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Preliminary communication

HYDRIDE REDUCTION OF THE CATION $[(\eta^5\text{-}C_5H_5)Fe(Ph_2PCH_2CH_2PPh_2)CO]PF_6$; FORMATION OF $(\eta^5\text{-}C_5H_5)FeH(CO)(Ph_2PCH_2CH_2PPh_2)$ AND ELIMINATION OF H_2 FROM $[(\eta^5\text{-}C_5H_5)FeH(CO)]_2(Ph_2PCH_2CH_2PPh_2)$

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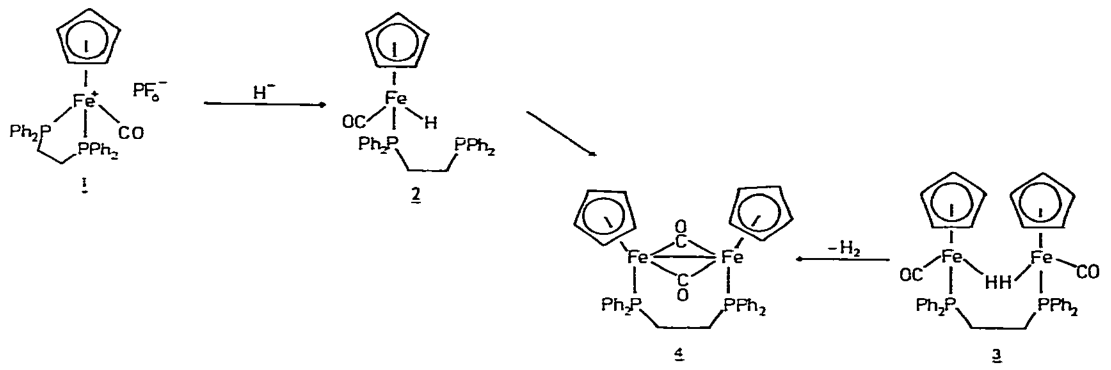
Summary

$(\eta^5\text{-}C_5H_5)FeH(CO)(Ph_2PCH_2CH_2PPh_2)$, formed in the $LiAlH_4$ reduction of the cation of $[(\eta^5\text{-}C_5H_5)Fe(Ph_2PCH_2CH_2PPh_2)CO]PF_6$, can be converted into $[(\eta^5\text{-}C_5H_5)FeH(CO)]_2(Ph_2PCH_2CH_2PPh_2)$, 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); ν(CO) 1910 cm^{-1} ; ^{1}H NMR [C_6D_6] τ 5.90 (C_5H_5 , d, *J*(PH) 1.3 Hz), 23.3 (FeH, d, *J*(PH) 74 Hz); ^{31}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 ($Ph_2PCH_2CH_2PPh_2$). Complex 3 may also be prepared by reaction of 2 with (η^5-C_5H_5)Fe(CO)$_2$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 (η^5-C_5H_5)Fe(diphos)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 andthus 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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