

Preliminary communication

HYDRIDE REDUCTION OF THE CATION

$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{CO}]\text{PF}_6$; FORMATION OF
 $(\eta^5\text{-C}_5\text{H}_5)\text{FeH}(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ AND ELIMINATION OF H_2 FROM
 $[(\eta^5\text{-C}_5\text{H}_5)\text{FeH}(\text{CO})]_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$

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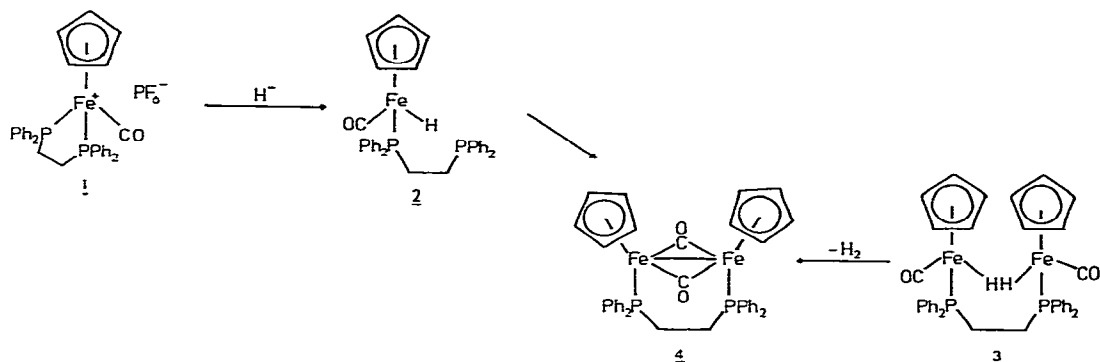
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Summary

$(\eta^5\text{-C}_5\text{H}_5)\text{FeH}(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$, formed in the LiAlH_4 reduction of the cation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{CO}]\text{PF}_6$, can be converted into $[(\eta^5\text{-C}_5\text{H}_5)\text{FeH}(\text{CO})]_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$, which undergoes thermal and photochemical elimination of hydrogen.

18-Electron cyclopentadienyl-organotransition metal cations undergo hydride addition at the cyclopentadienyl ligand in electron-poor complexes, i.e. when the other ligands are electron withdrawing. If the cation is electron-rich, however, attack at cyclopentadienyl is disfavoured [1]. We report here that hydride reduction of the cation 1 leads to the hydride 2. The dimetallic complex 3, formed by phosphine loss from 2, undergoes elimination of hydrogen both thermally and photochemically. There are a number of examples of thermal dinuclear elimination of hydrogen. These are thought to proceed by formation of a hydride-bridged species with concomitant loss of dihydrogen from either one metal centre in the intact dinuclear species [2] or from a mononuclear dihydride formed by cleavage of the hydride-bridged intermediate [3]. A key feature of such dinuclear species is the presence of a metal-metal bond and ligands that can be easily eliminated. The process of synchronous elimination of dihydrogen from two metal-hydride centres in a dinuclear species has not to our knowledge been reported, although a possible analogue has recently been published [4].

The reduction of 1 with LiAlH_4 in dichloromethane/tetrahydrofuran (1/1) at -78°C produces the iron hydride complex 2 (70%). Complex 2 was charac-



terised by IR (Nujol); $\nu(\text{CO})$ 1910 cm^{-1} ; $^1\text{H NMR}$ [C_6D_6] τ 5.90 (C_5H_5 , d, $J(\text{PH})$ 1.3 Hz), 23.3 (FeH, d, $J(\text{PH})$ 74 Hz); $^{31}\text{P NMR}$ δ (relative to external H_3PO_4) 84.8, -13.5, and gave satisfactory elemental analyses. Hydride addition to 1 proceeds either by direct attack on the metal or via initial attack on the carbonyl ligand followed by hydrogen migration to the metal. The third alternative, *exo*-attack on the cyclopentadienyl ring with subsequent transfer of the *endo*-hydrogen to the metal, is incompatible with the observed formation of the metal deuteride corresponding to 2 when 1 is reduced with LiAlD_4 . Phosphine substitution occurs when 2 is dissolved in toluene leading to the formation of the known dimetallic complex 3 [5] and diphos ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$). Complex 3 may also be prepared by reaction of 2 with $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{H}$. This substitution reaction is reversible since 3 in the presence of excess diphos produces 2.

On warming a toluene solution of 3 to 90°C in the absence of light the green diiron complex 4 [6] and an equimolar quantity of H_2 are produced together with a small amount of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{diphos})\text{H}$. Hydrogen was identified by rotational Raman spectroscopy [7]. Photolysis of 3 also led to the formation of 4.

Under similar conditions 4 is also produced thermally from 2. In the presence of excess diphos, however, to prevent the formation of 3, 2 does not undergo dehydrogenation. Compound 3 is coordinatively and electronically saturated and thus is unable to form a bridging hydride intermediate which could lead to elimination from one metal centre in a dinuclear species. These facts suggest that dihydrogen is eliminated from 3 in a synchronous manner involving both metal centres.

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References

- 1 S.G. Davies, M.L.H. Green and D.M.P. Mingos, *Tetrahedron*, **34** (1978) 3047; S.G. Davies, H. Felkin, T. Fillebeen-Khan, F. Tadj and O. Watts, *J. Chem. Soc. Chem. Commun.*, (1981) 431.
- 2 J.R. Norton, *Acc. Chem. Res.*, **12** (1979) 139.
- 3 T. Yoshida, T. Okano and S. Otsuka, *J. Amer. Chem. Soc.*, **102** (1980) 5966.
- 4 M. Berry, N.J. Cooper, M.L.H. Green and S.J. Simpson, *J. Chem. Soc. Dalton*, (1980) 29.
- 5 S.J. LaCroce, K.P. Menard and A.R. Cutler, *J. Organometal. Chem.*, **190** (1980) C79.
- 6 R.J. Haines and A.L. DuPreez, *Inorg. Chem.*, **11** (1972) 330.
- 7 F. Rasetti, *Phys. Rev.*, **34** (1929) 367; G.K. Teal and G.E. MacWood, *J. Chem. Phys.*, **3** (1935) 760.