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Preliminary communication

REDUCTIONS OF THE CATIONS $[(\eta^5\text{-}C_5H_5)Fe(L)_2CO]^+$ (L = tertiary phosphine): PRODUCT CONTROL BY VARIATION OF PHOSPHINE LIGANDS

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Summary

The reduction by $LiAlH_4$ of the carbonyl cations $[(\eta^5\text{-}C_5H_5)Fe(L)_2(CO)]^+$ ($L = Ph_3P$; L_2 = bis-tertiary phosphine) and $[(\eta^5\text{-}C_5H_5)Fe(L)(CO)_2]^+$ ($L = Ph_3P$, Me_3P) produces the corresponding carbonyl-hydride or -methyl complexes depending on the electron donating and chelating abilities of the phosphine ligands.

We have recently demonstrated that the electron-rich cation $[(\eta^5\text{-}C_5H_5)Fe(Ph_2PCH_2CH_2PPh_2)CO]^+$ (1) is attacked regioselectively at the carbonyl ligand to generate the formyl intermediate 2 which is in equilibrium with the carbonyl hydride 3 [1]. The two electron-donating phosphine ligands disfavour attack by hydride on the cyclopentadienyl ligand and thus favour attack on the carbonyl. Furthermore, the equilibration of 3 with 2 allows the disproportionation of 3 via 2 to the methyl complex 4 [2]. We were interested in studying the effect of variation of the phosphine ligands on the formyl to carbonyl hydride equilibrium, that is on the products obtained by reducing the cations $[(\eta^5\text{-}C_5H_5)Fe(L)_2CO]^+$ (L = tertiary phosphine). We describe here the lithium aluminium hydride reductions of the cations $[(\eta^5\text{-}C_5H_5)Fe(L)_2CO]^+$ ($L = PPh_3$ (5), $L_2 = Ph_2PCH_2CH_2CH_2PPh_2$ (8), (+)-DIOP* (10), *cis*-$Ph_2PCH = CHPPh_2$ (12), $Ph_2PCH_2PPh_2$ (14) and $Me_2PCH_2CH_2PMe_2$ (16)) and $[(\eta^5\text{-}C_5H_5)Fe(L)(CO)_2]^+$ ($L = Ph_3P$ (18) and Me_3P (21)) in the form of their hexafluorophosphate salts.

The bis-phosphine cations 5, 8, 10, 12 and 14 are readily available on treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Br$ or $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\text{isobutylene})]^+$ with an excess of phosphine followed in each case by trimethylamine *N*-oxide to effect the decarbonylation [3]. The cation 16 was prepared from $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ [4] or $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\text{tetrahydrofuran})]^+$ with $Me_2PCH_2CH_2PMe_2$ followed by

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*(+)-DIOP = (+)-2,3-*O*-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane.

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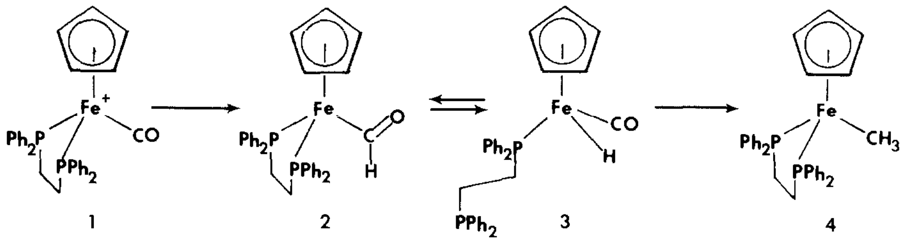
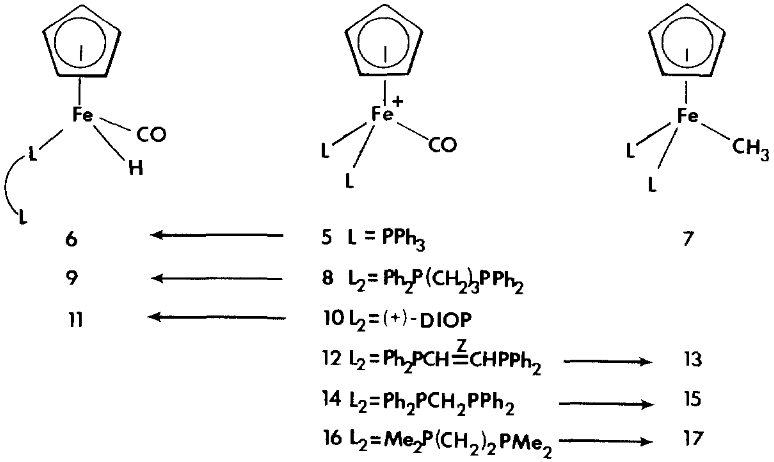
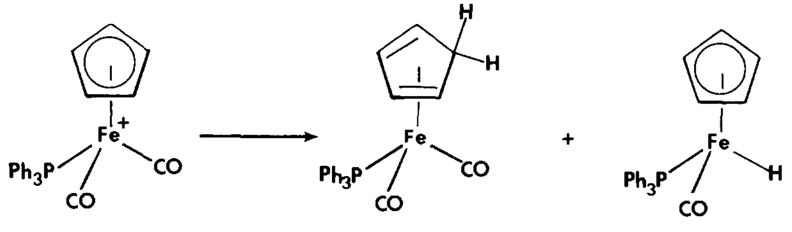


