

## Hydride Reduction of the Cations $\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[(\text{Ph}_2\text{PCH}_2)_3\text{CMe}]\text{PF}_6\}$ , $\{(\eta^5\text{-C}_5\text{H}_5)\text{-Ru}[(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh}]\text{PF}_6\}$ , and $\{(\eta^5\text{-C}_5\text{H}_5)\text{Ru}[(\text{Ph}_2\text{PCH}_2)_3\text{CMe}]\text{PF}_6\}$ : Regioselectivity and Mechanism

By STEPHEN G. DAVIES\*

*(The Dyson Perrins Laboratory, South Parks Road, Oxford, OX1 3QY)*

and HUGH FELKIN, TAUQIR FILLEBEEN-KHAN, FATEMEH TADJ, and OLIVER WATTS

*(Institut de Chimie des Substances Naturelles, 91190 Gif-sur-Yvette, France)*

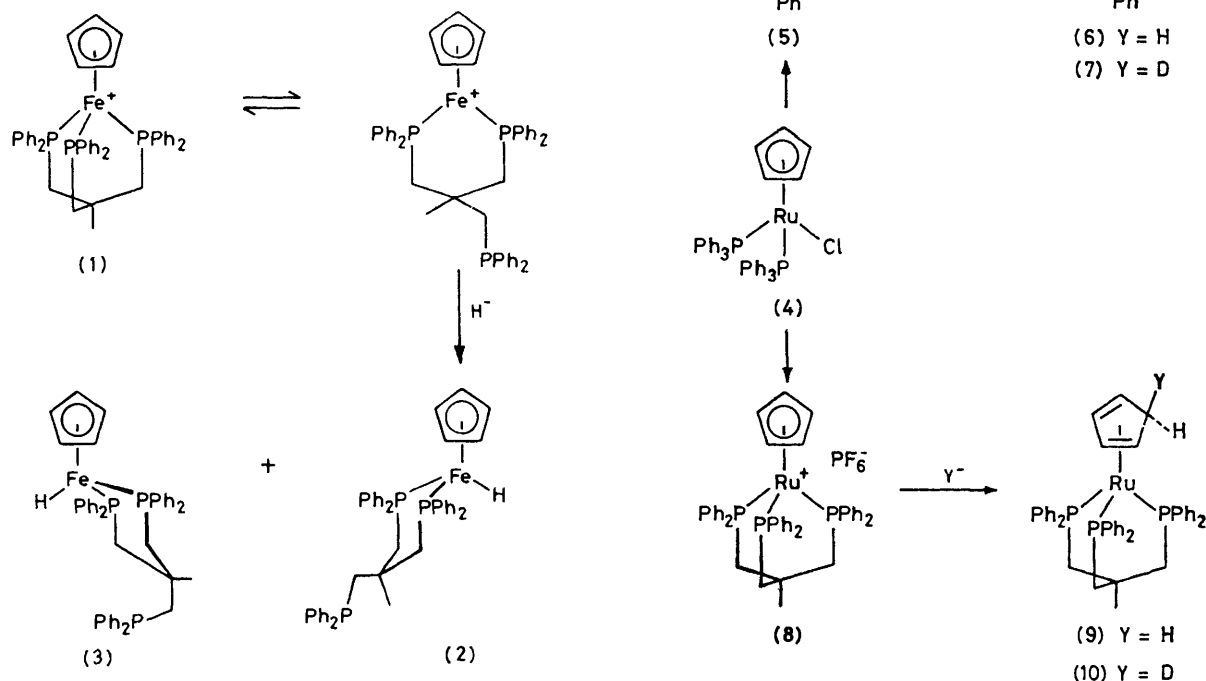
**Summary** Reduction of the cation  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{tripod})]\text{PF}_6$  with lithium aluminium hydride gives  $(\eta^5\text{-C}_5\text{H}_5)\text{FeH}(\text{tripod})$  via an  $S_N1$  mechanism, involving prior dissociation of a phosphine ligand leading to direct attack of hydride on the metal, in contrast with the related ruthenium cations  $[(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_3]\text{PF}_6$  ( $L_3 = \text{triphos}$  or tripod) which give the cyclopentadiene complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{RuL}_3$  via *exo*-hydride attack on the cyclopentadienyl ligand [tripod =  $(\text{Ph}_2\text{PCH}_2)_3\text{CMe}$ ; triphos =  $(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh}$ ].

