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Preliminary communication

REGIOSELECTIVITY OF HYDRIDE ADDITION TO $[(\eta^5\text{-}C_5H_5)Fe(Ph_2PCH_2CH_2PPh_2)CO]PF_6$ AND REARRANGEMENT OF $(\eta^5\text{-}C_5H_5)Fe(Ph_2PCH_2CH_2PPh_2)(CO)H$ TO $(\eta^4\text{-}C_5H_6)Fe(Ph_2PCH_2CH_2PPh_2)CO$

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Summary

In tetrahydrofuran at reflux $[(\eta^5\text{-}C_5H_5)Fe(Ph_2PCH_2CH_2PPh_2)CO]PF_6$ undergoes hydride attack both on CO and *exo* on the cyclopentadienyl ligand, whereas at −78°C hydride addition occurs regioselectivity at CO to give $(\eta^5\text{-}C_5H_5)Fe(Ph_2PCH_2CH_2PPh_2)(CO)H$. In toluene at 90°C the latter undergoes intramolecular rearrangement to $(\eta^4\text{-}C_5H_6)Fe(Ph_2PCH_2CH_2PPh_2)CO$.

The control and prediction of the regioselectivity of nucleophilic additions to organometallic cations containing unsaturated hydrocarbon ligands continues to attract attention. Few examples have been reported however, either of the temperature dependence of such regioselectivities or of subsequent rearrangements of kinetically formed products to more stable isomers [1]. Reduction of cation 1 with lithium aluminium hydride in dichloromethane/tetrahydrofuran (1/1) at −78°C produces the iron hydride complex 2 as the exclusive product [2]. Under these conditions hydride attack is occurring regioselectively at the carbonyl ligand to generate the corresponding formyl species which subsequently rearranges to 2 [3]. Reduction of 1 with lithium aluminium deuteride generates the corresponding iron deuteride 3 [2]. In tetrahydrofuran solution at 20°C the iron hydride 2 disproportionates to the iron methyl complex 4 [4]. In contrast in toluene solution at 20°C iron hydride 2 disproportionates to the dimetallic dihydride $[(\eta^5\text{-}C_5H_5)Fe(CO)H]_2$(diphos) (diphos = $Ph_2PCH_2CH_2PPh_2$) and free diphos. This latter disproportionation is however reversible and can be suppressed in the presence of excess diphos [2]. We report here that loss of regioselectivity in the reduction of cation 1 occurs at higher temperatures with both attack at CO and *exo* on the cyclopentadienyl ring being observed. On thermolysis in a non-polar solvent in the presence of excess diphos the carbonyl hydride

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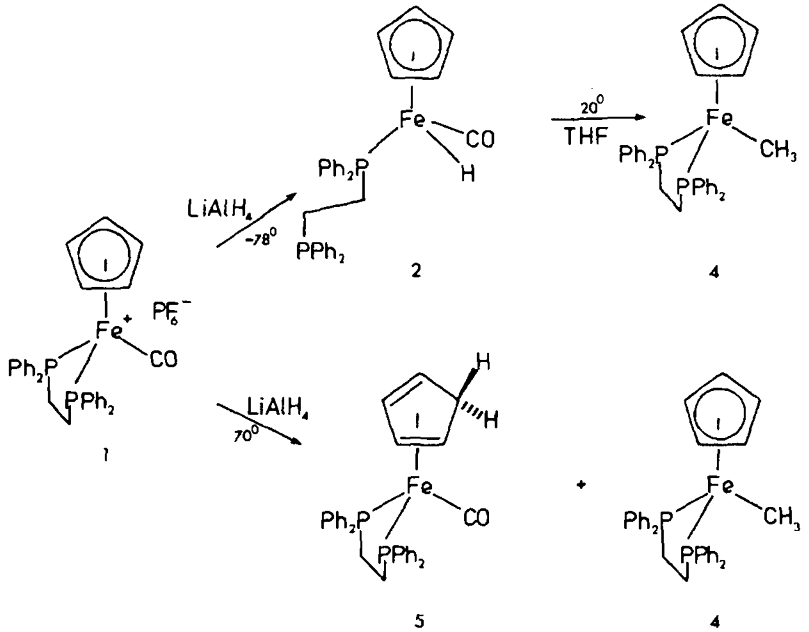
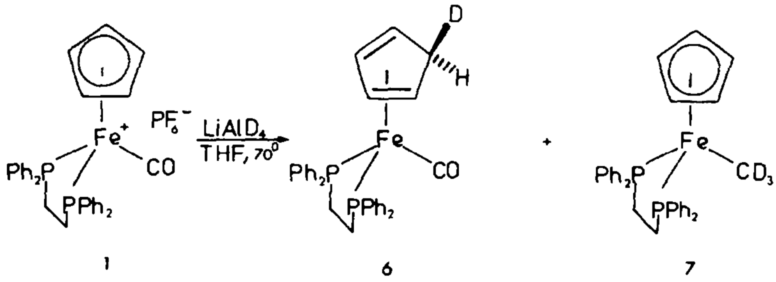
2 slowly rearranges to the corresponding cyclopentadiene complex 5 with hydrogen migration occurring intramolecularly to the *endo* position.

