

Phosphine photolabilisation studies of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{PPh}_3)(\text{CO})\text{-COR}$ ($\text{R} = \text{Me}, \text{Ph}, 2,6\text{-C}_6\text{H}_3\text{F}_2$) and $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{PPh}_3)(\text{CO})\text{-COR}$ ($\text{R} = \text{Me}, 2,6\text{-C}_6\text{H}_3\text{F}_2$) utilising NMR, laser desorption FT ICR MS and photofragmentation voltammetry analysis



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Received (in Cambridge) 6th January 1999, Accepted 11th March 1999

Photolysis of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{COR}$ ($\text{R} = 2,6\text{-C}_6\text{H}_3\text{F}_2, \text{Me}$) leads to preferential loss of the phosphine ligand to form the corresponding alkyl species $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{R}$, while photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{COR}$ ($\text{R} = \text{Me}, \text{Ph}, 2,6\text{-C}_6\text{H}_3\text{F}_2$) leads to loss of CO to form $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{R}$ which subsequently undergoes rapid phosphine exchange. A mechanism for this process is proposed which is corroborated using photofragmentation voltammetry. Laser desorption mass spectrometry was also used as a tool to probe whether phosphine loss was the primary photochemical process.

Introduction

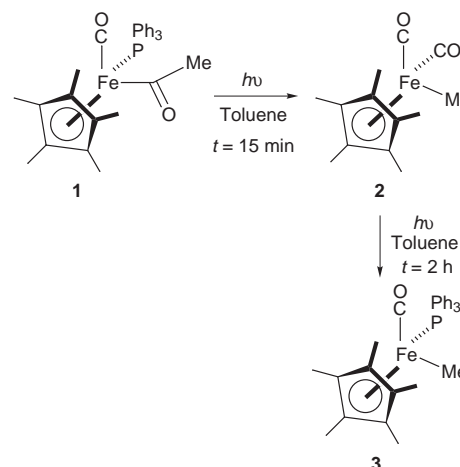
The photochemical decarbonylation of transition metal carbonyls containing an acyl group is a well documented process.¹ The chiral iron acyl complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{COR}$ have been extensively utilised in asymmetric synthesis² and the chirality at the pseudotetrahedral iron centre has been used to determine the stereochemical outcome of photochemical decarbonylations. Early studies established that the terminal CO rather than the acetyl CO is expelled under photolytic conditions to yield the alkyl species.³ In addition, it has been observed that no epimerisation occurs in the α position of the R group⁴ and that highly stereospecific decarbonylation occurs with inversion of configuration at the iron centre.⁵ In all of these studies, the mechanism for decarbonylation in the acyl species has been attributed to initial loss of the terminal CO to form a coordinatively unsaturated 16 electron intermediate with subsequent alkyl migration to yield the iron alkyl species. However, it has also been observed that prolonged photolysis of homochiral iron acyl species leads to racemic iron alkyl species.^{5c,6} These alkyl species possess high configurational instability at the iron centre such that photolysis of homochiral iron alkyl also leads to racemic iron alkyl species.

We have recently demonstrated that reversible photolytic phosphine rather than CO dissociation occurs in the homochiral aminocarbene complexes $\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PR}_3)[\text{C}(\text{NHR}^2)(\text{R}^1)]\}\text{BF}_4$ [$\text{R} = \text{Ph}, p\text{-Tol}$; $\text{R}^1 = \text{H}, \text{Me}, \text{Bu}$; $\text{R}^2 = \text{Me}, \text{CH}_2\text{Ph}, \text{CH}(\text{Me}), \text{Ph}$]⁷ and that epimerisation occurs exclusively at the iron centre. Further evidence for the intermediates involved in this process was provided by voltammetry experiments. We have also extended this study to the original iron acyl compounds and have determined that in the absence of other factors, the primary photochemical process is phosphine loss rather than the commonly accepted carbon monoxide dissociation.⁸ We now wish to report in full our studies on the iron acyl system and include further evidence for the original proposed mechanism.

Results

Photolysis studies of $(\eta^5\text{-C}_5\text{Me}_5)$ based complexes

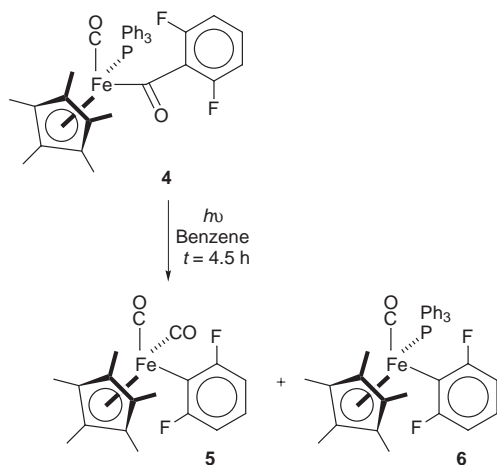
NMR Exchange experiments. The synthesis of the acetyl complex $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{COMe}$ **1** has been previously described,⁹ and the photochemical behaviour reported in a preliminary form.⁸ When a toluene solution of the complex **1** was photolysed and monitored by ¹H NMR spectroscopy, the only observable product after the first 5 minutes was $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Me}$ **2** (4.7%) and no $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$ **3** was observed. Only after 15 minutes of photolysis was a small quantity of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$ **3** observed (16% **2** and 6% **3**). After 30 minutes of photolysis, the proportion of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$ **3** increased substantially (20% **2** and 38% **3**). After a total time of 2 hours, the main product was $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$ **3** (89%) with no sign of the starting material (Scheme 1). The identity of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$ **3** was confirmed through independent synthesis of



Scheme 1

this compound by photolysis of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Me}$ in the presence of excess PPh_3 for 16.25 hours. Although a full analysis could not be obtained for this compound due to an inseparable excess of phosphine and phosphine oxide, all other spectroscopic data were identical to that reported in the literature.¹⁰

The complex $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{CO}(2,6\text{-C}_6\text{H}_3\text{F}_2)$ **4** was synthesised in an analogous fashion to the acetyl complex **1** with an overall yield of 19% from the starting dimer $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2]$. A solution of the desired complex **4** in benzene was photolysed and the reaction was monitored by IR spectroscopy (Scheme 2). A dicarbonyl intermediate (ν_{CO} 2007,



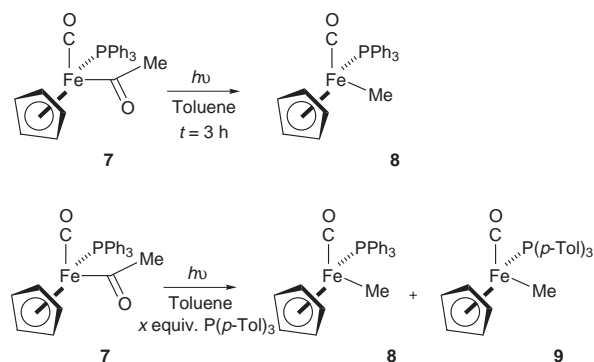
Scheme 2

1954 cm^{-1}) was observed after 5 min and its concentration increased with further irradiation to be eventually replaced by a new product with a single carbonyl frequency (ν_{CO} 1921 cm^{-1}) different to that of the starting acyl (ν_{CO} 1904 cm^{-1}). Purification by column chromatography proved unsuccessful as both compounds eluted together. However, full spectroscopic analysis (^1H , ^{13}C , ^{31}P and ^{19}F NMR) indicated the presence of both $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(2,6\text{-C}_6\text{H}_3\text{F}_2)$ **5** and $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(2,6\text{-C}_6\text{H}_3\text{F}_2)$ **6**.

An authentic sample of the suspected dicarbonyl intermediate **5** was prepared by treatment of a THF solution of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Br}$ with lithium 2,6-difluorobenzene. When a toluene solution of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(2,6\text{-C}_6\text{H}_3\text{F}_2)$ **5** (ν_{CO} 2010 , 1958 cm^{-1}) were replaced by a single carbonyl stretching frequency at ν_{CO} 1928 cm^{-1} . Purification by column chromatography and recrystallisation from diethyl ether at $-22\text{ }^\circ\text{C}$ afforded bright red crystals of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(2,6\text{-C}_6\text{H}_3\text{F}_2)$ **6** in 82% yield. Attempts to synthesise $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(2,6\text{-C}_6\text{H}_3\text{F}_2)$ **6** directly from $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Br}$ and lithium 2,6-difluorobenzene proved unsuccessful.

Photolysis studies of $(\eta^5\text{-C}_5\text{H}_5)$ based substrates

NMR Exchange experiments. Encouraged by these results we then proceeded to investigate in more detail the mechanism of photolabialisation of the corresponding $(\eta^5\text{-C}_5\text{H}_5)$ based complexes. A toluene solution of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{COMe}$ **7** was photolysed for 3 hours and led to clean formation of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$ **8** as determined from the methyl doublet in the ^1H NMR spectrum (Scheme 3). Photoirradiation of a toluene solution of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{COMe}$ **7** in the presence of one equivalent of $\text{P}(p\text{-Tol})_3$ for 3 hours resulted in the appearance of two methyl doublets in a 4:3 ratio. Interestingly, when the photolysis was performed for 5 hours, a 2:1 ratio of products was obtained. When the NMR sample was

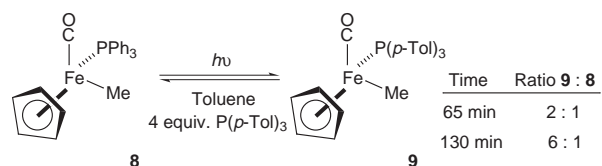


Photolysis Time	Equiv. $\text{P}(p\text{-Tol})_3$	Ratio 8 : 9
3 h	1	4 : 3
5 h	1	2 : 1
3 h	5	0 : 100

Scheme 3

doped with $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$ only the high frequency doublet increased in intensity. The second lower frequency doublet was due to the $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})[\text{P}(p\text{-Tol})_3]\text{Me}$ species **9** and was confirmed by comparison with an authentic sample of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})[\text{P}(p\text{-Tol})_3]\text{Me}$ **9**. When $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{COMe}$ **7** was photolysed for 3 hours in the presence of five equivalents of $\text{P}(p\text{-Tol})_3$, the only observable doublet in the NMR spectrum was due to $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})[\text{P}(p\text{-Tol})_3]\text{Me}$ **9** (Scheme 3). In a similar experiment, the reaction was monitored by ^1H NMR spectroscopy after 5, 15 and 30 minutes of photolysis. The first observable product after 5 minutes was $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$ **8**. After 15 minutes, a small amount of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})[\text{P}(p\text{-Tol})_3]\text{Me}$ **9** (5:2 ratio) was observed and after 30 minutes an equal amount of both products was observed in addition to unreacted starting material. In all cases, isolation of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})[\text{P}(p\text{-Tol})_3]\text{Me}$ **9** by column chromatography was unsuccessful as the complex either eluted with $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$ **8** or with excess $\text{P}(p\text{-Tol})_3$.

