Photofragmentation Voltammetry Studies of the Aminocarbene Complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)\{=C(NHR^1)(R^2)\}]BF_4$ [L = PPh_3, P(*p*-Tol)$_3$; R^1 = Me, CH_2Ph; R^2 =Me, Bu]

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The synthesis of the complexes $[(\eta^5\text{-}C_6H_6)Fe(CO)(L)\{=C(NHR^1)(R^2)\}]BF_4$ [L = PPh_3, P(*p*-Tol)$_3$; R^1 = Me, CH_2Ph; R^2 = Me, Bu] is described. Photofragmentation voltammetry is used to demonstrate that the primary photoprocess is loss of the phosphine ligand in all four carbene complexes. A common intermediate is observed when the analogous aminocarbenes are studied.

We have recently demonstrated that reversible phosphine rather than CO dissociation occurs in the homochiral aminocarbene complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)\{=C(NHR^2)(R^1)\}]BF_4$ [L = PPh_3, P(*p*-Tol)$_3$; R^1 = Me, Et; R^2 = CH_2Ph].[1] The method used only provided indirect evidence for this process. Photofragmentation voltammetry has been successfully used to detect transient species in a variety of inorganic systems.[2,3,4] The aminocarbenes $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)\{=C(NHMe)(Me)\}]BF_4$ [L = PPh_3, P(*p*-Tol)$_3$] were studied by this technique and direct evidence was found for initial loss of phosphine to produce a common residual iron intermediate.[5] We describe herein the synthesis of these two compounds in addition to $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)\{=C(NHCH_2Ph)(Bu)\}]BF_4$ [L = PPh_3, P(*p*-Tol)$_3$]. The full photofragmentation voltammetry studies on these four compounds is also presented.

Experimental

All reactions were performed under a nitrogen atmosphere using standard vacuum line techniques.[6] Solvents were dried and deoxygenated prior to use. The solvents tetrahydrofuran (THF), benzene and Et_2O were dried and distilled from sodium benzophenone while CH_2Cl_2 and CH_3CN were dried and distilled from CaH_2. Light petroleum [petroleum ether (PE)] refers to the redistilled hydrocarbon fraction, b.p. 40–60 °C. The complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(P(p\text{-}Tol)_3)C(O)Me$ (**1**),[1b] $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)C(O)Bu$ (**2**),[7] $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)\{=C(Me)(OMe)\}]BF_4$ [L = PPh_3 (**3**),[8] P(*p*-Tol)$_3$ (**4**)[1b]] were synthesized according to literature procedures. Butyllithium (1.6 mol dm^{-3} in hexane) (FMC corporation), P(*p*-Tol)$_3$ (Fluka), PrI (Aldrich) and $[Me_3O]BF_4$ (Aldrich) were used as supplied. Column chromatography was performed 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; ^{13}C, ^{31}P and ^{19}F NMR spectra were recorded on a Bruker AM250 spectrometer (at 62.9, 125.76 and 101.26 MHz respectively). *J* Values are given in Hz. IR spectra were recorded on a Perkin-Elmer 1750 fourier transform spectrophotometer using 0.05 mm NaCl cells. Elemental analyses were performed by Mrs. V. Lamburn of the Dyson Perrins Laboratory.

All standard photofragmentation voltammetry experiments were conducted using a channel electrode made of optical quality synthetic silica to standard construction and dimensions.[3,4,9] Electrolyte (volume) flow rates in the range 10^{-4}–10^{-1} $cm^3\ s^{-1}$ were employed. Working electrodes were fabricated from platinum foils (purity of 99.95%, thickness 0.025 mm) of approximate size 4 mm x 4 mm, supplied by Goodfellow Advanced Materials. Precise electrode 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*′-tetramethyl-1,4-phenylenediamine (TMPD) were observed. For this reason potentials are reported relative to the saturated calomel electrode (SCE), +0.20 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 (up to 200 V). Other methodological details were as described previously.[3,4,9] Irradiation was provided by a Wotan XBO 900 W/2 xenon arc lamp *via* a Jarrell-Ash 892–410 grating monochromator (maximum incident power 40 mW cm^{-2}). Variable light intensity measurements were made by attenuation of the beam as described previously.[3] UV/VIS measurements were made with a Perkin Elmer Lambda-5 spectrophotometer. Complementary rotating disc measurements were conducted using Oxford Electrodes equipment.

Experiments were performed using solutions of aminocarbene complex (*ca.* 10^{-4}–10^{-3} mol dm^{-3}) in dried[3] acetonitrile solution containing 0.1 mol dm^{-3} (recrystallised) tetrabutylammonium perchlorate (TBAP) (Fluka, purum) as supporting electrolyte. Solutions were purged of oxygen by outgassing with prepurified argon prior to electrolysis.