18-ELECTRON organometallic cations with unsaturated hydrocarbon ligands (*e.g.* cyclopentadienyl) usually undergo attack by hydrides on the hydrocarbon ligand from the *exo*-face rather than directly on the metal.<sup>1</sup> We have, however, recently demonstrated the first example of direct nucleophilic attack on the metal where, in the case of the cation  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{triphos})]\text{PF}_6$  [triphos =  $(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh}$ ], reduction with lithium aluminium hydride gave  $(\eta^5\text{-C}_5\text{H}_5)\text{FeH}(\text{triphos})$ .<sup>2</sup> Here we report that the lithium aluminium hydride reduction of the related iron cation (1) leads to a mixture of hydrides (2) and (3) whereas in contrast, reductions of the related ruthenium cations (5)

and (8) lead to the corresponding cyclopentadiene complexes (6) and (9) via *exo*-attack on the cyclopentadienyl ligand.†

Photolysis of a dichloromethane solution of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{isobutylene})]\text{PF}_6$ <sup>3</sup> in the presence of the tridentate ligand tripod [ $(\text{Ph}_2\text{PCH}_2)_3\text{CMe}$ ] gave the cation (1) after treatment with ammonium hexafluorophosphate. Reduction of (1) with lithium aluminium hydride in tetrahydrofuran produced a mixture of the hydrides (2) and (3). The <sup>1</sup>H n.m.r. spectrum of the mixture of (2) and (3) contained two triplets due to Fe-H at  $\tau$  26.1 ( $J$  70 Hz) and 25.9 ( $J$  70 Hz) in the ratio 60:40. An Fe-H absorption was observed in the i.r. spectrum at  $1840\text{ cm}^{-1}$ .<sup>2,4</sup>

The hydrides (2) and (3) are formed by direct attack on the metal, and not via *exo*-attack on the cyclopentadienyl ligand, followed by migration of the *endo*-hydrogen thus produced to the metal.<sup>1,2,5</sup> This is demonstrated by the



† All new compounds gave satisfactory elemental analyses and spectroscopic data.

formation of the metal deuterides corresponding to (2) and (3) when (1) is reduced under similar conditions using  $\text{LiAlD}_4$ ; the Fe-H i.r. absorptions for (2) and (3) were absent and the  $^1\text{H}$  n.m.r. spectrum indicated that there was no hydrogen bonded to the Fe.

The mechanism of direct attack on the metal is shown to be  $\text{S}_{\text{N}}1$  in character, involving prior dissociation of a phosphine, since both epimeric hydrides (2) and (3) are formed. An  $\text{S}_{\text{N}}2$  mechanism would lead, by inversion at Fe, only to (2). The mechanism is not initial formation of (2) followed by equilibration of (2)  $\rightleftharpoons$  (3). This is demonstrated by the stability of the major isomer, isolated from the mixture by successive recrystallisation, which also indicates that (2) and (3) are not conformational isomers.

Treatment of the chloride (4) with the tridentate ligands, triphos or tripod, in refluxing toluene gives by phosphine exchange and displacement of chloride the cations (5) and (8) after treatment with ammonium hexafluorophosphate.<sup>6</sup> Reduction of (5) with lithium aluminium hydride in tetrahydrofuran gives the complex (6). The  $^1\text{H}$  n.m.r. spectrum of (6) showed absorptions characteristic of a cyclopentadiene ligand and no Ru-H absorptions. The characteristic cyclopentadiene *exo*-H i.r. absorption<sup>7</sup> was present at  $2750\text{ cm}^{-1}$ . The cyclopentadiene complex (6) is formed by *exo*-attack on the cyclopentadienyl ligand and

not, as with the corresponding Fe cation,<sup>2</sup> by attack on the metal followed by migration of hydride from the metal to cyclopentadienyl. This is demonstrated by the formation of complex (7) containing *exo*-D when (5) is reduced under the same conditions with  $\text{LiAlD}_4$ . The *exo*-H i.r. absorption at  $2750\text{ cm}^{-1}$  was absent from the spectrum of (7) and had been replaced by *exo*-D absorption at  $2050\text{ cm}^{-1}$ . The mechanism involving attack at the metal would have led to *endo*-D with the product still containing *exo*-H.

Similarly, reduction of cation (8) with  $\text{LiAlH}_4$  and  $\text{LiAlD}_4$  affords the cyclopentadiene complexes (9) [*v*(*exo*-H) at  $2700\text{ cm}^{-1}$ ] and (10) [*v*(*exo*-D) at  $2000\text{ cm}^{-1}$ ] respectively.

The difference in regioselectivity observed between the Fe and the Ru cations can be attributed to strain present in the Fe cations, which promotes dissociation of a phosphine ligand to generate a 16-electron species prior to nucleophilic attack. The strain effects are different in the Fe and Ru cations because of their differing atomic sizes (Fe<sup>II</sup> radius =  $1.23\text{ \AA}$ ; Ru<sup>II</sup> radius =  $1.44\text{ \AA}$ ) and hence differing metal-phosphorus bond lengths.<sup>8</sup>

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