In related experiments, photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$ **8** in the presence of 4 equivalents of $\text{P}(p\text{-Tol})_3$ for 65 minutes resulted in the formation of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})[\text{P}(p\text{-Tol})_3]\text{Me}$ **9** in addition to starting material in a 2:1 ratio respectively (Scheme 4). Photolysis for 130 minutes resulted in



Scheme 4

increased formation of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})[\text{P}(p\text{-Tol})_3]\text{Me}$ **9** such that the ratio of product to starting material was 6:1.

Photolysis of toluene solutions of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})[\text{P}(p\text{-Tol})_3]\text{COMe}$ in the presence of 5 equivalents of PPh_3 formed both $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$ **8** and $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})[\text{P}(p\text{-Tol})_3]\text{Me}$ **9** in a 3:1 ratio, respectively. Authentic $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})[\text{P}(p\text{-Tol})_3]\text{Me}$ **9** was prepared by photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})[\text{P}(p\text{-Tol})_3]\text{COMe}$ for 3 hours. Purification by column chromatography and treatment of a toluene solution with MeI to remove the phosphine contaminant afforded the pure product, albeit in low yield.

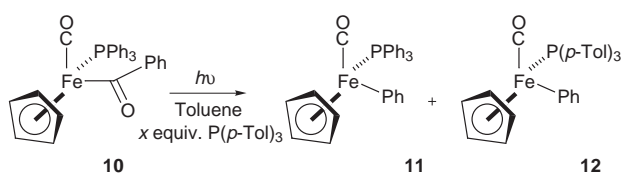
The literature preparation of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{COPh}$ **10** by the photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{COPh}$ in the presence of PPh_3 only proceeded in 37.5% yield. An appreciable amount of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Ph}$ was also formed in this reaction presumably *via* the decarbonylation of the intermediate phenyl

Table 1

Complex	% PR ₃ Me ⁺ <i>m/z</i> (%)	% PR ₄ ⁺ <i>m/z</i> (%)	[CpFe(PR ₃)] ⁺ <i>m/z</i> (%)	[CpFeO(PR ₃)] ⁺ <i>m/z</i> (%)
CpFe(CO)(PPh ₃)COMe 7	277 (15)	339 (35)	383 (100)	399 (4)
CpFe(CO)(PPh ₃)COMe 7 ^a	277 (32)	339 (60)	383 (66)	399 (18)
CpFe(CO)(PPh ₃)Me 8	277 (100)	339 (62)	383 (22)	399 (14)
CpFe(CO)(PPh ₃)Me 8 ^a	277 (72)	339 (22)	383 (25)	399 (25)
CpFe(CO)(PPh ₃)Ph 11	—	339 (100)	383 (10)	399 (18)
CpFe(CO)[P(<i>p</i> -Tol) ₃]Me 9	319 (100)	395 (42)	425 (22)	441 (11)

^a Sample recorded in the presence of a matrix.

acyl species ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)(PPh₃)COPh which has been previously observed in the literature.¹¹ The desired compound was also readily prepared by treating ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)(PPh₃)H with BuLi–TMEDA and quenching the novel iron anion with (Ph₃CO)₂O. No evidence of ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)(PPh₃)Bu was observed in this reaction. Photolysis of ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)(PPh₃)COPh **10** in the presence of one equivalent of P(*p*-Tol)₃ for 3 hours resulted in the formation of a 3:2 mixture of ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)[P(*p*-Tol)₃]Ph **12** and ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)(PPh₃)Ph **11** as determined by ¹H NMR spectroscopy (Scheme 5). These



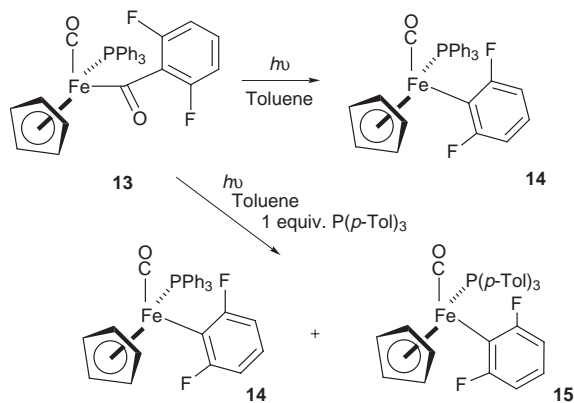
Photolysis Time	Equiv. P(<i>p</i> -Tol) ₃	Ratio 11 : 12
3 h	1	2 : 3
6–8 h	5	0 : 100

Scheme 5

two were separable by chromatography and the identity of the tolyl analogue was confirmed by comparison with the literature data.¹¹ Photolysis in the presence of 5 equivalents of P(*p*-Tol)₃ for 6–8 hours resulted in essentially quantitative conversion to ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)[P(*p*-Tol)₃]Ph **12** as determined by comparison with the authentic sample obtained above.

In a similar experiment, the reaction was monitored after 5, 15 and 30 minutes of irradiation by ¹H NMR spectroscopy. The first observable product after 5 minutes was ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)(PPh₃)Ph **11**. Only after 30 minutes was a small amount of ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)[P(*p*-Tol)₃]Ph **12** observed (**11** : **12** = 7.5 : 1).

The novel complex ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)(PPh₃)CO(2,6-C₆H₃F₂) **13** was readily prepared in 53% isolated yield by treating ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)(PPh₃)H with BuLi–TMEDA and quenching the anion with 2,6-C₆H₃F₂COCl. Photolysis of this complex resulted in clean formation of ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)(PPh₃)-(2,6-C₆H₃F₂) **14** (Scheme 6). Photolysis in the presence of



Scheme 6

one equivalent of P(*p*-Tol)₃ resulted in a 1:1 mixture of ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)(PPh₃)-(2,6-C₆H₃F₂) **14** and ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)[P(*p*-Tol)₃](2,6-C₆H₃F₂) **15** as determined by ¹H NMR spectroscopy. These two were separable by chromatography and the tolyl analogue was characterised.

Photolabilitation studies using laser desorption FT ICR MS.

Observation of the intermediates generated in the photolysis would provide further evidence to indicate that photolabilitation of phosphine is facile for such iron acyl complexes and enable rapid screening of other similar complexes which should undergo photodissociation. Using nitrogen laser desorption, the frequency of which (337 nm) corresponds to one of the major absorption bands of the complexes, we considered that it would be possible to use MALDI FT ICR MS without a matrix to determine both the mass and elemental composition of the intermediates from the photolabilitation process.

Thus samples of the alkyl and acyl complexes **7–9**, **11** were subjected to nitrogen laser photolysis with and without a matrix and analysed by FT ICR MS. The results are summarised in Table 1. In general, major decomposition products were the quaternary phosphine species PR₃Me⁺, PR₄⁺ and iron containing ions [CpFe(PR₃)]⁺, [CpFeO(PR₃)]⁺. In addition, photolysis in the presence of a matrix led to the introduction of an ion at *m/z* 263 corresponding to PPh₃⁺ which was not observed in samples photolysed without a matrix. The individual spectra of PPh₃ and P(*p*-Tol)₃ were also recorded for comparison purposes as well as a sample of a mixture of PPh₃ and P(*p*-Tol)₃ which gave a spectrum which contained four species Ph₄P⁺ (*m/z* 339, 30%), P(*p*-Tol)₄⁺ (*m/z* 395, 100%), [PPh(*p*-Tol)₃]⁺ (*m/z* 381, 10%), and [PPh₃(*p*-Tol)]⁺ (*m/z* 353, 10%).

Photofragmentation voltammetric studies. In previous studies on the photolysis of the related iron aminocarbene complexes, key intermediates in the photodissociation process were identified by means of photofragmentation voltammetry.^{7b,c} This method was thus employed for the complex ($\eta^5\text{-C}_5\text{H}_5$)Fe(PPh₃)COMe **7** in an attempt to provide further evidence for intermediates in the photochemical pathway previously proposed. Preliminary experiments were first performed in the absence of light to identify the dark electrochemical behaviour of complex **7**. Cyclic voltammetry conducted under no flow conditions in the range 0.0–0.60 V (vs. SCE) using a scan rate of 100 mV s⁻¹ revealed a chemically reversible oxidation with a formal potential of +0.36 (±0.05) V (vs. SCE) as shown in Fig. 1.

On extending the range of the cyclic voltammetry scan to higher potentials three new voltammetric features were observed at the following peak potentials (measured on the forward scan) as shown in Fig. 2. It was found that if the potential was reversed after wave 1 the height of the reduction peak associated with the feature at 0.36 V was reduced.