Synthesis of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{=C(NHMe)(Me)\}]BF_4$ (**5**).—To a THF suspension (30 cm^3) of **3** (2.00 g, 3.60 mmol) at 0 °C was added $MeNH_2$ (3 cm^3; 40% aq solution, 36.0 mmol) dropwise resulting in the immediate formation of an orange-red solution. The reaction was stirred at 0 °C for 2 h, filtered through Celite to afford a bright orange solution which was then added to diethyl ether at 0 °C. The resultant bright yellow precipitate was washed twice with diethyl ether and dried under reduced pressure (1.89 g, 95%). M.p. 184–187 °C (dec) (Found: C, 58.32; H, 5.11; N, 2.48. Calcd. for $C_{27}H_{27}BF_4FeNOP$: C, 58.42; H, 4.91; N, 2.52%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1956 (CO) and 1057 (BF_4^-); $\delta_H(CDCl_3)$ 9.83 (br s, 1 H, N-H), 7.53–7.47 (m, 9 H, PPh_3), 7.32–7.27 (m, 6 H, PPh_3), 4.78 (d, 5 H, J_{PH} 1.41, C_5H_5), 3.00 (d, 3 H, J_{HH} 4.80, N-Me) and 2.18 (s, 3 H, Fe=C–Me); $\delta_C(CDCl_3)$ 264.54 (d, J_{PC} 22.60, Fe=C), 217.95 (d, J_{PC} 28.63, Fe-CO), 133.37 (d, J_{PC} 45.28, ipso-PPh_3), 132.81 (d, J_{PC} 9.19, *o*-PPh_3), 131.02 (s, *p*-PPh_3), 129.08 (d, J_{PC} 9.31, *m*-PPh_3), 85.50 (s, C_5H_5), 37.22 (s, N-CH_3) and 36.99 (s, Fe=C–CH_3); $\delta_F(CDCl_3)$ − 154.09 (s) and −154.15 (s) (1:3); $\delta_P(CDCl_3)$ 66.83.

Synthesis of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{{=}C(Bu)(OMe)\}]BF_4$ (**6**).—A CH_2Cl_2 solution (150 cm^3) of **2** (5.00 g, 10.1 mmol) was treated with $[Me_3O]BF_4$ (1.94 g, 13.1 mmol) and stirred at room temp. for 18 h. The reaction mixture was concentrated to 20 cm^3 and the product was precipitated by the addition of cold diethyl ether. The resultant yellow precipitate was washed with diethyl ether and dried under reduced pressure (5.79 g, 96%). M.p. 172–174 °C (dec) (Found: C, 60.52; H, 5.53. Calcd. for $C_{30}H_{32}BF_4FeO_2P$: C, 60.23; H, 5.4%); ν_{max}(THF)/cm^{-1} 1962 (CO) and 1093 (BF_4^-); δ_H($CDCl_3$) 7.63–7.45 (m, 9 H, PPh_3), 7.32–7.30 (m, 6 H, PPh_3), 4.88 (s, 5 H, C_5H_5), 4.29 (s, 3 H, OMe), 2.77 (m, 1 H, $C\mathit{H}_2CH_2CH_2CH_3$), 2.50 (m, 1 H, $C\mathit{H}_2CH_2CH_2CH_3$), 1.73 (m, 1 H, $CH_2C\mathit{H}_2CH_2CH_3$), 1.50 (m, 1 H, $CH_2C\mathit{H}_2CH_2CH_3$), 1.37 (m, 2 H, $CH_2CH_2C\mathit{H}_2CH_3$) and 0.87 (t, 3 H, J_{HH} 6.41, $CH_2CH_2CH_2C\mathit{H}_3$); δ_C($CDCl_3$) 259.37 (d, J_{PC} 23.31, Fe=C), 216.11 (d, J_{PC} 26.94, Fe–CO), 132.73 (d, J_{PC} 48.03, ipso-PPh_3), 131.40 (d, J_{PC} 9.96, *o*-PPh_3), 131.40 (s, *p*-PPh_3), 129.10 (d, J_{PC} 9.89, *m*-PPh_3), 87.34 (s, C_5H_5), 65.65 (s, OMe), 56.18 (s, $\mathit{C}H_2CH_2CH_2CH_3$), 27.62 (s, $CH_2\mathit{C}H_2CH_2CH_3$), 22.48 (s, $CH_2CH_2\mathit{C}H_2CH_3$) and 13.19 (s, $CH_2CH_2CH_2\mathit{C}H_3$); δ_F($CDCl_3$) − 154.76 (s) and − 154.81 (s) (1 : 3); δ_P($CDCl_3$) 61.86. Note that in all attempts to synthesize this compound a small amount (15%) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)]BF_4$ (**7**) was also produced as determined by both ^1H and ^{31}P NMR spectroscopy.

