

Preliminary communication

MECHANISMS OF NUCLEOPHILIC ATTACK AT COORDINATED CARBON MONOXIDE

II * IODIDE ADDITION TO A CARBON MONOXIDE LIGAND IN $[\text{Fe}(\text{CO})_3(1-5-\eta\text{-DIENYL})]^+$ CATIONS (DIENYL = C_6H_7 , C_7H_9 , 2-MeOC₆H₆)

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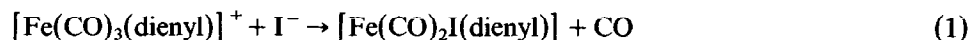
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Summary

Nucleophilic addition to a carbonyl ligand has been shown to compete with attack at the metal or dienyl ring in the reactions of $[\text{Fe}(\text{CO})_3(1-5-\eta\text{-dienyl})]^+$ cations with iodide ion. Thus, the novel acyl iodide complex $[\text{Fe}(\text{CO})_2(\text{COI})(1-5-\eta\text{-C}_6\text{H}_7)]$ is found to be a major product from the reaction of $[\text{Fe}(\text{CO})_3(1-5-\eta\text{-C}_6\text{H}_7)]^+$ with I^- in nitromethane or acetone solvents. The other major initial product is the ring adduct $[\text{Fe}(\text{CO})_3(1-4-\eta\text{-IC}_6\text{H}_7)]$. Exposure of the acyl iodide species to light causes its rapid decomposition. Analogous behaviour towards I^- is shown by the related $[\text{Fe}(\text{CO})_3(1-5-\eta\text{-C}_7\text{H}_9)]^+$ and $[\text{Fe}(\text{CO})_3(1-5-\eta\text{-2-MeOC}_6\text{H}_6)]^+$ cations.

Attack by nucleophiles on tricarbonyl(dienyl)iron cations of the type $[\text{Fe}(\text{CO})_3(1-5-\eta\text{-dienyl})]^+$ (I, dienyl = C_6H_7 ; II, dienyl = C_7H_9) may occur at the dienyl ring, the metal, or a carbonyl ligand [1,2]. With the vast majority of nucleophiles (tertiary phosphines and phosphites, primary and secondary amines, anilines, pyridines, heterocyclics, activated aromatics, and the anions H^- , CN^- , NCS^- , NCSe^- , NCO^- , $\text{R}_2\text{NCS}_2^{2-}$) only ring addition has been reported [1–3].

One of the few examples involving nucleophilic attack at the iron centre is reaction 1, where dienyl = C_6H_7 or C_7H_9 , which is the standard route for the synthesis of $[\text{Fe}(\text{CO})_2\text{I}(1-5-\eta\text{-dienyl})]$ compounds [4]. Spectroscopic studies reported here show that reaction 1 is considerably more complex than simple carbonyl displacement, and that it involves initial attack at both the dienyl ring and a carbonyl ligand in CH_3NO_2 or acetone solvents.



* For part 1 see ref. 8a.

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The reaction between $[\text{Fe}(\text{CO})_3(1-5-\eta\text{-C}_6\text{H}_7)]^+$ (I) ($[\text{Fe}] = 6 \times 10^{-3} \text{ mol dm}^{-3}$) and Et_4NI ($[\text{I}^-] \geq 3 \times 10^{-2} \text{ mol dm}^{-3}$) was carried out in the dark under dinitrogen in a variety of solvents. At the completion of the reaction in CH_3NO_2 (as evidenced by the complete disappearance of the initial dienyl $\nu(\text{CO})$ bands at 2110 and 2060 cm^{-1}), four strong $\nu(\text{CO})$ bands were observed at 2080, 2040, 2030 (sh) and 1967 cm^{-1} . Significantly, there was only a small amount ($< 5\%$) of the reported [4] product $[\text{Fe}(\text{CO})_2 \text{I}(1-5-\eta\text{-C}_6\text{H}_7)]$ ($\nu(\text{CO})$ in CH_3NO_2 : 2030, 1987 cm^{-1}), as shown by a weak shoulder at ca. 1985 cm^{-1} . The solid product mixture isolated from an analogous preparative procedure exhibited a further medium intensity $\nu(\text{CO})$ band at 1730 cm^{-1} (Nujol mull).

