# Stepwise Reduction of Iron(II) Co-ordinated CO by $NaBH_4$. Access to New Hydroxymethyl and Hydride Complexes

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$NaBH_4$ reduction of $[FpCO]^+PF_6^-$ (**1**) [Fp = $(C_5Me_5)Fe(CO)_2$] gives FpH (**4**), $FpCH_2OH$ (**2**), and FpMe (**3**), selectively, depending on the solvent.

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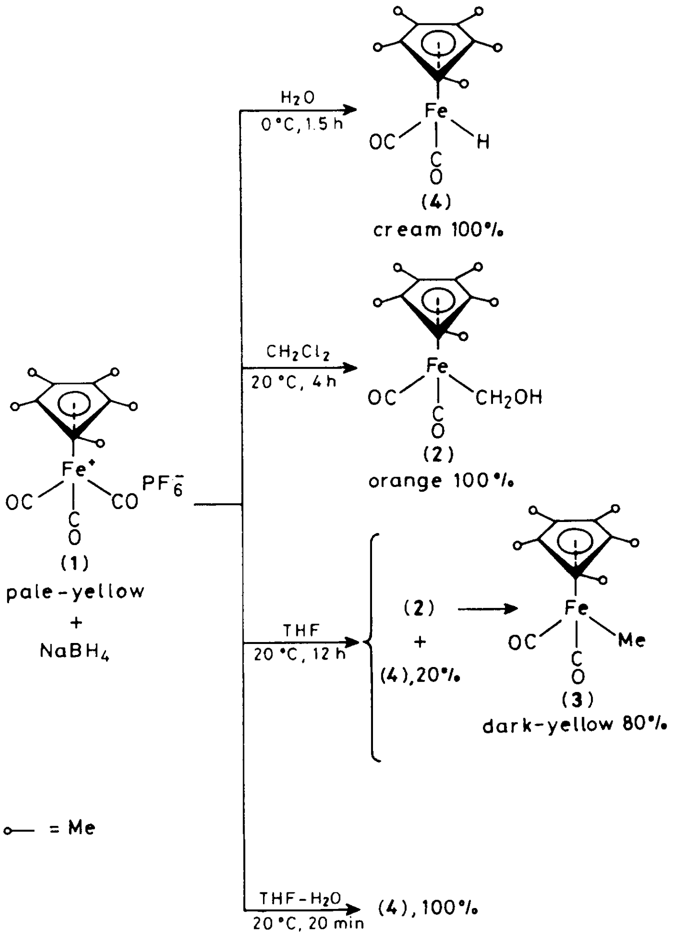
The catalytic reduction of CO, a process of intense interest owing to the prospect of petroleum shortages,[1] has been successfully modelled by Graham,[2] Casey,[3] and Gladysz[4] using rhenium complexes. We report here a stepwise reduction of CO co-ordinated to iron, the metal operating as a catalyst in the Fischer–Tropsch process. Wilkinson and Green's pioneering study[5] showed that $NaBH_4$ reduction of $[FpL]^+$ [Fp = $(C_5H_5)Fe(CO)_2$, L = CO or $PPh_3$] gives $Fp_2$ (L = CO) or $(\eta^4\text{-}C_5H_6)Fe(CO)_3$ (L = $PPh_3$), whereas Cutler[6] recently reported the $NaBH_3CN$ reduction of $[FpCO]^+$ in MeOH to give $FpCH_2OMe$. We have now used $[(C_5Me_5)Fe(CO)_3]^+PF_6^-$ (**1**)[7] as a model substrate to avoid reduction of the cyclopentadienyl moiety and to stabilise intermediates of CO reduction.

The degree of reduction of CO in (**1**) depends on the solvent (Scheme 1). In tetrahydrofuran (THF), the reduction proceeds to the methyl complex (**3**) at 20 °C in 12 h [80% spectroscopic yield, $^1H$ n.m.r.; 20% of the hydride (**4**) was also detected]. Monitoring this reaction by $^1H$ n.m.r. also allowed the detection of the hydroxymethyl complex (**2**) (20% after 2 h) and its slow but complete transformation to (**3**). The percentage of the hydride (**4**) formed in this reaction (20% by $^1H$ n.m.r.) is the same after 2 or 12 h. Since neither (**2**) nor (**3**) gave (**4**), this argues for a possible formyl complex or its $BH_3$ adduct as intermediate. The only complex detected by $^1H$ n.m.r. after reduction of (**1**) in $CH_2Cl_2$ (4 h, 20 °C) was the new hydroxymethyl species (**2**). Crystallization from pentane gave an 80% yield of orange microcrystals stable for several days at 0 °C.† The reduction of (**1**) in $H_2O$ (0 °C, 1.5 h) followed by extraction with cold pentane gave a high yield (apparently quantitative from $^1H$ n.m.r.) of the new hydride (**4**). The complex (**4**) can be isolated in 85% yield of cream microcrystals from this



Scheme 1

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† (**2**): $^1H$ n.m.r. ($CD_3COCD_3$) δ (p.p.m. from $Me_4Si$): 1.78 (s, 15H, $CH_3$), 1.15 (d, 2H, $CH_2$), and 4.72 (d, 1H, OH); $J_{CH_2OH}$ 3 Hz; $^{13}C$ n.m.r. ($CD_2Cl_2$) δ (p.p.m. from $Me_4Si$): 97.2 ($C_5Me_5$), 11.1 ($CH_3$), 220.7 (CO), and 67.2 ($CH_2OH$; triplet in the off-resonance spectrum).

reaction.‡ Reduction of (**1**) in THF–water gave the same results. When one or two ancillary carbonyl groups are replaced by $PPh_3$ or $Ph_2PCH_2CH_2PPh_2$, the reduction of the cationic iron(II) complexes gives neither the hoped-for neutral formyl complex nor any other CO reduction products.

In conclusion, the dramatic solvent dependence of the reduction of iron(II) co-ordinated CO results from the interaction of the solvent with the borane adducts of the intermediates of CO reduction, as already noted by Graham in the related rhenium chemistry.[2] We also observed an easy synthesis of a rare hydroxymethyl metal complex and the extreme instability of the probable formyl intermediate. We are at present investigating the reactivities of the hydroxymethyl and hydride complexes (**2**) and (**4**).

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‡ (**4**): $^1H$ n.m.r. ($C_6D_6$) $\delta$ (p.p.m. from $Me_4Si$): $-11.74$ (s, 1H, FeH) and 1.65 (s, 15H, $CH_3$); $^{13}C$ n.m.r. ($C_6D_6$) $\delta$ (p.p.m. from $Me_4Si$): 94.7 ($C_5Me_5$), 8.7 (Me), and 219 (CO). Satisfactory elemental analyses were obtained.

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