Synthesis of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{{=}C(NHCH_2Ph)(Bu)\}]BF_4$ (**8**).—To a THF suspension (30 cm^3) of **6** (500 mg, 0.84 mmol) at 0 °C was added $PhCH_2NH_2$ (0.90 cm^3, 8.36 mmol) dropwise resulting in the immediate formation of an orange-red solution. The reaction was stirred at 0 °C for 2 h and the solvent was removed under reduced pressure. The red oil was dissolved in a minimum amount of CH_2Cl_2 (10 cm^3) and added dropwise to diethyl ether at 0 °C. The resultant bright yellow precipitate was washed twice with diethyl ether and dried under reduced pressure (0.447 g, 80%). The product was recrystallised from CH_2Cl_2–diethyl ether to yield a bright yellow crystalline solid (0.367 g, 65%). M.p. 171–173 °C (dec) (Found: C, 64.08; H, 5.43; N, 2.02. Calcd. for $C_{36}H_{37}BF_4FeNOP$: C, 64.22; H, 5.54; N, 2.08%); ν_{max}(CH_2Cl_2)/cm^{-1} 1963 (CO) and 1088 (BF_4^-); δ_H($CDCl_3$) 10.19 (br s, 1 H, N-H), 7.48–7.35 (m, 9 H, PPh_3), 7.24–6.94 (m, 11 H, PPh_3 and $CH_2\mathit{Ph}$), 4.90 (s, 5 H, C_5H_5), 4.89–4.82 (m, 1 H, N-$C\mathit{H}_2Ph$), 4.53–4.47 (m, 1 H, N-$C\mathit{H}_2Ph$), 2.70–2.61 (m, 1 H, $C\mathit{H}_2CH_2CH_2CH_3$), 2.09–2.00 (m, 1 H, $C\mathit{H}_2CH_2CH_2CH_3$), 1.73–1.65 (m, 1 H, $CH_2C\mathit{H}_2CH_2CH_3$), 1.42–1.35 (m, 2 H, $CH_2CH_2C\mathit{H}_2CH_3$), 1.19–1.11 (m, 1 H, $CH_2C\mathit{H}_2CH_2CH_3$) and 0.91 (t, 3 H, J_{HH} 7.19, $CH_2CH_2CH_2C\mathit{H}_3$); δ_C(CD_2Cl_2) 269.91 (d, J_{PC} 23.44, Fe=C), 218.59 (d, J_{PC} 28.80, Fe–CO), 135.80 (s, ipso-$CH_2\mathit{Ph}$), 133.25 (d, J_{PC} 9.83, *o*-PPh_3), 133.23 (d, J_{PC} 45.48, ipso-PPh_3), 131.53 (s, *p*-PPh_3), 129.08 (d, J_{PC} 8.90, *m*-PPh_3), 129.50 (br s, *o*-$CH_2\mathit{Ph}$), 129.04 (s, *p*-$CH_2\mathit{Ph}$), 128.52 (s, *m*-$CH_2\mathit{Ph}$), 85.91 (s, C_5H_5), 53.70 (s, N-$\mathit{C}H_2Ph$), 49.48 (s, $\mathit{C}H_2CH_2CH_2CH_3$), 29.44 (s, $CH_2\mathit{C}H_2CH_2CH_3$), 23.45 (s, $CH_2CH_2\mathit{C}H_2CH_3$) and 15.52 (s, $CH_2CH_2CH_2\mathit{C}H_3$); δ_F($CDCl_3$) −153.00 (s) and −153.05 (s) (1 : 3); δ_P($CDCl_3$) 67.31. Note that in all attempts to synthesize this compound a small amount (15%) of **7** was also produced as determined by IR, ^1H and ^{31}P NMR spectroscopy.