The $\nu(\text{CO})$ bands at 2040 and 1967 cm^{-1} are typical of neutral tricarbonyl-(diene)iron species, and are assigned to the ring adduct $[\text{Fe}(\text{CO})_3(1-4-\eta\text{-IC}_6\text{H}_7)]$ (III). Brown et al. [2] have also recently reported III as a major product from the reaction of I with I^- . Most significantly, we assign the $\nu(\text{CO})$ product bands at 2080, 2030, and 1735 cm^{-1} to the novel acyl iodide complex $[\text{Fe}(\text{CO})_2(\text{COI})(1-5-\eta\text{-C}_6\text{H}_7)]$ (IV). The 1735 cm^{-1} band is attributed to the COI ligand, being very similar to the peak at 1715 cm^{-1} reported [5] for an acyl iodide intermediate in the reaction of $\text{Fe}(\text{CO})_5$ with iodine.

Exposure of the product mixture (either solid or in CH_3NO_2) to normal laboratory light resulted in the rapid (minutes) disappearance of the $\nu(\text{CO})$ bands associated with IV. This was not accompanied by the growth of any other $\nu(\text{CO})$ bands. The instability of IV to light is consistent with its acyl iodide formulation, since organic acyl iodides are known [6] to undergo CO dissociation upon irradiation (eq. 2). The failure to generate any $[\text{Fe}(\text{CO})_2\text{I}(1-5-\eta\text{-C}_6\text{H}_7)]$ from exposure



of IV to sunlight may arise from rapid decomposition subsequent to CO release, before attachment of I^- to the vacated metal site can occur.

Prolonged (hours) examination of product mixtures revealed a slow conversion of adduct III to the carbonyl-displaced product $[\text{Fe}(\text{CO})_2\text{I}(1-5-\eta\text{-C}_6\text{H}_7)]$ (V). This may explain why V is the product reported in previous investigations [4] of reaction 2.

The nature of the reaction between I and iodide ion is strongly solvent dependent. Thus, while we found closely analogous results to the above in acetone solvent, no evidence was observed for an acyl iodide product (IV) in CH_3CN . Similarly, Brown et al. [2] reported only III and V as products in a dichloromethane/water (2/1) mixture as solvent. However, in the latter case it is possible that the failure to observe III may arise from the presence of light.

Finally, spectroscopic studies of the reactions of the related cations II and $[\text{Fe}(\text{CO})_3(1-5-\eta\text{-2MeOC}_6\text{H}_6)]^+$ with iodide ion in CH_3NO_2 reveal very similar behaviour to the cyclohexadienyl substrate. All the above results are consistent with the general mechanism outlined in Scheme 1 ($\text{A} = \text{H}$ or MeO ; $n = 1$ or 2). Similar behaviour, involving competing nucleophilic attack at the dienyl ring and a CO ligand, has previously been reported for alkoxide [7] and hydroxide [8] ions.

Kinetic studies are in progress for the reactions outlined in Scheme 1, from which it is hoped to determine quantitatively for the first time the relative ease of nucleophilic addition to dienyl (k_2) and carbonyl (k_1) ligands.

Acknowledgements

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References

- 1 L.A.P. Kane-Maguire, E.D. Honig, and D.A. Sweigart, *Chem. Rev.*, 84 (1984) 525, and refs. therein.
- 2 D.A. Brown, N.J. Fitzpatrick, W.K. Glass, and P.K. Sayal, *Organometallics*, 3 (1984) 1137, and refs. therein.
- 3 A.J. Birch, P.E. Cross, J. Lewis, D.A. White, and S.B. Wild, *J. Chem. Soc. (A)*, (1968) 332.
- 4 M.A. Hashmi, J.D. Munro, P.L. Pauson, and J.M. Williamson, *J. Chem. Soc. A*, (1967) 240.
- 5 K. Noack, *J. Organomet. Chem.*, 13 (1968) 411.
- 6 A. Wojcicki, *Adv. Organomet. Chem.*, 11 (1973) 88.
- 7 D.A. Brown, S.K. Chawla, W.K. Glass and F.M. Hussein, *Inorg. Chem.*, 21 (1982) 2726.
- 8 (a) J.G. Atton and L.A.P. Kane-Maguire, *J. Organomet. Chem.*, 246 (1983) C23; (b) J.G. Atton, K. Gilmore, and L.A.P. Kane-Maguire, unpublished results.