trimethylamine *N*-oxide. Reductions of cations **5**, **8**, and **10** with lithium aluminium hydride gave the corresponding carbonyl hydrides **6**, **9** and **11** respectively. Complex **11** was obtained as a mixture of diastereomers in the ratio 5/4; The carbonylhydride **6** was stable in solution since even in the presence of a very large excess of triphenylphosphine or trimethylphosphine no formation of **7** could be detected. Furthermore complex **6** did not undergo phosphine exchange in the latter case. Carbonyl hydrides **9** and **11** were also stable in solution for long periods. Reductions of cations **12**, **14** and **16** gave the methyl complexes **13**, **15** and **17** directly.

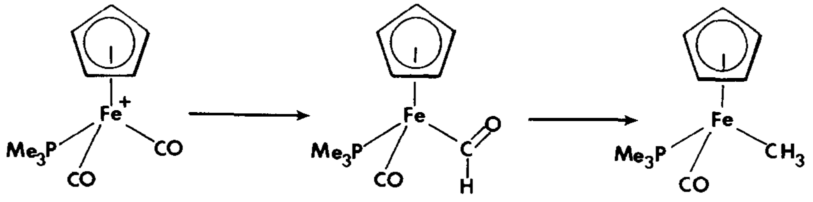


Reduction of cation **1** occurs regioselectively at CO to give the formyl **2** which rearranges to the more stable carbonyl hydride **3** [1]. Complexes **2** and **3** are however in equilibrium and this allows disproportionation of **3** via the formyl **2** to give the methyl complex **4** [2]. The products obtained from the reductions of cations **5**, **8**, **10**, **12**, **14** and **16** are also consistent with regioselective attack onto CO. The carbonyl hydrides **6**, **9** and **11** are however, in contrast to **3**, stable towards disproportionation to methyl complexes. In carbonyl hydrides **6**, **9** and **11** equilibrations with formyl complexes are more unfavourable for reasons of entropy than in the case of **3**. For the phosphine ligands in cations **12**, **14** and **16** coordination of both phosphines is favoured and this would be expected to stabilise the initially formed formyl intermediates sufficiently for complete reduction to the methyl complexes, **13**, **15** and **17** respectively, to occur.



18 19 20

The monophosphine cations **18** and **21** were prepared by treatment of the phosphines with $(\eta^5\text{-}C_5H_5)Fe(CO)_2Br$ in tetrahydrofuran or $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{(isobutylene)}]^+$ in acetone. Cation **21** can also be obtained by phosphine exchange on **18** in acetone solution. Reduction of cation **18** gave the expected [5] cyclopentadiene complex **19** together with the carbonyl hydride **20** (ratio **19**/**20** = 1/2). In contrast, reduction of cation **21** led to the exclusive formation of the methyl complex **23**. The intermediate formyl complex **22** (δ(CHO) 15.4 ppm, d, J(PH) 5 Hz) was observed by monitoring this reduction by NMR spectroscopy.



21 22 23

The regioselective attack on CO is controlled by the electron-richness of the cation. For example, reduction of the monotriphenylphosphine cation **18** occurs both at cyclopentadienyl and at CO to give the complexes **19** and **20** respectively. Again carbonyl hydride **20** would be expected to arise by loss of CO from the initially formed formyl complex. In order to demonstrate clean reduction of CO in iron cations containing two CO ligands we reasoned that it would be necessary to use the very electron donating phosphine ligand trimethylphosphine. Indeed reduction of cation **21** cleanly gave the methyl complex **23**; the Me_3P ligand not only directing attack towards CO but also stabilising the initial formyl **22** towards ligand loss and hence allowing complete reduction to methyl.

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