The voltammetric behaviour was next observed for the oxidation of **7** at an illuminated channel electrode. Fig. 3 shows the photofragmentation voltammogram measured in a solution containing 0.50 × 10⁻³ mol dm⁻³ of **7** in 0.1 M tetrabutylammonium perchlorate (TBAP)–acetonitrile using a wavelength of 310 nm to irradiate the electrode. For comparison the corresponding ‘dark’ hydrodynamic voltammogram is also

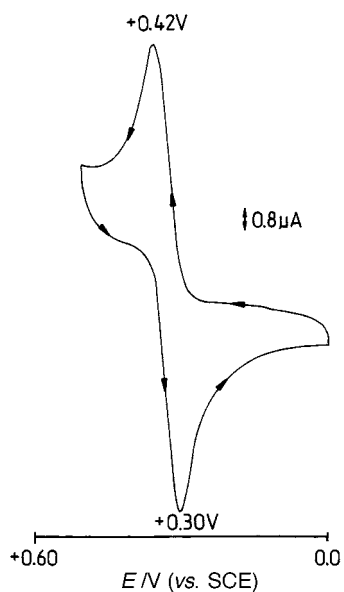


Fig. 1

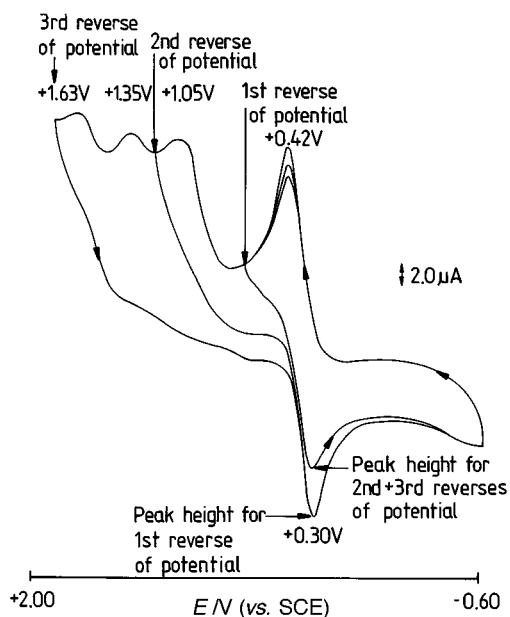


Fig. 2

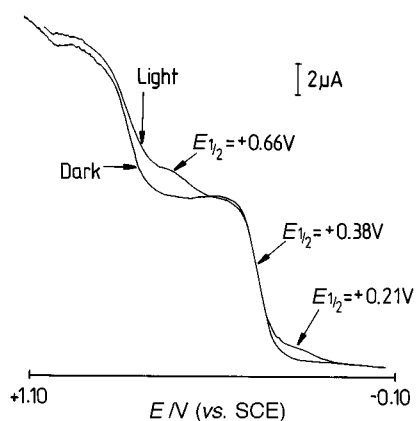


Fig. 3

displayed. Two new voltammetric signatures were observed in addition to that observed previously. The two new waves were found to have half wave potentials of $+0.21 (\pm 0.05)$ V and

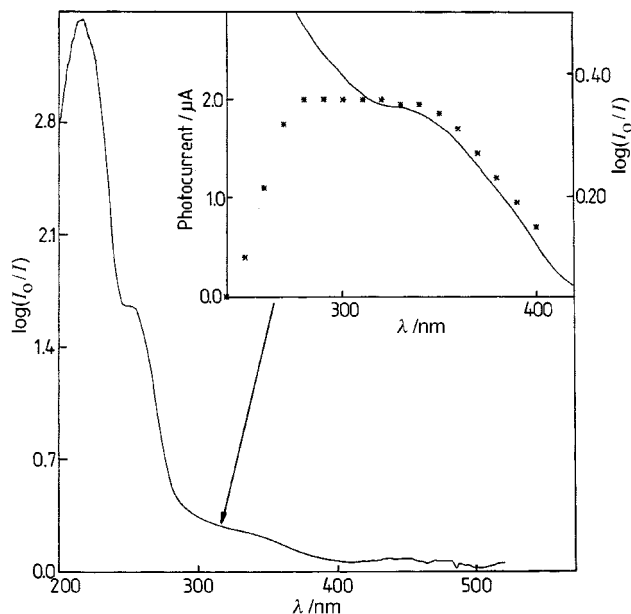


Fig. 4

$+0.66 (\pm 0.05)$ V. The ratio of the currents of these two waves was close to 2.

Quantitative measurements of the reaction mechanism were also carried out. Initially the photocurrents were optimised as a function of the wavelength of the exciting radiation. The resulting action spectrum, shown in Fig. 4, was identical for the pre and post photo-waves with a broad maximum at around 300–340 nm. The UV/VIS spectrum of **7**, also shown in Fig. 4, reveals two absorption bands in the UV region at 220 and 250 nm (which are likely to be charge transfer bands) together with a broad absorption, of much lower extinction coefficient, between 300 and 340 nm. A wavelength of 310 nm was used for the quantitative mechanistic work described below.

It was observed that under direct irradiation of the electrode extreme electrode fouling occurred, as manifested by a discernible yellow layer on the electrode after continual irradiation of the solution directly over the electrode for a period of tens of minutes. This led to photo-currents which systematically decreased with time and precluded quantitative interpretation. However this problem was overcome by irradiating immediately upstream of the electrode only, and incorporating a platinum foil (at open-circuit and unconnected with the working electrode) in the zone of irradiation. The latter served to 'mop up' minority species responsible for electrode passivation and the irradiation products were swept to the unpassivated electrode for voltammetric interrogation. With this protocol, combined with electrochemical cleaning of the working electrode using a highly cathodic potential between voltage scans, passivation was eliminated and reproducible, quantitative measurements of transport limited currents and their flow rate dependence were achieved. The experimental arrangement is sketched schematically in Fig. 5. Experiments were carried out in the concentration range $0.5 < [7]/\text{mM} < 1.0$; higher concentrations led to renewed electrode passivation and lower concentrations gave photo-currents too low for accurate measurement. Figs. 6 and 7 show representative plots of the flow rate dependence of the photo-current for the 0.21 V prewave and two different concentrations of **7**.

One possible intermediate in the photodissociative mechanism is the dicarbonyl species $\text{CpFeMe}(\text{CO})_2$ which was found to undergo two oxidation processes in acetonitrile with half wave potentials of $E_{1/2} = +1.01$ V and $+1.20$ V (vs. SCE) although extended measurements were hampered by severe electrode passivation effects. An alternative intermediate in the mechanism was the complex $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$ **8** which was

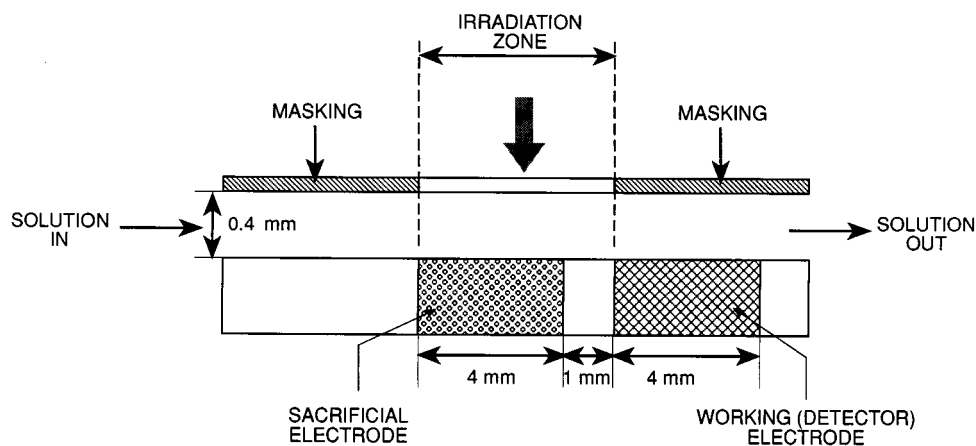


Fig. 5

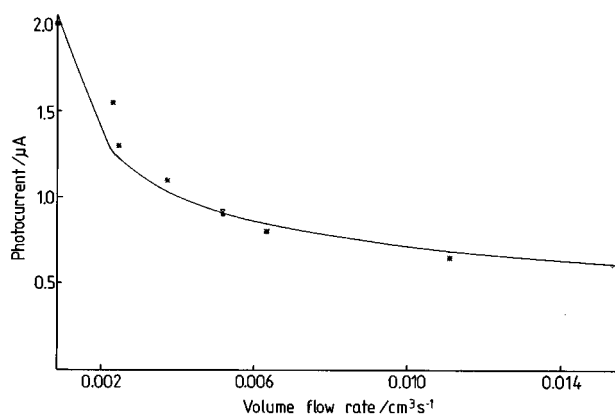


Fig. 6

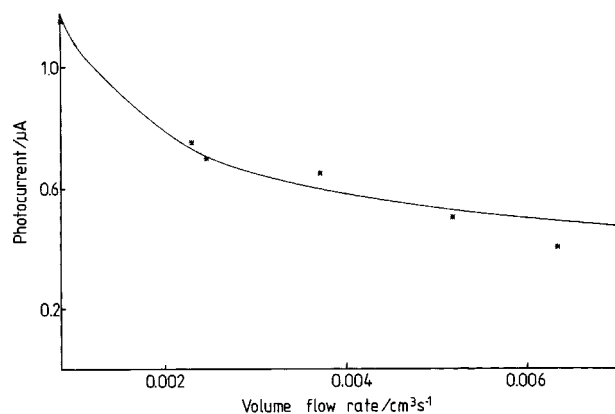


Fig. 7

found to undergo two oxidation processes in acetonitrile with half wave potentials of +0.23 (± 0.05) V and +0.59 (± 0.05) V (*vs.* SCE), as shown in Fig. 8.

Discussion

NMR Exchange studies

Our previous experience of the photolysis of transition metal complexes led us to propose that phosphine loss in these systems was the primary photoprocess, *unless* other steric and/or electronic factors influenced the photodissociation.

