spectrum of a $C_6D_5CD_3$ solution of (**4**) which had been allowed to stand at 20 °C for 18 h showed the strong double doublet Fe–H resonance, while the i.r. spectrum contained a new absorption at 2280 cm^{-1} in the position expected for the C–D stretch of the C_5H_4D ligand.

A mechanism for this H–D scrambling process is shown in Scheme 2. Hydrogen shift reactions have been observed previously for several transition metal complexes containing unsaturated hydrocarbon ligands.[3] In all other cases, however, these hydrogen migrations require elevated temperatures and it is always the *endo*-H that undergoes migration, *via* the metal. The scrambling process reported here appears to be the first example of an *exo*-hydrogen sigmatropic shift around a hydrocarbon ligand bonded to a transition metal.

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