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

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Summary Reduction of the cation $[(\eta^{5}-C_{5}H_{5})Fe(triphos)]$ -PF₆ with lithium aluminium deuteride gives $(\eta^{5}-C_{5}H_{5})FeD-(triphos)$ which slowly undergoes H–D scrambling at **20** °C (triphos = Ph₂PCH₂CH₂PPhCH₂CH₂PPh₂)

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 (Ph₂PCH₂)₂PPh (triphos) led to the



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 ¹H 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 ¹H 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 ¹H 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.

We thank Mme R. Brière (D.R.F., C.E.A., Grenoble) for her interest.

(Received, 13th November 1979; Com. 1189.)

¹S. G. Davies, M. L. H. Green, and D. M. P. Mingos, Tetrahedron Report No. 57, Tetrahedron, 1978, 34, 3047.

 ² T. H. Whitesides and J. Selly, J. Organometallic Chem., 1975, 92, 215.
³ G. A. M. Munro and P. L. Pauson, J.C.S. Chem. Comm., 1976, 134, and references therein.