

Disproportionation of the Iron Carbonyl Hydride $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{H}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ to the Iron Methyl $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Me}$

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The iron carbonyl hydride $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{H}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ disproportionates *via* the iron formyl $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)(\text{CHO})$ to the methyl complex $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Me}$.

The mechanism of the homogeneous reduction of carbon monoxide in the presence of transition metal catalysts is believed to proceed sequentially *via* metal formyl, metal hydroxymethyl, and metal carbene complexes.¹ Some recent extensive studies have demonstrated all these steps.^{2,3} In general, however, external electrophilic catalysis is necessary to produce metal methyl from metal formyl in these model systems. We have demonstrated previously that lithium aluminium hydride reduction of the cation (1) produces after work-up the iron hydride (3).⁴ The mechanism of this reduction involves initial attack of hydride onto the carbon monoxide ligand followed by rearrangement of the thus formed formyl complex (2) (Figure 1).³ We report here that the hydride (3) disproportionates *via* the formyl (2) to generate the methyl complex (4).

Pure carbonyl hydride (3) left at 20 °C for 3 days was observed to produce an oil whose ¹H n.m.r. spectrum contained the characteristic methyl resonance of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Me}$ (4) (δ -1.3, t, J_{PH} 7 Hz).⁵ In solution (in tetrahydrofuran) (3) was similarly observed to decompose completely, again with formation of the methyl complex (4) (ca. 30%). It has not proved possible, so far, to identify the other iron-containing species in this reaction; however, the necessary stoichiometry of the reaction suggests complex (5) (Figure 2).

Under the latter conditions but in the presence of LiAlH_4 , tetrahydrofuran solutions of (3) gave after work-up the iron methyl (4) and the carbonyl hydride (3) in the ratio 1:2. The hydride (3) isolated in this case would come from LiAlH_4 reduction of (5) [equivalent to $2(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)^+$]. Complete conversion of all the iron species into the methyl complex (4) is not observed in this case. This is consistent with the initial reduction of the cation (1) to give exclusively the carbonyl hydride (3) with no further reduction to methyl being observed even after prolonged reaction times in the presence of excess of LiAlH_4 . Presumably in both cases co-ordination of the unbound phosphine to AlH_3 prevents equilibration with the formyl (2) and hence further reaction.

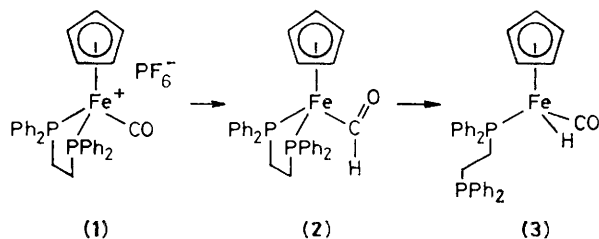


Figure 1

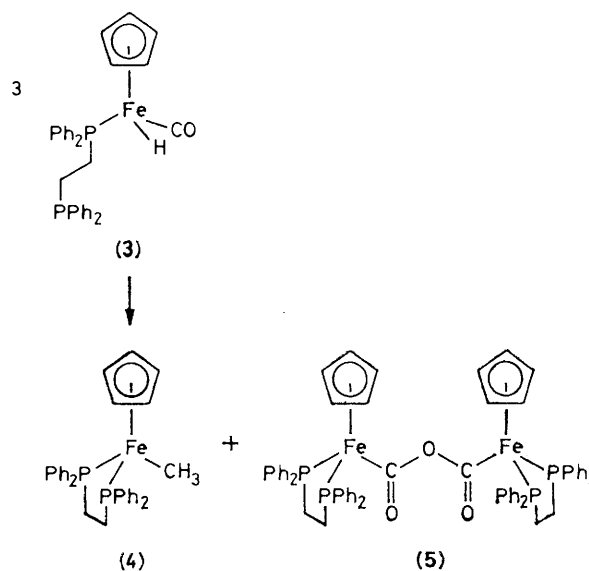


Figure 2

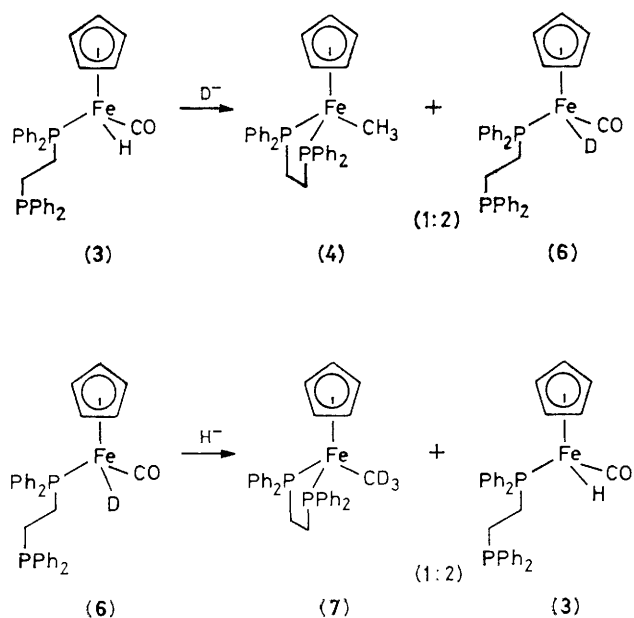
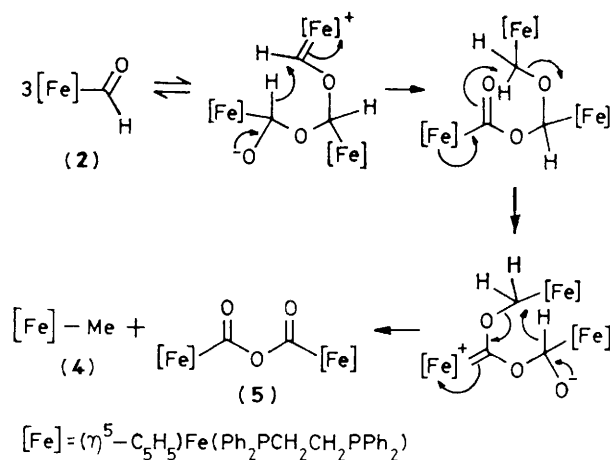


Figure 3

All the hydrogen atoms in the methyl group of (4) originate from the carbonyl hydride (3) and not from $LiAlH_4$. The carbonyl hydride (3) in the presence of $LiAlD_4$ gives after work-up the methyl compound (4) and the carbonyl deuteride (6). Similarly the carbonyl deuteride (6) in the presence of $LiAlH_4$ gives after work-up the $[^2H_3]$ methyl complex (7) and the carbonyl hydride (3) (Figure 3).

A mechanism for the disproportionation of (2) to (4) by analogy with aldehyde trimerisations and the Cannizzaro and related hydride transfer reactions, is given in Scheme 1.



Scheme 1. The disproportionation mechanism.

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