Synthesis of $[(\eta^5\text{-}C_5H_5)Fe(CO)(P(p\text{-}Tol)_3)\{{=}C(NHMe)(Me)\}]BF_4$ (**9**).—Into a yellow CH_2Cl_2 solution (40 cm^3) of **4** (2.16 g, 3.61 mmol) stirred over 4 Å sieves was bubbled $MeNH_2$ gas. A rapid colour change to bright red occurred immediately and an IR spectrum at this point exhibited a single ν_{CO} (1957 cm^{-1}) with no starting material (ν_{CO} 1986 cm^{-1}). The solution was filtered to remove the sieves, the solvent was reduced to 5 cm^3 and cannulated onto dry diethyl ether to form a bright yellow precipitate. This was kept at −30 °C for 1 h after which time the solvent was removed *via* cannula. The precipitate was washed with diethyl ether and dried under reduced pressure to afford **9** as a bright yellow analytically pure solid (1.74 g, 81%) (Found: C, 60.54; H, 5.84; N, 2.34. Calcd. for $C_{30}H_{33}BF_4FeNOP$: C, 60.33; H, 5.57; N, 2.35%); ν_{max}(CH_2Cl_2)/cm^{-1} 1957 (CO) and 1066 (BF_4^-); δ_H($CDCl_3$) 9.72 (br s, 1 H, N-H), 7.3–7.1 [m, 12 H, $P(p\text{-}CH_3C_6\mathit{H}_4)_3$], 4.74 (d, 5 H, J_{PH} 1.32, C_5H_5), 3.01 (d, 3 H, J_{HH} 4.63, N-CH_3), 2.40 [s, 9 H, $P(p\text{-}C\mathit{H}_3C_6H_4)_3$] and 2.19 (s, 3 H, Fe=C–CH_3); δ_C($CDCl_3$) 264.91 (d, J_{PC} 22.16, Fe=C), 218.28 (d, J_{PC} 29.18, Fe–CO), 141.43 [s, *p*-$P(p\text{-}CH_3\mathit{C}_6H_4)_3$], 132.97 [d, J_{PC} 9.62, *o*-P-$(p\text{-}CH_3\mathit{C}_6H_4)_3$], 130.42 [d, J_{PC} 47.51, ipso-P-$(p\text{-}CH_3\mathit{C}_6H_4)_3$], 129.75 [d, J_{PC} 9.88, *m*-$P(p\text{-}CH_3\mathit{C}_6H_4)_3$], 85.43 (s, C_5H_5), 37.06 (s, N–CH_3), 36.77 (s, Fe=*C*–CH_3) and 21.30 [s, $P(p\text{–}\mathit{C}H_3C_6H_4)_3$]; δ_F($CDCl_3$) −154.27 (s) and −154.32 (s) (1 : 3); δ_P($CDCl_3$) 68.31.

Synthesis of $(\eta^5\text{-}C_5H_5)Fe(CO)(P(p\text{-}Tol)_3)C(O)Bu$ (**10**).—A THF solution (40 cm^3) of **1** (2.63 g, 5.30 mmol) at −78 °C was treated with BuLi (3.7 cm^3, 5.92 mmol). The resultant dark red solution was stirred for 1 h after which time PrI (0.60 cm^3, 6.15 mmol) was added. The orange solution was stirred for 1 h and warmed to room temp. The solvent was removed under reduced pressure and the orange product was chromatographed on silica with diethyl ether (20%) in PE to elute **10** (2.51 g, 88%) leaving residual starting material on the column (Found: C, 71.37; H, 6.60. Calcd. for $C_{32}H_{35}FeO_2P$: C, 71.38; H, 6.55%); ν_{max}(CH_2Cl_2)/cm^{-1} 1910 (CO) and 1599 (acyl); δ_H($CDCl_3$) 7.38 [dd, 6 H, J_{HH} 10.14 and 8.12, *o*-$P(p\text{-}CH_3C_6\mathit{H}_4)_3$], 7.15 [d, 6 H, J_{HH} 6.32, *m*-$P(p\text{-}CH_3C_6\mathit{H}_4)_3$], 4.40 (d, 5 H, J_{PH} 1.12, C_5H_5), 2.95–2.76 (m, 1 H, $C\mathit{H}_2CH_2CH_2CH_3$), 2.64–2.45 (m, 1 H, $C\mathit{H}_2CH_2CH_2CH_3$), 2.36 [s, 9 H, $P(p\text{-}C\mathit{H}_3C_6H_4)_3$], 1.28–1.12 (m, 1 H, $CH_2C\mathit{H}_2CH_2CH_3$), 1.10–0.86 (m, 3 H, $CH_2C\mathit{H}_2C\mathit{H}_2CH_3$) and 0.76 (t, 3 H, J_{HH} 7.02, $CH_2CH_2CH_2C\mathit{H}_3$); δ_C($CDCl_3$) 277.17 [d, J_{PC} 22.46, Fe-*C*(O)CH_3], 220.95 (d, J_{PC} 31.03, Fe–CO), 139.55 [s, *p*-$P(p\text{-}CH_3\mathit{C}_6H_4)_3$], 133.59 [d, J_{PC} 49.84, ipso-P-$(p\text{-}CH_3\mathit{C}_6H_4)_3$], 133.36 [d, J_{PC} 9.48, *o*-$P(p\text{-}CH_3\mathit{C}_6H_4)_3$], 128.70 [d, J_{PC} 8.9, *m*-$P(p\text{-}CH_3\mathit{C}_6H_4)_3$], 85.21 (s, C_5H_5), 65.96 (s, $\mathit{C}H_2CH_2CH_2CH_3$), 27.37 (s, $CH_2\mathit{C}H_2CH_2CH_3$), 22.26 (s, $CH_2CH_2\mathit{C}H_2CH_3$), 21.23 (s, $P(p\text{-}\mathit{C}H_3C_6H_4)_3$] and 13.92 (s, $CH_2CH_2CH_2\mathit{C}H_3$); δ_P($CDCl_3$) 73.66.