Photolysis of the acetyl complex ($\eta^5\text{-C}_5\text{Me}_5$)Fe(CO)(PPh₃)-COMe **1** over a period of time led to slow conversion to the dicarbonyl complex ($\eta^5\text{-C}_5\text{Me}_5$)Fe(CO)₂Me **2** followed by subsequent formation of the alkyl complex ($\eta^5\text{-C}_5\text{Me}_5$)Fe(CO)(PPh₃)Me **3**. The dicarbonyl complex **2** has been independently shown to be transformed to the alkyl complex **3** by photolysis,

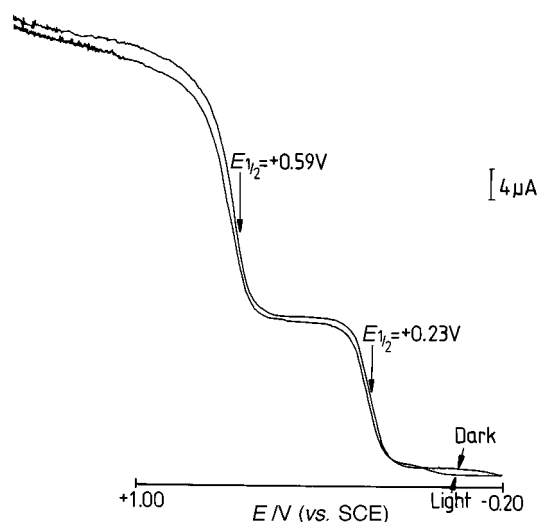
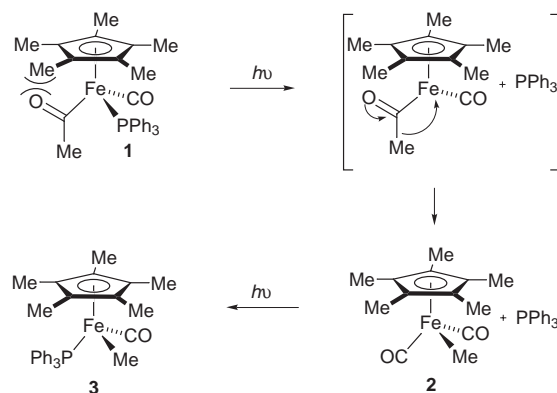


Fig. 8

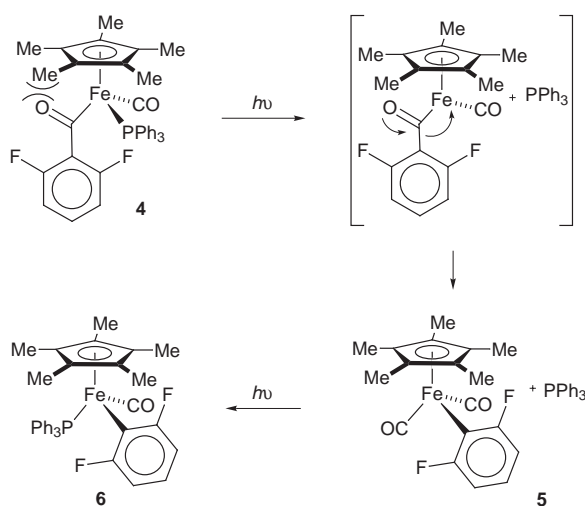
thus resulting in a two step photoprocess whereby acyl complex **1** undergoes primary loss of phosphine with alkyl migration to form the dicarbonyl complex **2**, followed by photodissociation of carbon monoxide and trapping with previously ejected phosphine. Preferential phosphine loss is observed since severe steric interactions between the pentamethylcyclopentadienyl ring and the acetyl group disfavour the arrangement of the carbonyl functionality in an antiperiplanar fashion to facilitate intramolecular displacement of carbon monoxide (Scheme 7).



Scheme 7

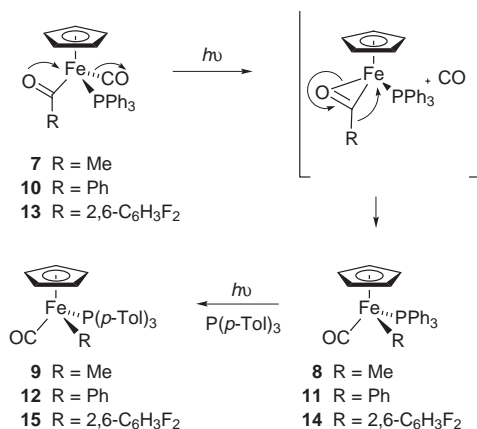
In addition, the electron donating cyclopentadienyl ring serves to weaken the iron–phosphorus bond and strengthen the iron–carbon bonds, thus further inducing phosphine loss.

Further investigation of blocking the intramolecular carbonyl displacement was carried out using the 2,6-difluorobenzene iron complexes **4–6**. When $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{CO}(2,6\text{-C}_6\text{H}_3\text{F}_2)$ **4** was photolysed, the dicarbonyl intermediate $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(2,6\text{-C}_6\text{H}_3\text{F}_2)$ **5** was observed in the IR spectrum. Its intensity grew with time and then decreased with further photolysis. The eventual product in the reaction was $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(2,6\text{-C}_6\text{H}_3\text{F}_2)$ **6** with a small amount of the dicarbonyl product **5** (20%). The suspected dicarbonyl intermediate was synthesised independently and was found to have the same IR carbonyl stretching frequencies as those observed during the photolysis reaction and all spectroscopic data correlated with the small amount of the dicarbonyl product obtained in the photolytic reaction. When a sample of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(2,6\text{-C}_6\text{H}_3\text{F}_2)$ **5** was photolysed in the presence of 3 equivalents of PPh_3 , the only observable product was the expected $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(2,6\text{-C}_6\text{H}_3\text{F}_2)$ **6**. This is again consistent with the above hypothesis whereby adverse steric effects prevent intramolecular displacement of carbon monoxide leading to the phosphine loss as the primary photo-process (Scheme 8).



Scheme 8

Photolysis of the cyclopentadienyl complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{COR}$ ($\text{R} = \text{Me}$ **7**, Ph **10**, $2,6\text{-C}_6\text{H}_3\text{F}_2$ **13**) readily resulted in decarbonylation to form the corresponding alkyl or aryl species. When photolyses of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{COR}$ ($\text{R} = \text{Me}$ **7**, Ph **10**, $2,6\text{-C}_6\text{H}_3\text{F}_2$ **13**) were carried out in the presence of excess $\text{P}(p\text{-Tol})_3$ and monitored by ^1H NMR spectroscopy, the initial products were PPh_3 containing iron alkyls $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{R}$ ($\text{R} = \text{Me}$ **8**, Ph **11**, $2,6\text{-C}_6\text{H}_3\text{F}_2$ **14**), which only after photolysis for an extended period of time led to the $\text{P}(p\text{-Tol})_3$ complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})[\text{P}(p\text{-Tol})_3]\text{R}$ ($\text{R} = \text{Me}$ **9**, Ph **12**, $2,6\text{-C}_6\text{H}_3\text{F}_2$ **15**). These results indicate that a different reaction mechanism was operating than in the pentamethylcyclopentadienyl substrates. The absence of dicarbonyl complexes and the $\text{P}(p\text{-Tol})_3$ intermediates which would have resulted from photolysis of these complexes implied that the primary photochemical process was loss of CO not PPh_3 . The cyclopentadienyl system is more electron deficient than the pentamethyl analogue, thus negating the electronic effects which led to the strengthening and weakening of the iron-carbon and iron-phosphorus bonds in the latter. In addition, the cyclopentadienyl analogue is much less sterically demanding than the pentamethyl complex, which can facilitate intramolecular participation *via* an η^2 -acyl complex, and subsequent rearrangement. This process implies that stereospecific formation of the iron alkyl occurs, which then undergoes photoinduced phosphine exchange and hence racemisation under prolonged photolysis conditions, a process which has been previously demonstrated for related iron alkyl complexes

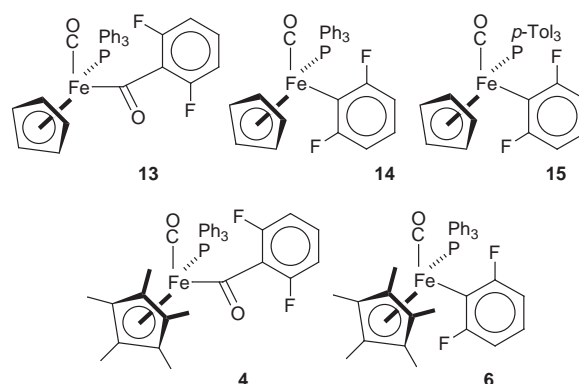


Scheme 9

(Scheme 9).^{5b,6} Exclusive phosphine loss in these iron alkyl complexes is more facile than in the acyl precursors since they are now more electron rich, and behave in a similar manner to the pentamethylcyclopentadienyl complexes, weakening the iron-phosphorus bond and strengthening the iron-carbon bond.

Properties of the $(2,6\text{-C}_6\text{H}_3\text{F}_2)$ complexes

Broadening of the triphenylphosphine aryl signals in the ^{13}C NMR spectra of some of the 2,6-difluorobenzene complexes **4**, **6**, **13**, **14**, **15** implied that the close proximity of the fluorine



atoms in the aryl ring to the cyclopentadienyl group was causing hindered rotation. This phenomenon was probed by observing the ^{31}P and ^{19}F NMR spectra of these compounds at different temperatures.

