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Preliminary communication

EVIDENCE FOR THE IRON FORMYL $(\eta^5\text{-}C_5H_5)Fe(Ph_2PCH_2CH_2PPh_2)(CHO)$

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Summary

Evidence for $(\eta^5\text{-}C_5H_5)Fe(Ph_2PCH_2CH_2PPh_2)(CHO)$ as an intermediate in the reduction of $[(\eta^5\text{-}C_5H_5)Fe(Ph_2PCH_2CH_2PPh_2)CO]PF_6$ to $(\eta^5\text{-}C_5H_5)Fe(CO)H(Ph_2PCH_2CH_2PPh_2)$ and for a metal-carbonyl hydride-formyl equilibrium is described.

The mechanisms of the reduction and reductive polymerisation of carbon monoxide continue to attract a great deal of attention [1]. An essential feature of many of the proposed mechanisms is the equilibrium between a metal carbonyl hydride and a metal formyl species. No examples of such an equilibrium have to our knowledge been demonstrated. We recently reported that lithium aluminium hydride reduction of cation 1 leads to the formation of the iron hydride 2. Deuteration studies indicated that hydride addition to 1 proceeded either by direct attack on the metal or via initial attack on the carbonyl ligand followed by hydrogen migration from the formyl thus produced to the metal [2]. We describe here evidence supporting the formation of the iron formyl 3.

$LiAlH_4$ or $Li(Et_3BH)$ were added to solutions of cation 1 in tetrahydrofuran-d_8 at —78°C. These solutions were monitored by ^1H NMR spectroscopy as the temperature was slowly raised. Between —70 and —50°C both solutions developed a resonance at δ 11.53 ppm characteristic of a metal formyl proton [3]. Above —50°C the formyl rapidly disappeared. Work-up led to the isolation of 2 as the sole product strongly supporting the hypothesis of the formyl species 3 being an intermediate in these reductions.

The formation of 2 via the formyl 3 suggested the possibility that these two compounds might be in equilibrium in solution at room temperature. Such an equilibrium is considered to be an essential feature of Fischer-Tropsch and related reactions. A ^{31}P NMR saturation transfer experiment in which one of the phosphorus atoms of the carbonyl hydride 2 was saturated and completely in-

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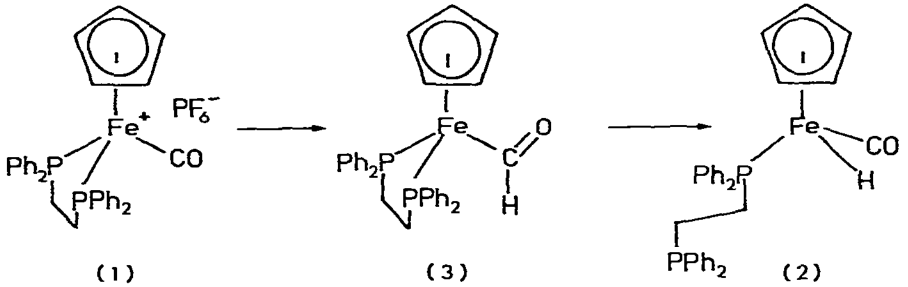
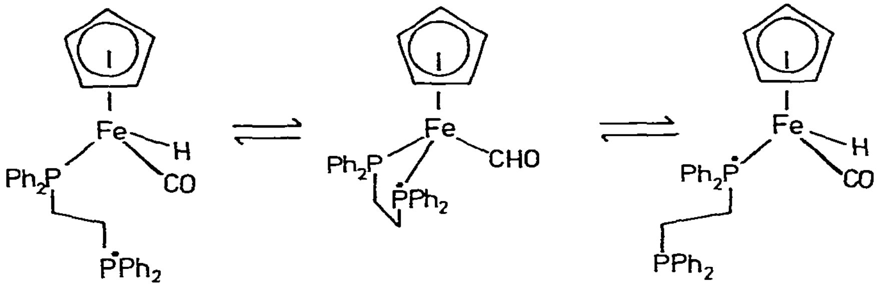


(1) (3) (2)

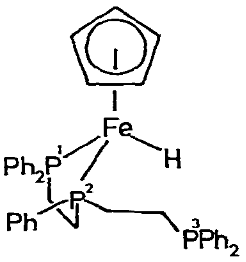
verted by means of a DANTE sequence [4] clearly demonstrated that the two phosphorus atoms in 2 were rapidly equilibrating (k 0.24 s^{-1} ; $\Delta G^{\ddagger}_{297}$ 18 kcal mol^{-1}) with each other but not with free diphos. No exchange of phosphorus atoms could be detected in $(\eta^5\text{-}C_5H_5)Fe[PhP(CH_2CH_2PPh_2)_2]H$ (4) [5]. Exchange via the formyl 3 is the only possible mechanism for 2 that is unavailable to 4 (Scheme 1).



(2) (3) (2)

SCHEME 1. Phosphorus exchange mechanism.

The P—P coupling constants observed in the hydride 4 are $J(P^1P^2)$ 28 and $J(P^2P^3)$ 35 Hz. These are consistent with the expected thermodynamically most stable *anti* conformation being adopted by P^2 and P^3 (dihedral angle 180°) while the dihedral angle between P^2 and P^3 will be 25—50° [6]. In contrast for hydride 2 the P—P coupling constant is close to zero implying that in $(\eta^5\text{-}C_5H_5)$-$Fe(CO)H(Ph_2PCH_2CH_2PPh_2)$ the dihedral angle in the bis-phosphine ligand is approximately 90°. The thermodynamic disadvantage inherent in such a conformation is presumably compensated for by a metal—phosphorus interaction indicating that 5 is a better representation of the structure than 2.



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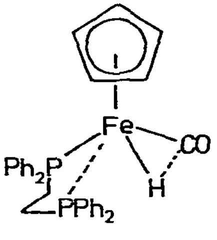

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