Synthesis of $[(\eta^5\text{-}C_5H_5)Fe(CO)(P(p\text{-}Tol)_3)\{{=}C(OMe)Bu\}]BF_4$ (**11**).—In a typical reaction, a CH_2Cl_2 solution (40 cm^3) of **10** (0.704 g, 1.31 mmol) was treated with $[Me_3O]BF_4$ (0.25 g, 1.69 mmol) and stirred at room temp. for 7 h. The IR spectrum at this point indicated the presence of the desired product (ν_{CO} 1972 cm^{-1}) in addition to a small amount of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(P(p\text{-}Tol)_3)]BF_4$ (**12**) (ν_{CO} 2056 and 2013 cm^{-1}). The solution was filtered, the solvent was reduced to 3 cm^3 and 250 cm^3 diethyl ether added to form a yellow solution. The schlenk was stored under nitrogen at −30 °C overnight after which time fine yellow crystals grew. The mother liquor was removed and the product dried under reduced pressure (0.735 g, 87%); ν_{max}(CH_2Cl_2)/cm^{-1} 1972 (CO); δ_H($CDCl_3$) 7.41–7.18 [m, 12 H, $P(p\text{-}CH_3C_6H_4)_3$], 4.85 (d, 5 H, J_{PH} 1.20, C_5H_5), 4.30 (s, 3 H, OMe), 2.88–2.63 (m, 1 H, $C\mathit{H}_2CH_2CH_2CH_3$), 2.41 [br s, 10 H, $C\mathit{H}_2CH_2CH_2CH_3$ and $P(p\text{-}C\mathit{H}_3C_6H_4)_3$], 1.5–1.15 (m, 4 H, $CH_2C\mathit{H}_2C\mathit{H}_2CH_3$) and 0.87 (t, 3 H, J_{HH} 6.74, $CH_2CH_2CH_2C\mathit{H}_3$); δ_C($CDCl_3$) 141.96 [s, *p*-$P(p\text{-}CH_3\mathit{C}_6H_4)_3$], 132.74 [d, J_{PC} 8.69, *o*-$P(p\text{-}CH_3\mathit{C}_6H_4)_3$], 130.24 [d, J_{PC} 32.62, ipso-$P(p\text{-}CH_3\mathit{C}_6H_4)_3$], 129.83 [d, J_{PC} 10.21, *m*-$P(p\text{-}CH_3\mathit{C}_6H_4)_3$], 87.44 (s, C_5H_5), 65.99 (s, $\mathit{C}H_2CH_2CH_2CH_3$), 27.80 (s, $CH_2\mathit{C}H_2CH_2CH_3$), 22.66 (s, $CH_2CH_2\mathit{C}H_2CH_3$), 21.33 [s, $P(p\text{-}\mathit{C}H_3C_6H_4)_3$] and 13.32 (s, $CH_2CH_2CH_2\mathit{C}H_3$); δ_F($CDCl_3$) − 153.71 (s) and − 153.76 (s) (1 : 3); δ_P($CDCl_3$) 20.45. The above product was contaminated with **12** and satisfactory elemental analysis could therefore not be obtained.