The simplest complex, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{CO}(2,6\text{-C}_6\text{H}_3\text{F}_2)$ **13** showed no sign of restricted rotation giving sharp signals at -117.0 ppm and 70.0 ppm in the ^{19}F and ^{31}P NMR spectra respectively. This is not surprising since the combination of the carbonyl 'spacer' and a relatively unhindered cyclopentadienyl ring should allow free rotation of the aryl ring. However, the corresponding aryl complex **14** exhibited an apparent triplet at 72.2 ppm ($J = 9.2$ Hz) in the ^{31}P NMR spectrum and a broad singlet at -76.17 ppm in the ^{19}F NMR spectrum at room temperature. Upon cooling to -70 °C, the signals in the ^{19}F NMR resolved into a singlet at -76.85 ppm and a doublet at -76.17 ppm ($J = 9.2$), while at -40 °C the signal in the ^{31}P NMR spectrum was partially resolved into a doublet (72.3 ppm, $J = 9.2$). This corresponds to a situation where one fluorine atom lies very close in space to the adjacent phosphorus atom, thus exhibiting through space coupling, while the other is distant from the phosphorus and thus does not experience this effect (Fig. 9).

Through space P-F coupling has been observed previously for *ortho*- CF_3 substituted triphenylphosphines,¹² but this phenomenon is not common in organometallic species. From variable temperature ^{19}F NMR studies of complex **14** the free

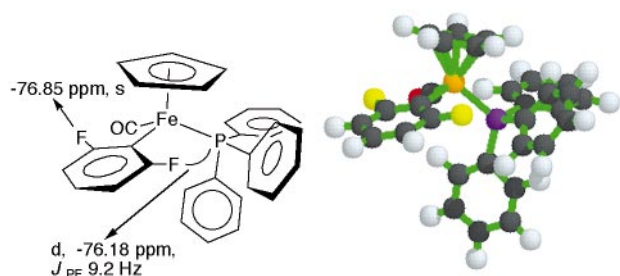


Fig. 9 Molecular model of complex **14** demonstrating the close proximity of the phosphorus and fluorine atoms.

energy of activation for this rotation was calculated to be 12.9 kJ mol^{-1} at 276 K. The $\text{P}(p\text{-Tol})_3$ analogue **15** gave a doublet at -74.65 ppm ($J = 5.0 \text{ Hz}$) in the ^{19}F NMR spectrum and an apparent triplet at 73.3 ppm ($J = 5.0 \text{ Hz}$) in the ^{31}P NMR spectrum, which is similar to the above complex **14** except that partial resolution of the ^{19}F NMR spectrum had occurred at room temperature. This implies that complex **15** exhibits greater restricted rotation than complex **14** at the same temperature.

The pentamethylcyclopentadienyl complexes **4** and **6** would be expected to demonstrate even more pronounced effects due to the increased steric bulk of the C_5Me_5 unit. The ^{31}P NMR spectrum of the acyl complex **4** displayed a singlet at 68.5 ppm , while the ^{19}F NMR spectrum contained a peak at -113.70 ppm which was due to the desired complex **4**, as well as a minor signal which corresponded to the dicarbonyl complex **2**. Upon warming this sample to approximately 70°C in order to investigate any possible rotational properties, the singlet at -113.70 ppm slowly reduced in height while the signal due to the dicarbonyl complex **2** increased in intensity. Upon cooling the sample to 25°C the predominant species was now the dicarbonyl complex **2**. This suggests that although complex **4** does not exhibit any restricted rotation, it is thermally unstable and readily decomposes upon warming to the dicarbonyl complex **2**.

The aryl complex **6** gave a doublet at -76.00 ppm ($J 13.4 \text{ Hz}$) and a singlet at -79.39 ppm in the ^{19}F NMR spectrum. The coupling constant of the doublet corresponded to the complementary signal observed in the ^{31}P NMR spectrum (69.5 ppm , $J_{\text{PF}} 13.4 \text{ Hz}$) which confirmed that due to the close proximity of the phosphorus and fluorine atoms, an analogous through-space P–F coupling was operating. The magnitude of the coupling constant was greater in this compound compared to the cyclopentadienyl complex **14** probably due to more efficient overlap of the lone pairs of the fluorine atom with the acceptor phosphorus orbitals which is enforced by the sterically demanding pentamethylcyclopentadienyl ring.¹³ Variable temperature ^{19}F NMR was performed on complex **6** and although the two signals did not coalesce with increasing temperature, they did move closer together allowing the free energy of activation to be calculated as 57.4 kJ mol^{-1} at 309 K, which demonstrates that the increased steric requirement of the pentamethylcyclopentadienyl ring essentially inhibits rotation of the aryl ring of this complex.

Laser desorption FT ICR MS studies

The mass spectra of the products arising from laser desorption of the iron acyl and alkyl complexes consisted of two peaks due to iron containing species $[\text{CpFe}(\text{PR}_3)]^+$ and $[\text{CpFeO}(\text{PR}_3)]^+$, and two peaks due to phosphine containing species PR_3Me^+ and PR_4^+ . In the case of the complex $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Ph}$, no peak was observed for the ion PPh_3Me^+ which must therefore originate from recombination of PPh_3 with the attached alkyl or acyl group.

Although the same key ions are apparent in the spectra of both the alkyl and acyl complexes, the relative abundances of the peaks due to quaternary phosphines are significantly greater

for the alkyl and aryl complexes **8**, **9**, **11**, while the acyl complex **7** showed significantly reduced ions due to phosphine loss. This is entirely consistent with the results obtained from the NMR exchange experiments where phosphine loss is the primary photochemical event in the alkyl and aryl complexes. Thus, although this technique cannot provide a quantitative method for determining phosphine lability from organometallic complexes, it can be used as a tool to rapidly screen such compounds for similar photochemistry.

Photofragmentation voltammetric studies

The initial hydrodynamic voltammetry performed on acyl complex $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{PPh}_3)\text{COMe}$ **7** using both channel and rotating disc electrodes corresponded to an electrochemically reversible one electron process as evidenced by (i) mass transport corrected Tafel analysis of the waveshape,¹⁴ which for both electrode types gave plots of electrode potential against $\log_{10}\{I^{-1} - I_{\text{lim}}^{-1}\}$ which were good straight lines of slope 62 (± 3) mV per decade, and (ii) Levich analysis of the mass transport dependence of the limiting current, I_{lim} . I_{lim} showed a direct linear dependence on both (flow rate)^{1/3} (ChE) or (rotation speed)^{1/2} (ChE) which permitted the determination of the diffusion coefficient of **7** as $1.37 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.¹⁵ It was inferred that the cationic complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{PPh}_3)\text{COMe}]^+$ which was stable on the voltammetric timescale was formed as a result of the oxidation.

Further studies at higher potential led to three peak potentials (measured on the forward scan):

$$\text{Wave 1: } E_p = +1.05 (\pm 0.05) \text{ V}$$

$$\text{Wave 2: } E_p = +1.35 (\pm 0.05) \text{ V}$$

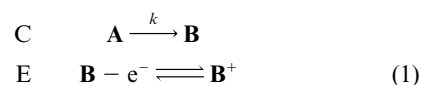
$$\text{Wave 3: } E_p = +1.63 (\pm 0.05) \text{ V}$$

It was found that if the potential was reversed after wave 1 the height of the reduction peak associated with the feature at 0.36 V was reduced. This suggests that wave 1 is associated with a second oxidation of **7** to form a dicationic complex, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{PPh}_3)\text{COMe}]^{2+}$, which then decomposes. The products of this decomposition then give rise to waves 2 and 3. The latter can be assigned to the oxidation of phosphine, PPh_3 .^{7b}

This suggests that **7** (partly) decomposes on photolysis into a species which undergoes a one-electron oxidation at +0.21 V and a subsequent two-electron oxidation at +0.66 V. A crucial observation is that for all photochemical experiments conducted, the sum of transport limited currents due to the 0.21 V prewave and to the direct oxidation of **7** was identical to that observed in the dark for the direct oxidation of **7** alone under corresponding conditions. This indicates that, within voltammetric experimental error, the sole product of the photolysis is the species which undergoes oxidation at 0.21 V and that any other process must be insignificant ($< 2\%$) on the experimental timescale.

The UV/VIS spectrum of **7**, also shown in Fig. 4, reveals two absorption bands in the UV region at 220 and 250 nm (which are likely to be charge transfer bands) together with a broad absorption, of much lower extinction coefficient, between 300 and 340 nm. The latter region corresponds to the measured action spectrum suggesting that the photolysis arises from the absorption of visible light in the parent, probably through the stimulation of a d–d transition(s).

Established computational procedures^{7b,15} were used to theoretically predict the photo-current/flow rate behaviour for the proposed 'photo-CE' mechanism [eqn. (1)], where **A** is



the parent molecule and **B** is the photolysis product which undergoes oxidation at 0.21 V. The first order rate constant, k , was optimised to give the best fit with experiment. In all cases good agreement was found between experiment and theory confirming the mechanism suggested. The best fit rate constant was $k = 1.1 (\pm 0.4) \times 10^{-2} \text{ s}^{-1}$ for an incident light intensity of $80 (\pm 10) \text{ mW cm}^{-2}$ and wavelength of 310 nm; the optimised rate constant was independent of the concentration of **A** studied over the range studied. The best fit rate constant together with the data of Fig. 4 permits the deduction of a quantum yield of approximately 0.01 for the conversion of **A** to **B**.¹⁵

One possible intermediate in the photodissociative mechanism is the dicarbonyl species $\text{CpFeMe}(\text{CO})_2$ which accordingly was considered as a candidate for species **B**. The two waves observed did not correspond to any electrode process observed in the voltammogram of **7** so ruling out the photochemical formation of $\text{CpFeMe}(\text{CO})_2$. An alternative was the photolytic expulsion of CO and the subsequent formation of $(\eta^5\text{-C}_5\text{H}_5)\text{-Fe}(\text{CO})(\text{PPh}_3)\text{Me}$. This complex was found to undergo two oxidation processes in acetonitrile with half wave potentials of $+0.23 (\pm 0.05) \text{ V}$ and $+0.59 (\pm 0.05) \text{ V}$ (*vs.* SCE), as shown in Fig. 8. These potentials correspond to the oxidation potentials of the photo-products observed in the PFV of **7**. Further, the ratio of the transport limited currents of the two waves is the same as seen in the photofragmentation voltammogram in Fig. 3. These observations suggest that the photo-product **B** is $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$ **8**.

