Contrasting Ligand Photolabilisations in the Acetyl Complexes $[(\eta^5\text{-}C_5R_5)Fe(CO)(PPh_3)COMe]$ (R = H, Me)

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While the primary photochemical process for $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe]$ is exclusive loss of carbon monoxide to generate $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)Me]$, that for $[(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)COMe]$ is exclusive loss of triphenylphosphine to generate $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2Me]$.

Photolysis of the iron acyl complexes $[(\eta^5\text{-}C_5H_5)\text{-}Fe(CO)(PPh_3)COR]$ results in formation of the corresponding alkyl complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)R]$ with overall loss of carbon monoxide. Extensive studies that have been in the literature for some time[1] have established that one, but not necessarily the only, mechanism is direct loss of the carbon monoxide to generate after rearrangement, stereospecifically the iron alkyl complexes with inversion of configuration at iron (Scheme 1).

The loss of carbon monoxide could not be established as the exclusive mechanism since the reaction was never observed even at low conversion to proceed completely stereospecifically; the observed 16–60% loss of stereochemical integrity being due at least in part to photoracemisation of the product alkyl complex by an unspecified mechanism. However, triphenylphosphine loss competing as the primary photochemical process would not be inconsistent with the observations.

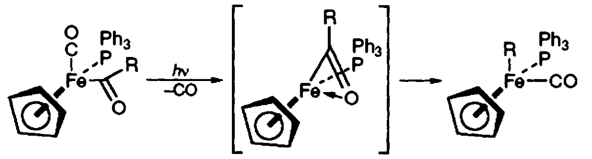
We have established recently that phosphine loss is the primary and exclusive photolabilisation process for related cationic aminocarbene complexes[2] and describe herein mechanistic evidence for the photolyses of the acetyl complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe]$ **1** and $[(C_5Me_5)Fe(CO)(PPh_3)COMe]$ **4**, which show exclusive carbon monoxide loss for the former and exclusive triphenylphosphine loss for the latter.

The cyclopentadienyl complexes **1–3** were synthesised by standard literature methods.[3] Each complex in the series was clearly recognisable by the characteristic methyl resonances in their ^1H NMR spectra. Photolysis of toluene solutions of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe]$ **1** led to clean formation of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)Me]$ **2**. In the presence of a large excess (>5 equiv.) of $(p\text{-Tol})_3P$ prolonged photolysis of **1** gave $\{(\eta^5\text{-}C_5H_5)Fe(CO)[P(p\text{-Tol})_3]Me\}$ **3**. Monitoring this latter experiment over time showed the only observable product after 5 min (3.5% conversion) to be **2**. After 15 min (15% conversion) a mixture of **2** and **3** (70 : 30) was apparent and after 30 mins (29% conversion) approximately equal proportions of **2** and **3** were observed. The initial formation of only complex **2** is consistent with exclusive loss of carbon monoxide being the primary photochemical process for the acetyl complex **1**, with complex **3** being formed subsequently by photoinduced phosphine exchange in **2** (Scheme 2). In agreement with this treatment of **2** with a large excess of $(p\text{-Tol})_3P$ in the dark did not lead to the formation of **3**, which was, however, formed rapidly on photolysis.

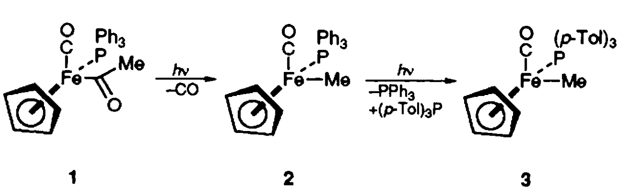
The pentamethylcyclopentadienyl complexes **4–6** were prepared as described previously,[4] and again were readily recognisable by ^1H NMR spectroscopy. When a toluene solution of complex **4** was photolysed and monitored by ^1H NMR spectroscopy the only detectable product after 5 min (5% conversion) was $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2Me]$ **5**, with none of complex **6** being detectable (ratio **5** : **6** > 99 : 1). After 15 min (22% conversion) both **5** and **6** were present (70 : 30), after 30 min (58% conversion) the ratio of **5** : **6** was 35 : 65, while after 120 min (100% conversion) the ratio was 10 : 90. The initial formation of only complex **5** is consistent with exclusive loss of triphenylphosphine being the primary photochemical process for the acetyl complex **4**, which subsequently undergoes a photoinduced ligand exchange reaction to generate **5** (Scheme 3). In agreement with this prolonged photolysis of complex **5** in the presence of an excess of triphenylphosphine cleanly produced complex **6**.

Photolysis of the iron acetyl complex $[(\eta^5\text{-}C_5H_5)\text{-}Fe(CO)(PPh_3)COMe]$ **1** leads to exclusive labilisation of the carbon monoxide ligand. This is in complete contrast to the related methyl complex **2**, aminocarbene cations[2] and the pentamethylcyclopentadienyl iron acetyl complex **4**, all of which undergo photolabilisation of the phosphine ligand. While a definitive explanation for these differences must await many more examples, we are working on the hypothesis that except for exceptional cases phosphine will always be photolabilised in preference to carbon monoxide, a phenomenon consistent simply with the relative bond strengths. Exceptions to this tenet will arise when the carbon monoxide is labilised by other factors. In the case of the acetyl complex **1** the carbon monoxide is labilised by neighbouring group participation of the acetyl oxygen leading to the η^2-acetyl intermediate (Scheme 1) necessary to explain the stereospecificity of the decarbonylation.[1] In complex **4** the phosphine and carbon monoxide ligands are less and more tightly bound respectively than in complex **1** due to the superior electron donation from the pentamethylcyclopentadienyl ligand and neighbouring group participation by the acetyl is disfavoured because the required antiperiplanar arrangement of the acetyl oxygen to the carbon monoxide ligand is prevented by the bulk of the pentamethylcyclopentadienyl ligand.

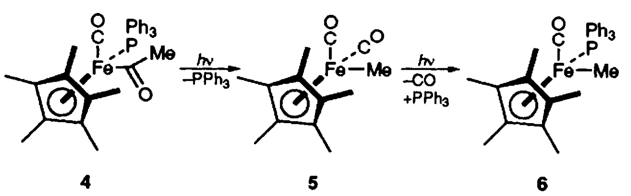
These photolabilisation studies indicate the need for caution when assigning reaction mechanisms on the basis of products alone. Furthermore, given that these phosphine exchanges are even promoted by the low levels of normal



Scheme 1



Scheme 2



Scheme 3

laboratory lighting, many other ligand exchange processes previously assumed to be thermally induced may turn out to be photoinitiated.

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