Synthesis of $[(\eta^5\text{-}C_5H_5)Fe(CO)(P(p\text{-}Tol)_3)\{{=}C(NHCH_2Ph)(Bu)\}]BF_4$ (**13**).—A CH_2Cl_2 solution (40 cm^3) of **11** (2.76 g, 4.32 mmol) was treated with benzylamine (1.0 cm^3, 9.15 mmol) and stirred at room temp. over 4 Å sieves. An IR spectrum after 10 min exhibited carbonyl stretching frequencies due to **12**, **11** and a new peak at 1910 cm^{-1}. The latter indicates the presence of a neutral species which may be due to the presence of **10**. However, the acyl stretch was concealed by the stretching frequency of the amine used in the reaction. Thus we were unsure as to the identity of the neutral species at this point. Another aliquot of benzylamine (1.0 cm^3) was added and an IR spectrum taken 10 min after the second addition indicated an increase in the amount of the neutral species. The reaction mixture was stirred for an additional 2 h with no change in the IR spectrum. The same results were obtained when 10 equiv. of benzylamine were added. The solution was filtered through Celite and the solvent was removed under reduced pressure. The product was dissolved in 7 cm^3 CH_2Cl_2, layered with 200 cm^3 diethyl ether and stored at −30 °C for 1 h. A small amount of yellow precipitate formed and the mother liquor was decanted. The IR spectrum of the precipitate in CH_2Cl_2 indicated the presence of **12** and a small amount of **13** (ν_{CO} 1956 cm^{-1}). This was discarded as it proved impossible to remove **12** from **13**. The IR spectrum of the mother liquor indicated the presence of the neutral species in addition to the desired product in a 2 : 1 ratio. This was filtered through a pad of silica which was washed with diethyl ether in the hope of leaving the carbene on the silica and washing through the neutral species. The IR spectrum of the diethyl ether eluent was identical to that previously observed. The diethyl ether fraction slowly developed bright yellow crystals upon standing (0.342 g, 11%) (Found: C, 65.18; H, 6.10; N, 1.82. Calc. for $C_{39}H_{43}BF_4FeNOP$: C, 65.48; H, 6.06; N, 1.96%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1955 (CO) and 1055 (BF_4^-); $\delta_H(CDCl_3)$ 10.14 (br s, 1 H, N–H), 7.25–7.13 [m, 9 H, $P(p\text{-}CH_3C_6\mathit{H}_4)_3$ and $CH_2\mathit{Ph}$], 7.0–6.90 [m, 8 H, $P(p\text{-}CH_3C_6\mathit{H}_4)_3$ and CH_2Ph), 4.85 (s, 5 H, $C_5\mathit{H}_5$), 4.81 (dd, 1 H, J_{NHH} 14.58 and J_{HH} 4.50, $C\mathit{H}_2Ph$), 4,49 (dd, 1 H, J_{NHH} 14.31 and J_{HH} 7.56, $C\mathit{H}_2Ph$), 2.64 (dt, 1 H, J_{HH} 11.68 and J_{HH} 3.82, $C\mathit{H}_2CH_2CH_2CH_3$), 2.39 [s, 9 H, $P(p\text{-}CH_3C_6H_4)_3$], 2.13 (dt, 1 H, J_{HH} 12.00 and J_{HH} 4.49, $C\mathit{H}_2CH_2CH_2CH_3$), 1.69 (m, 1 H, $CH_2C\mathit{H}_2CH_2CH_3$), 1.38 (m, 2 H, $CH_2CH_2C\mathit{H}_2CH_3$), 1.17 (m, 1 H, $CH_2C\mathit{H}_2CH_2CH_3$) and 0.91 (t, 3 H, J_{HH} 7.33, $CH_2CH_2CH_2C\mathit{H}_3$); $\delta_C(CDCl_3)$ 268.69 (d, J_{PC} 37.73, Fe=C), 141.33 [s, $p\text{-}P(p\text{-}CH_3\mathit{C}H_6)_3$], 135.55 (s, ipso-$CH_2\mathit{Ph}$), 132.68 [d, J_{PC} 9.35, $o\text{-}(p\text{-}CH_3C_6H_4)_3$], 129.76 [d, J_{PC} 44.4, ipso-$P(p\text{-}CH_3\mathit{C}_6H_4)_3$], 129.69 [d, J_{PC} 9.78, $m\text{-}P(p\text{-}CH_3\mathit{C}_6H_4)_3$], 129.58 (s, $o\text{-}CH_2\mathit{Ph}$), 128.75 (s, $m\text{-}CH_2\mathit{Ph}$), 127.74 (s, $p\text{-}CH_2\mathit{Ph}$), 85.46 (s, C_5H_5), 53.17 (s, $N\mathit{C}H_2Ph$), 48.79 (s, $\mathit{C}H_2CH_2CH_2CH_3$), 29.01 (s, $CH_2\mathit{C}H_2CH_2CH_3$), 22.89 (s, $CH_2CH_2\mathit{C}H_2CH_3$), 21.30 [s, $P(p\text{-}\mathit{C}H_3C_6H_4)_3$] and 13.60 (s, $CH_2CH_2CH_2\mathit{C}H_3$); $\delta_F(CDCl_3)$ −153.39 (s) and −153.44 (s) (1 : 3); $\delta_P(CDCl_3)$ 68.73. The solvent of the now red mother liquor was removed under reduced pressure and the product was dissolved in CH_2Cl_2, layered with diethyl ether and stored at −30 °C. Both bright yellow and bright red crystals developed. The solvent was removed *via* cannula and the crystals were dried under reduced pressure. A ^1H NMR spectrum in benzene (the yellow precipitate was insoluble in benzene) indicated only **10**. The crystals were then extracted with benzene to recover **10** (0.806 g, 35%) leaving behind 0.010 g of **13**.