The conclusion of this study is that the photolysis of **7** is a 'photo-CE process' which involves photoexpulsion of CO to form a 16 electron species with rapid migration of Me to form $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$ **8**. This species is then oxidised at $+0.21 \text{ V}$ (and $+0.66 \text{ V}$) leading to the photo-currents seen in photofragmentation voltammograms such as shown in Fig. 3. This is again consistent with the solution phase chemistry of this complex and provides further evidence for the proposed mechanism.

Conclusion

We have demonstrated that the photolysis of cyclopentadienyl iron complexes in the *absence of other steric or electronic effects* involves initial loss of phosphine followed by rapid phosphine exchange and racemisation of the iron alkyl or aryl complexes formed. Evidence has been provided in the form of NMR phosphine exchange experiments and photofragmentation voltammetry to support this mechanism. In addition we have used FT ICR MS to provide a means of rapidly screening the photolability of phosphine ligands in organometallic complexes.

Experimental

All reactions were performed under a nitrogen atmosphere using standard vacuum line techniques. The solvents THF, Et₂O and toluene were dried and distilled from sodium benzophenone while CH₂Cl₂ was dried and distilled from CaH₂ all under a nitrogen atmosphere. PE refers to redistilled petroleum ether boiling between 40–60 °C. The complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{COR}$ (R = Me **7**,¹⁶ Ph **10**¹¹), $(\eta^5\text{-C}_5\text{H}_5)\text{-Fe}(\text{CO})(\text{PPh}_3)\text{R}$ (R = Me **8**,¹⁷ Ph **11**¹¹), $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{-}[\text{P}(p\text{-Tol})_3]\text{COMe}$ **16**,¹⁸ $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{H}$ **17**,¹⁹ $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)]\text{PF}_6$ **19**,⁹ $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Me}$ **2**,²⁰ $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Br}$ **20**²¹ and $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{-COMe}$ **1**⁹ were synthesised according to their respective literature procedures. *n*-Butyllithium (1.6 M in hexane) was used as supplied by the FMC Corporation, P(*p*-Tol)₃ (Fluka), PhCOCl (Aldrich), 2,6-C₆H₄F₂ (Aldrich) and 2,6-C₆H₃F₂COCl (Aldrich) were used without further purification. Photolyses were carried out with a Hanovia 450 watt medium pressure mercury lamp in

a quartz Schlenk tube unless otherwise stated. Column chromatography was performed on grade I (active) alumina or on silica gel (Merck Kieselgel 60). ¹H NMR spectra were recorded on either a Varian-Gemini 200 (200 MHz) or a Bruker AM500 (500.13 MHz) spectrometer. ¹³C, ³¹P and ¹⁹F NMR spectra were recorded on a Bruker AM250 spectrometer (at 62.9, 125.76 and 101.26 MHz respectively). IR spectra were recorded on a Perkin-Elmer 1750 Fourier transform spectrophotometer using 0.05 mm NaCl cells. Microanalyses were performed by Mrs V. Lamburn of the Dyson Perrins Analytical Service.

FT ICR Laser desorption mass spectra

Nitrogen laser desorption mass spectra of compounds **7–9**, **11** were measured with and without a matrix from the MALDI probe of a Bruker 4.7 BioApex MALDI FT ICR mass spectrometer in both broad band and narrow band modes, or a Micromass ToF Spec E in reflectron mode. The elemental compositions of the ionic species were determined from the narrow band spectra.

Voltammetric studies

All regular photofragmentation voltammetry experiments were conducted using a channel electrode (ChE) made of optical quality synthetic silica to standard construction and dimensions¹⁵ capable of delivering flow rates in the range 10^{-4} – $10^{-1} \text{ cm}^3 \text{ s}^{-1}$. Platinum foils (purity of 99.95%, thickness 0.025 mm) of approximate size 4 mm × 4 mm, supplied by Goodfellow Advanced Materials, were used as working electrodes. Precise dimensions were determined using a travelling microscope. A silver wire pseudo-reference electrode was positioned in the flow system upstream and a platinum gauze counter electrode located downstream of the channel electrode. The silver wire reference electrode was found to be steady throughout the period of our experiments: consistent values for the oxidation potential of *N,N,N',N'*-tetramethylphenylene-1,4-diamine (TMPD) were observed. Hence potentials are reported relative to the saturated calomel electrode, $+0.20 \text{ V}$ being subtracted from the measured values to obtain the potentials quoted. Electrochemical measurements were made using an Oxford Electrodes potentiostat modified to boost the counter electrode voltage by up to 200 V. Other methodological details were as described previously.¹⁵ Irradiation was provided by a Wotan X130 900 W/2 xenon arc lamp *via* a Jarrell-Ash 82-410 grating monochromator (maximum incident power 40 mW cm⁻²). Variable light intensity measurements were made by attenuation of the beam as described previously.^{15b} UV/VIS measurements were made with a Perkin-Elmer Lambda-5 spectrometer. Complementary rotating disc electrode (RDE) measurements were conducted using Oxford Electrodes equipment. Experiments were performed using solutions of the electroactive material (*ca.* 10^{-4} – 10^{-3} M) in dried acetonitrile (Fisons, dried, distilled) solution containing 0.1 M (recrystallised) tetrabutylammonium perchlorate (TBAP) (Fluka, *purum*) as supporting electrolyte. Solutions were purged of oxygen by outgassing with prepurified argon prior to electrolysis.

General procedure for the photolysis of the iron complexes

A benzene or toluene solution (30 mL) of the complex (1.0 mmol) was photolysed for a period of time and monitored by NMR, TLC, or IR analysis. When the reaction was deemed to be complete, the solvent was evaporated and the crude product purified by chromatography. In cases where phosphine exchange experiments were carried out, treatment of a toluene solution of crude product with MeI helped to remove excess phosphine.

Synthesis of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$ **3**

A toluene solution of **2** (1.454 g, 5.54 mmol) and PPh₃ (3.1 g,

11.82 mmol) was photolysed for 16.25 h and was monitored by ^1H NMR spectroscopy. At the end of this time the methyl doublet of the starting material had disappeared and a new doublet had appeared at -0.54 ppm. An excess amount of MeI (2 mL, 32.13 mmol) was added to the reaction mixture and allowed to stand overnight after which a copious amount of $(\text{PPh}_3\text{Me})\text{I}$ had precipitated out of solution. The solution was filtered through Celite and the solvents were removed under reduced pressure. The ^1H NMR spectrum indicated that PPh_3 was still present. The product was extracted with PE but some PPh_3 was still observed in the ^1H NMR spectrum. All attempts to chromatograph the product (on silica or alumina) only resulted in complete decomposition of the product. $\nu_{\text{max}}/\text{cm}^{-1}$ (CH_2Cl_2) 1924; $\delta_{\text{H}}(\text{CDCl}_3)$ -0.54 (3 H, d, J_{PH} 6.7, FeCH_3), 1.39 (15 H, s, C_5Me_5), 7.28–7.38 (12 H, m, PPh_3), 7.38–7.78 (3 H, m, PPh_3); $\delta_{\text{C}}(\text{CDCl}_3)$ 129.0 (s, C_5Me_5), 133.6 (d, J_{PC} 9.0, *ortho*- PPh_3), 136.5 (d, J_{PC} 35.9, *ipso*- PPh_3), 224.7 (d, J_{PC} 29.6, Fe-CO); $\delta_{\text{P}}(\text{CDCl}_3)$ 84.2 (s); *m/z* (FAB) 496 (5), 468 (20), 453 (93), 279 (100).

Synthesis of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{CO}(2,6\text{-C}_6\text{H}_3\text{F}_2)$ **4**

A THF solution (50 mL) of lithium 2,6-difluorobenzene was prepared by treating 2,6-difluorobenzene (800 μL , 8.26 mmol) with 5.05 mL *n*-BuLi (1.5 M, 7.75 mmol) and stirring at -78°C for 2 h. This solution was added dropwise to a THF solution (50 mL) of **19** (4.29 g, 6.89 mmol) at -78°C and the mixture stirred for 30 min followed by 30 min at -40°C . The reaction was quenched with MeOH and the solvents were removed under reduced pressure. The residue was extracted with CH_2Cl_2 , filtered through alumina and the solvent was removed to form a yellow–brown foam. Chromatography on silica with diethyl ether (5%) in PE removed unidentifiable mixtures. Increasing the polarity to 50% eluted the desired product as an analytically pure yellow–orange foam (820 mg, 19%) (Found: C, 69.2; H, 5.6. $\text{C}_{36}\text{H}_{33}\text{F}_2\text{FePO}_2$ requires C, 69.45; H, 5.30%); $\nu_{\text{max}}/\text{cm}^{-1}$ (CH_2Cl_2) 1904, 1613; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.51 (15 H, s, C_5Me_5), 6.45 (2 H, t, $^3J_{\text{HH}} = ^3J_{\text{FH}}$ 8.2, *meta*- $\text{C}_6\text{H}_3\text{F}_2$), 6.82–7.00 (1 H, m, *para*- $\text{C}_6\text{H}_3\text{F}_2$), 7.20–7.48 (15 H, m, PPh_3); $\delta_{\text{C}}(\text{CDCl}_3)$ 9.4 (s, C_5Me_5), 95.8 (s, C_5Me_5), 111.1 (d, $^2J_{\text{CF}}$ 27.5, *meta*- $\text{C}_6\text{H}_3\text{F}_2$), 127.6 (s, *para*- $\text{C}_6\text{H}_3\text{F}_2$), 127.7 (d, J_{PC} 9.3, *meta*- PPh_3), 129.2 (s, *para*- PPh_3), 133.5 (br, *ortho*- PPh_3), 157.4 (dd, $^1J_{\text{CF}}$ 249.7, $^3J_{\text{CF}}$ 8.3, *ortho*- $\text{C}_6\text{H}_3\text{F}_2$), 223.2 (d, J_{PC} 27.6, Fe-CO), 272.3 (d, J_{PC} 27.6, Fe-COC $_6\text{H}_3\text{F}_2$); $\delta_{\text{F}}(\text{CD}_3\text{C}_6\text{D}_5)$ -113.70 (s); $\delta_{\text{P}}(\text{CDCl}_3)$ 68.5 (s).

