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Preliminary communication

STEPWISE OXIDATIVE DECARBONYLATIONS OF ORGANOMETALLIC CATIONS OF IRON

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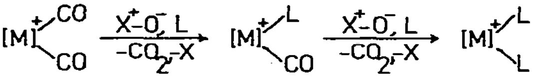
Summary

Controlled stepwise removal by nucleophilic oxidants of one or two carbon monoxide ligands from $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^+PF_6^-$ with replacement by another ligand (L = phosphine or phosphite) is demonstrated.

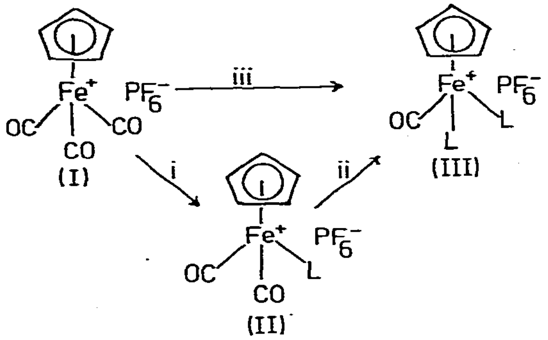
An attractive alternative to the photolytic or thermal displacement of carbon monoxide from transition metal carbonyl complexes is oxidation using a nucleophilic oxidant. This process has however seldom been exploited [1] except for the complete destruction of organotransition metal complexes for the recovery of organic ligands [2]. We were interested in developing a general synthesis of cationic organotransition metal complexes containing several phosphine ligands. We anticipated that a nucleophilic oxidant in the presence of a ligand L would readily react with cations containing carbon monoxide ligands to remove CO as CO_2 and replace it with L. One would expect also that for cations containing several CO ligands this process would be stepwise: the more CO ligands are replaced by L the more electron-rich is the cation and thus the slower the attack by the oxidant.



SCHEME 1

We have discovered that it is possible to replace one of the carbon monoxide ligands of $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^+PF_6^-$ (I) by a ligand L in this manner with dimethyl sulphoxide as the oxidant. The cation I and L were dissolved in dimethyl sulphoxide under nitrogen and stirred at 20°C for 10 min. Work-up gave the cations II. Cations II with L = $PPh_2(CH_2)_nPPh_2$ (n = 2, 3), PPh_3 and $P(OMe)_3$ were prepared in this way. Prolonged exposure to dimethyl sulphoxide in the presence of excess L leads to slow replacement of a second carbon monoxide ligand.

A second carbon monoxide ligand may be readily replaced by using Me_3NO as oxidant. The complexes II and L were dissolved in acetone and treated with an excess of Me_3NO hydrate. Work-up gave III. The reaction with Me_3NO appears to be instantaneous at 20°C. Rapid removal of the second carbon monoxide may also be achieved using alkaline hydrogen peroxide (alk. H_2O_2). Complexes III may also be prepared directly from cation I with two equivalents of L and an excess of Me_3NO or alkaline hydrogen peroxide as oxidant. Cations III with L_2 = $PPh_2(CH_2)_nPPh_2$ (n = 1, 2, 3), $(PPh_3)_2$ and $[P(OMe)_3]_2$ were prepared by these methods.



SCHEME 2. (i) L = dimethyl sulphoxide; (ii) L = Me_3NO or alk. H_2O_2; (iii) 2L = Me_3NO or alk. H_2O_2.

All of the above reactions were essentially quantitative. The methods described above for the preparation of the cations $[(\eta^5\text{-}C_5H_5)Fe(CO)_2L]^+PF_6^-$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)L_2]^+PF_6^-$ are more efficient and practically easier than existing methods. For the phosphite complexes the usual complications arising from Michaelis—Arbuzov type rearrangements of phosphite complexes to phosphonate complexes [3] are avoided.

References

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