Results and Discussion

We summarise first the voltammetry of the free phosphines, PPh_3 and $P(p\text{-}Tol)_3$, as previously reported.[5] Separate voltammetric experiments on PPh_3 in 0.1 mol dm^{-3} TBAP–acetonitrile using both a channel electrode and a platinum rotating disc showed a reproducible (irreversible) one-electron oxidation with a half-wave potential of +1.55 (+/−0.10) V in rigorously dry solvent in agreement with the general consensus of opinion from previous studies.[10,11] Analogous behaviour was seen for the case of $P(p\text{-}Tol)_3$ except that the half-wave potential was lowered to +1.41 (+/−0.10) V.

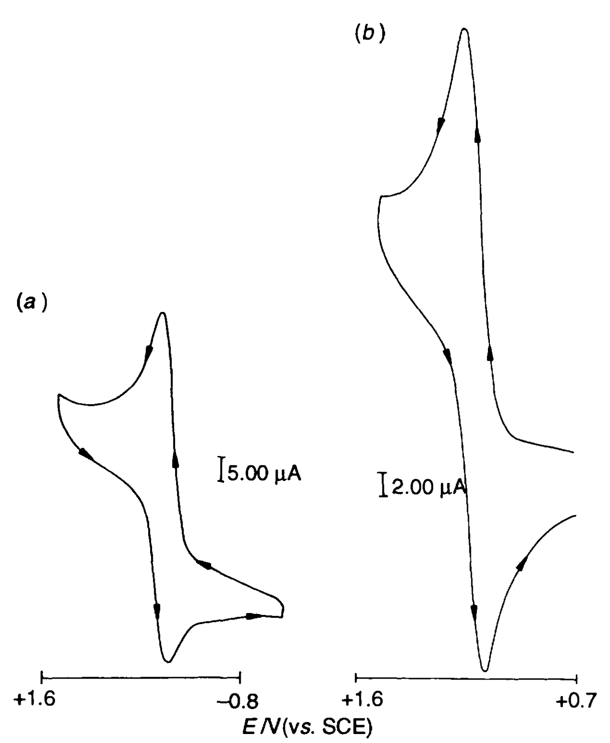

Fig. 1 Cyclic voltammogram obtained from the oxidation of (*a*) **8** and (*b*) **13** in 0.1 mol dm^{-3} TBAP–acetonitrile solution at a platinum electrode. A voltage scan rate of 100 mV s^{-1} was used.

We report next experiments performed, in the absence of light, to identify the 'dark' electrochemical behaviour of **8** and **13**, that of **5** and **9** having been previously studied. Considering first **8**, Fig. 1(*a*) shows a typical voltammogram obtained under no-flow conditions using a scan rate of 100 mV s^{-1}. An electrochemically reversible one-electron feature was seen with a formal potential of +1.13 (+/−0.05) V. Next, Fig. 1(b) shows the corresponding measurements for **13**; again a reversible one-electron oxidation is seen [formal potential of +1.15 (+/−0.05) V]. For both **8** and **13** the ratio of anodic to cathodic peak currents is close to unity suggesting that the dication resulting from the oxidation is stable on the voltammetric timescale (at low scan rates < 100 mV s^{-1}). All this 'dark' volammetric behaviour is analogous to that found[5] for **5** and **9** for which the formal oxidation potentials were +1.11 (+/ 0.05) V and + 1.06 (+/−0.05) V respectively.