Synthesis of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(2,6\text{-C}_6\text{H}_3\text{F}_2)$ **5**

A THF solution (10 mL) of lithium 2,6- $\text{C}_6\text{H}_3\text{F}_2$ was prepared by treating 2,6- $\text{C}_6\text{H}_3\text{F}_2$ (170 μL , 1.73 mmol) with *n*-BuLi (1.13 mL, 1.82 mmol) and stirring the solution at -78°C for 2 h. A THF solution (15 mL) of **20** (513 mg, 1.57 mmol) was added and stirred at -78°C for 30 min and then at -40°C for 2 h. The reaction mixture was allowed to warm to room temperature and was quenched with MeOH. The solvents were removed under reduced pressure, the product extracted with PE and the resultant solution filtered through Celite. The solvent was removed under reduced pressure and the product purified by chromatography on silica with diethyl ether (1%) in PE to elute a dark yellow band of analytically pure $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(2,6\text{-C}_6\text{H}_3\text{F}_2)$ (134 mg, 24%).

Recrystallisation from diethyl ether at -40°C gave dark yellow crystals (Found: C, 59.95; H, 5.00. $\text{C}_{18}\text{H}_{18}\text{F}_2\text{FeO}_2$ requires C, 60.0; H, 5.0%); $\nu_{\text{max}}/\text{cm}^{-1}$ (CH_2Cl_2) 2010, 1957; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.75 (15 H, s, C_5Me_5), 6.70 (2 H, t, 3J 7.4, *meta*- $\text{C}_6\text{H}_3\text{F}_2$), 6.9 (1 H, q, 3J 7.4, *para*- $\text{C}_6\text{H}_3\text{F}_2$); $\delta_{\text{C}}(\text{CDCl}_3)$ 9.5 (s, C_5Me_5), 96.6 (s, C_5Me_5), 109.9 (dd, $^2J_{\text{CF}}$ 32.57, $^4J_{\text{CF}}$ 3.3, *meta*- $\text{C}_6\text{H}_3\text{F}_2$), 125.3 (t, $^3J_{\text{CF}}$ 10.0, *para*- $\text{C}_6\text{H}_3\text{F}_2$), 170.2 (dd, $^1J_{\text{CF}}$ = 229.8, $^3J_{\text{CF}}$ 19.7, *ortho*- $\text{C}_6\text{H}_3\text{F}_2$), 217.3 (t, J_{PH} 4.3, Fe-CO); $\delta_{\text{F}}(\text{CDCl}_3)$ -81.99 (s).

Increasing the polarity to 50% diethyl ether eluted $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2]_2$ (12 mg, 1.5%) and $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Br}$ **20** (263 mg, 51%).

Preparation of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(2,6\text{-C}_6\text{H}_3\text{F}_2)$ **6**

A toluene solution (20 mL) of **4** (130 mg, 0.36 mmol) and PPh_3 (290 mg, 1.1 mmol) was photolysed for 6 h at room temperature. During this time the carbonyl stretching frequencies of the starting material (ν_{CO} 2010, 1958 cm^{-1}) were replaced by a single carbonyl stretching frequency at ν_{CO} 1928 cm^{-1} . The solvent was removed under reduced pressure to give a dark red oil which was purified by chromatography on silica eluting with diethyl ether (1%) in PE to remove excess PPh_3 , followed by 20% diethyl ether in PE to elute a dark red band of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(2,6\text{-C}_6\text{H}_3\text{F}_2)$ **3**. Recrystallisation from diethyl ether at -40°C gave dark red crystals (184 mg, 82%) (Found: C, 70.6; H, 5.65. $\text{C}_{35}\text{H}_{33}\text{F}_2\text{FeOP}$ requires C, 70.7; H, 5.55%); $\nu_{\text{max}}/\text{cm}^{-1}$ (CH_2Cl_2) 1927; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.50 (15 H, s, C_5Me_5), 6.12 (1 H, t, $^3J_{\text{HH}} = ^3J_{\text{FH}}$ 7.2, *meta*- $\text{C}_6\text{H}_3\text{F}_2$), 6.48–6.71 (2 H, m, *para*- and *meta*- $\text{C}_6\text{H}_3\text{F}_2$), 7.10–7.40 (15 H, m, PPh_3); $\delta_{\text{C}}(\text{CDCl}_3)$ 9.8 (s, C_5Me_5), 92.4 (s, C_5Me_5), 108.6 (d, J 34.3, *meta*- $\text{C}_6\text{H}_3\text{F}_2$), 123.5 (t, J 10.2, *para*- $\text{C}_6\text{H}_3\text{F}_2$), 127.7 (br, ArCH), 128.6 (ArCH), 128.8 (ArCH), 128.9 (ArCH), 129.2 (br, ArCH), 132.4 (d, J 9.7), 133.8 (ArC $_{\text{ipso}}$), 134.2 (ArC $_{\text{ipso}}$), 137.5 (d, J 10.6, ArC $_{\text{ipso}}$), 170.2 (dd, $^1J_{\text{CF}}$ 229.5 and $^3J_{\text{CF}}$ 20.8, *ortho*- $\text{C}_6\text{H}_3\text{F}_2$), 224.6 (dd, J 29.4 and J 12.0, Fe-CO); $\delta_{\text{F}}(\text{CD}_3\text{C}_6\text{D}_5)$ -76.00 (d, J_{PF} 13.4, *syn*), -79.39 (s, *anti*); $\delta_{\text{P}}(\text{CD}_3\text{C}_6\text{D}_5)$ 69.5 (d, J_{PF} 13.4).

Synthesis of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})[\text{P}(p\text{-Tol})_3]\text{Me}$ **9**

A toluene solution (30 mL) of **16** (0.436 g, 0.878 mmol) was photolysed for 3 h at the end of which a red solution was obtained. The solvent was removed under reduced pressure and the reaction mixture was chromatographed on silica eluting with diethyl ether (5%) in PE to give a dark red band of product **9** (0.115 g) which was contaminated with $\text{P}(p\text{-Tol})_3$ as determined by ^1H NMR spectroscopy. Increasing the polarity of the solvent then eluted a red band of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ and finally starting material **16** (0.113 g). The product **9** was extracted with PE to remove more phosphine to form an orange foam upon solvent removal, which was redissolved in toluene, an excess of MeI was added and the solution was stirred for 5 h. Filtration through alumina afforded a red product **9** which was no longer contaminated with phosphine. $\nu_{\text{max}}/\text{cm}^{-1}$ (CH_2Cl_2) 1902; $\delta_{\text{H}}(\text{CDCl}_3)$ -0.20 (3 H, d, $^3J_{\text{PH}}$ 6.4, Fe- CH_3), 2.36 [9 H, s, $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$], 4.24 (5 H, d, $^3J_{\text{PH}}$ 1.0, C_5H_5), 7.10–7.40 [12 H, m, $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$]; $\delta_{\text{C}}(\text{CDCl}_3)$ -22.4 (d, $^3J_{\text{PC}}$ 22.3, Fe- CH_3), 21.2 [s, $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$], 84.3 (s, C_5H_5), 128.6 [d, J_{PC} 8.5, *meta*- $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$], 133.0 [d, J_{PC} 9.4, *ortho*- $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$], 133.9 [d, J_{PC} 41.0, *ipso*- $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$], 139.1 [s, *para*- $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$], 223.1 (d, J_{PC} 31.2, Fe-CO); $\delta_{\text{P}}(\text{CDCl}_3)$ 82.4 (s).

Synthesis of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{COPh}$ **10**

A THF solution (40 mL) of **17** (450 mg, 1.10 mmol) at -78°C was treated with *n*-BuLi (1.25 mmol) and TMEDA (0.188 mL, 1.25 mmol) and stirred for 1 h. The resultant purple solution of the anion was then treated with $(\text{Ph}_2\text{CO})_2\text{O}$ (316 mg, 1.4 mmol) and the resultant orange–brown solution stirred for 2 h, then quenched with methanol. Chromatography on silica eluting with CH_2Cl_2 (50%) in PE eluted **10** (200 mg, 35%); $\nu_{\text{max}}/\text{cm}^{-1}$ (CH_2Cl_2) 1920, 1596; $\delta_{\text{H}}(\text{CDCl}_3)$ 4.58 (5 H, d, $^3J_{\text{PH}}$ 1.2, C_5H_5), 7.00–7.15 (3 H, m, *meta*- and *para*-ArCH), 7.15–7.55 (17 H, m, PPh_3 and *ortho*-ArCH); $\delta_{\text{C}}(\text{CDCl}_3)$ 85.5 (s, C_5H_5), 126.1 (s, *meta*-Ph), 127.4 (s, *para*-Ph), 128.3 (d, J_{PC} 9.2, *meta*- PPh_3), 129.3 (s, *ortho*-Ph), 130.0 (s, *para*- PPh_3), 133.7 (d, J_{PC} 9.5, *ortho*- PPh_3), 136.5 (d, J_{PC} 43.7, *ipso*- PPh_3), 152.8 (d, J_{PC} 4.6, Fe-COC $_6\text{H}_5$), 221.5 (d, J_{PC} 32.8, Fe-CO).