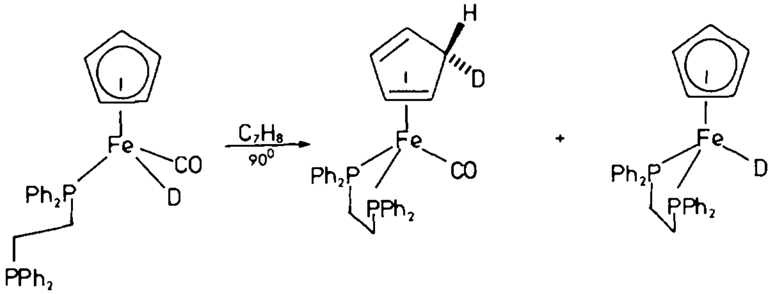
Reduction of cation 1 with lithium aluminium hydride in tetrahydrofuran at reflux results in the formation of only two products, the cyclopentadiene complex 5 and the methyl complex 4 in the ratio 2/3 respectively. The novel cyclopentadiene complex 5 was characterised by elemental analysis and high resolution mass spectroscopy (M^+ = 548.1119); In the 300 MHz ^{1}H NMR spectrum (toluene-d_8) of 5, H_{exo} (δ 2.75) and H_{endo} (δ 3.03) could be readily assigned since only H_{exo} exhibited coupling to phosphorus [5]. The characteristic H_{exo} IR absorption [6] was present at 2740 cm^{-1}.



Reduction of cation 1 with lithium aluminium deuteride in tetrahydrofuran at reflux results in the formation of the deuterated compounds 6 and 7. The deuterium was shown to be in the *exo* position by the complete absence of H_{exo} in the ^{1}H NMR spectrum of 6, while D_{exo}, but no D_{endo}, was observed by ^{2}H NMR spectroscopy. In confirmation of this the H_{exo} IR absorption was absent for 6 and had been replaced by D_{exo} absorption at 2045 cm^{-1}.



Thermolysis of the carbonyl hydride **2** in toluene at 90°C for 20 h in the presence of excess diphos results in complete isomerisation of **2** to the cyclopentadiene complex **5** together with a small amount (< 5%) of $(\eta^5\text{-}C_5H_5)Fe(Ph_2PCH_2CH_2PPh_2)H$ (**8**). The proportion of **8** increases with temperature. Thermolysis of the corresponding carbonyl deuteride **3** under the same conditions results in formation of the deuterated compound **9** and a small amount of **10**. By the same criteria as described above for **6** the deuterium in **9** was shown to be in the *endo* position ($\nu(D_{endo})$ 2170 cm^{-1}). The rearrangements of **2** and **3** to **5** and **9** respectively were found to be first order and the isotope effect k_H/k_D had a value close to unity.



3 9 10

In contrast to the low temperature reduction of **1**, at elevated temperatures regioselectivity is lost and *exo* hydride attack on the cyclopentadienyl ligand competes with attack at CO. In the polar solvent, tetrahydrofuran, at reflux the initially formed carbonyl hydride **2** rapidly disproportionates to the methyl complex **4** and does not undergo rearrangement to the cyclopentadiene complex **5**. In the less polar solvent toluene, however, no disproportionation of **2** to **4** is observed even at elevated temperatures, instead the relatively slow migration of hydride from the metal in **2** to the *endo* cyclopentadiene position in **5** occurs.

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