Synthesis of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})[\text{P}(p\text{-Tol})_3]\text{Ph}$ **12**

An orange toluene solution (20 mL) of **10** (0.282 g, 0.546 mmol) and $\text{P}(p\text{-Tol})_3$ (0.170 g, 0.556 mmol) was photolysed for 3 h. The resultant red solution was filtered through Celite and the solvent was removed under reduced pressure to form a red oil. Chromatography on silica eluting with diethyl ether (5%) in

PE eluted a dark red band and increasing the polarity to 50% eluted the starting material. The ^1H NMR spectra of the red band indicated it to be a 3:2 mixture of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{-}[\text{P}(p\text{-Tol})_3]\text{Ph}$ **12** and the corresponding complex $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Ph}$ **11** as determined by the Cp resonances. Chromatography on alumina (grade I) eluting with diethyl ether (2%) in PE afforded two red fractions, the leading fraction of which was determined to be **12** (0.148 g) with $\text{P}(p\text{-Tol})_3$ contamination. Attempts to further purify the product by chromatography or by adding MeI were unsuccessful. $\nu_{\text{max}}/\text{cm}^{-1}$ (CH_2Cl_2) 1916; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.35 [9 H, s, $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$], 4.48 (5 H, d, $^3J_{\text{PH}}$ 1.04, C_5H_5), 6.67–6.76 (3 H, m, *meta*-Ph, *para*-Ph), 7.10–7.12 [12 H, m, $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$], 7.49–7.62 (2 H, m, *ortho*-Ph); $\delta_{\text{C}}(\text{CDCl}_3)$ 21.2 [s, $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$], 84.7 (s, C_5H_5), 120.7 (s, *meta*-Ph), 125.7 (s, *para*-Ph), 128.5 [d, J_{PC} 8.9, *meta*- $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$], 133.3 [d, J_{PC} 8.5, *ortho*- $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$], 139.4 [s, *para*- $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$], 157.2 (d, J_{PC} 25.1, *ipso*-Ph) 146.57 (s, *ortho*-Ph), 222.2 (d, J_{PC} 31.5, Fe-CO); $\delta_{\text{P}}(\text{CDCl}_3)$ 75.6 (s). The trailing fraction was determined to be **11** by comparison with an authentic sample.

Synthesis of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{CO}(2,6\text{-C}_6\text{H}_3\text{F}_2)$ **13**

A THF solution (40 mL) of **17** (530 mg, 1.29 mmol) at -78°C was treated with *n*-BuLi (1.4 mmol) and TMEDA (1.4 mmol) and stirred for 1 h. The resultant purple solution of the anion was then treated with 2,6- $\text{C}_6\text{H}_3\text{F}_2\text{COCl}$ (0.22 mL, 1.5 mmol) to form a green–yellow solution which was stirred for 2 h and then quenched with MeOH. The reaction mixture was filtered through deactivated alumina and the solvent removed under reduced pressure to form an orange solid. Chromatography on silica eluting with PE (25%) in CH_2Cl_2 first gave unreacted **17** followed by **13**. This was rechromatographed and recrystallised from CH_2Cl_2 –pentane (375 mg, 53%) (Found: C, 67.7; H, 4.2. $\text{C}_3\text{H}_3\text{F}_2\text{FePO}_2$ requires C, 67.4; H, 4.20%); $\nu_{\text{max}}/\text{cm}^{-1}$ (CH_2Cl_2) 1931, 1587; $\delta_{\text{H}}(\text{CDCl}_3)$ 4.50 (5 H, d, $^3J_{\text{PH}}$ 1.1, C_5H_5), 6.69 (2 H, t, $^3J_{\text{HH}} = ^3J_{\text{FH}}$ 7.9, *meta*- $\text{C}_6\text{H}_3\text{F}_2$), 7.00–7.15 (1 H, m, *para*- $\text{C}_6\text{H}_3\text{F}_2$), 7.31–7.62 (15 H, m, PPh_3); $\delta_{\text{C}}(\text{CDCl}_3)$ 86.3 (s, C_5H_5), 111.4 (d, $^2J_{\text{CF}}$ 25.8, *meta*- $\text{C}_6\text{H}_3\text{F}_2$), 127.7 (s, *para*- $\text{C}_6\text{H}_3\text{F}_2$), 128.0 (d, J_{PC} 9.3, *meta*- PPh_3), 129.8 (s, *para*- PPh_3), 131.0 (br, *ipso*- $\text{C}_6\text{H}_3\text{F}_2$), 133.5 (d, J_{PC} 9.5, *ortho*- PPh_3), 136.1 (d, J_{PC} 43.8, *ipso*- PPh_3), 156.12 (dd, $^1J_{\text{CF}}$ 248.1 and $^3J_{\text{CF}}$ 9.0, *ortho*- $\text{C}_6\text{H}_3\text{F}_2$), 220.3 (d, J_{PC} 31.5, Fe-CO), 266.9 (d, J_{PC} 31.1, Fe-COC $_6\text{H}_3\text{F}_2$); $\delta_{\text{F}}(\text{CDCl}_3)$ –117.10 (s); $\delta_{\text{P}}(\text{CDCl}_3)$ 70.0 (s).

Synthesis of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(2,6\text{-C}_6\text{H}_3\text{F}_2)$ **14**

An orange benzene solution (30 mL) of **13** (350 mg, 0.63 mmol) was photolysed for 2.5 h with a 100 W medium pressure Hg lamp. The solvent was removed under reduced pressure and the product chromatographed on silica eluting with CH_2Cl_2 (50%) in PE to give a dark red band of product which was recrystallised from diethyl ether and pentane to afford deep red crystals of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(2,6\text{-C}_6\text{H}_3\text{F}_2)$ **14** (260 mg, 78%) (Found: C, 68.8; H, 4.35%. $\text{C}_3\text{H}_3\text{F}_2\text{FePO}$ requires C, 68.7; H, 4.40%); $\nu_{\text{max}}/\text{cm}^{-1}$ (CH_2Cl_2) 1940; $\delta_{\text{H}}(\text{CDCl}_3)$ 4.59 (5 H, d, $^3J_{\text{PH}}$ 1.2, C_5H_5), 6.36 (2 H, br, *meta*- $\text{C}_6\text{H}_3\text{F}_2$), 6.70 (1 H, quintet, $^4J_{\text{FH}} = ^3J_{\text{HH}}$ 7.3, *para*- $\text{C}_6\text{H}_3\text{F}_2$), 7.15–7.45 (15 H, m, PPh_3); $\delta_{\text{C}}(\text{CD}_2\text{Cl}_2)$ 83.5 (s, C_5H_5), 108.8 (d, $^2J_{\text{CF}}$ 33.7, *meta*- $\text{C}_6\text{H}_3\text{F}_2\text{Ph}$), 124.3 (t, $^3J_{\text{CF}}$ 10.4, *para*- $\text{C}_6\text{H}_3\text{F}_2$), 128.1 (d, J_{PC} 9.3, *meta*- PPh_3), 129.7 (s, *para*- PPh_3), 133.5 (d, J_{PC} 9.5, *ortho*- PPh_3), 136.1 (d, J_{PC} 40.7, *ipso*- PPh_3), 171.4 (dd, $^1J_{\text{CF}}$ 225.9 and $^3J_{\text{CF}} = 20.0$, *ortho*- $\text{C}_6\text{H}_3\text{F}_2$), 221.1 (d, J_{PC} 31.5, Fe-CO); $\delta_{\text{F}}(\text{CDCl}_3)$, room temp.) –76.17 (s, br); -70°C , –76.17 (d, J_{PF} 9.2, *syn*), –76.85 (s, *anti*); $\delta_{\text{P}}(\text{CDCl}_3)$ 72.2 (apparent t, J_{PF} 9.2); -40°C , 72.3 (d, J_{PF} 9.2).

$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})[\text{P}(p\text{-Tol})_3](2,6\text{-C}_6\text{H}_3\text{F}_2)$ **15**

A toluene solution (20 mL) of **13** (94.1 mg, 0.17 mmol) and $\text{P}(p\text{-Tol})_3$ (52 mg, 0.17 mmol) was photolysed for 3.75 h. The solvent was removed under reduced pressure to form a red oil,

which was purified by chromatography on alumina eluting with diethyl ether (20%) in PE to give a red band which was collected in fractions. The leading fractions were determined to be **15** with a small amount of $\text{P}(p\text{-Tol})_3$ contamination and were redissolved in toluene, an excess amount of MeI added and the solution stirred for 12 h. Filtration through a pad of alumina gave the product (10 mg) with only a small amount of phosphine contaminant; $\nu_{\text{max}}/\text{cm}^{-1}$ (CH_2Cl_2) 1939; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.33 [9 H, s, $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$], 4.55 (5 H, d, $^3J_{\text{PH}}$ 1.1, C_5H_5), 6.36 (2 H, br, *meta*- $\text{C}_6\text{H}_3\text{F}_2$), 6.70 (1 H, quintet, $^3J_{\text{HH}} = ^4J_{\text{FH}}$ 7.3, *para*- $\text{C}_6\text{H}_3\text{F}_2$), 7.02–7.11 [12 H, m, $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$]; $\delta_{\text{C}}(\text{CDCl}_3)$ 21.2 [s, $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$], 83.4 (s, C_5H_5), 108.6 (d, $^2J_{\text{CF}}$ 33.8, *meta*- $\text{C}_6\text{H}_3\text{F}_2$), 123.9 (t, $^3J_{\text{CF}}$ 10.3, *para*- $\text{C}_6\text{H}_3\text{F}_2$), 128.5 [d, J_{PC} 9.1, *meta*- $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$], 133.2 [d, J_{PC} 9.2, *ortho*- $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$], 139.4 [s, *para*- $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$], 171.3 (dd, $^1J_{\text{CF}}$ 209.5, $^3J_{\text{CF}}$ 19.0, *ortho*- $\text{C}_6\text{H}_3\text{F}_2$), 222.5 (d, J_{PC} 17.6, Fe-CO); $\delta_{\text{F}}(\text{CDCl}_3)$ –74.65 (d, J_{PF} 5.0); $\delta_{\text{P}}(\text{CDCl}_3)$ 73.3 (apparent t, J_{PF} 5.0).

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