Next we consider the photofragmentation voltammetry of the aminocarbene complexes **5**, **8**, **9** and **13**, building on our preliminary observations[5] that visible light induced the preferential expulsion of phosphine over carbon monoxide from **5** and **9** in acetonitrile leaving a common residual iron fragment. Fig. 2 shows the photofragmentation voltammogram measured in a solution containing 5.9 × 10^{-4} mol dm^{-3} **8** in 0.1 mol dm^{-3} TBAP–acetonitrile using light of wavelength 370 nm. For comparison the corresponding 'dark' hydrodynamic voltammogram is also displayed. Two new voltammetric fingerprints, in addition to that of the simple oxidation of **8**, are noticeable in the presence of light. First the wave at $E_{1/2}$ = +1.55 (+/−0.10) V may, on the basis of the results presented above for the oxidation of the free phosphines, be attributed to the oxidation of PPh_3, and second the prewave [$E_{1/2}$ = +0.48 (+/−0.05) V] may be inferred to result from the oxidation of the iron-

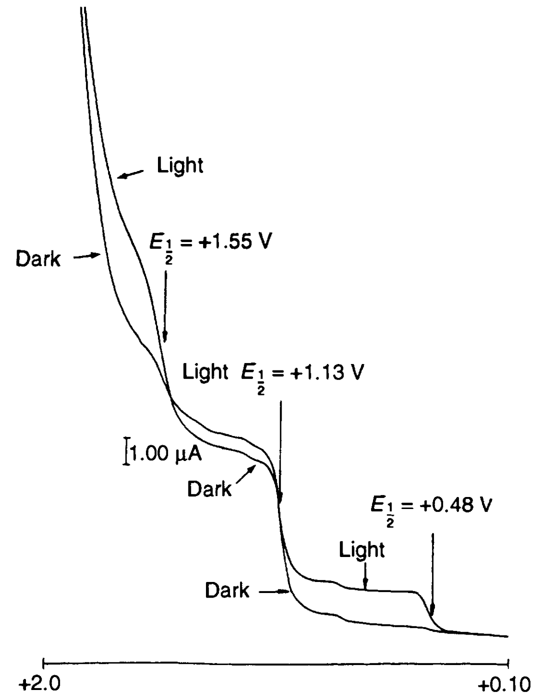

Fig. 2 Photofragmentation voltammogram for the oxidation of **8** measured at a platinum channel electrode using a flow rate of 7.2 × 10^{-4} cm^3 s^{-1}

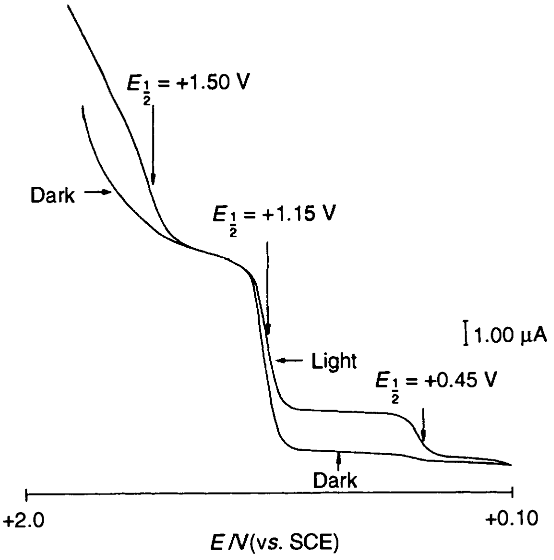

Fig. 3 Photofragmentation voltammogram for the oxidation of **13** measured at a platinum channel electrode using a flow rate of 2.0 × 10^{-3} cm^3 s^{-1}

containing photofragment formed through the loss of PPh_3. Fig. 3 shows the analogous photofragmentation voltammogram for **13** (4.2 × 10^{-4} mol dm^{-3}) under identical conditions except that a wavelength of 365 nm was required to induce fragmentation. Again two new voltammetric waves result; one attributable to free phosphine, $P(p\text{-Tol})_3$, $[E_{1/2} = +1.50(+/-0.10)$ V] and the second—the pre-wave—to the residual photofragment $[E_{1/2} = +0.45\ (+/-0.05)$ V]. Comparison of Figs. 2 and 3 shows that the pre-wave occurs at an essentially identical halfwave potential for both **8** and **13** suggesting the formation of a common species from the two precursors, namely $[(\eta^5\text{-}C_5H_5)Fe(CO)(CH_3CN)\{=C(NHCH_2Ph)(Bu)\}]BF_4$ (**14**). Also the voltammetric fragment seen in each case at potentials more positive than the 'dark' electro-oxidation is observed at a half-way potential consistent with that expected for the relevant free phosphine. Similar conclusions may be drawn from Figs. 4 and 5 which show the corresponding behaviour seen for **5** and **9**. These closely parallel those for **8** and **13** except that the iron containing photofragment (now of different structure) has the formal oxidation potential of +0.43 V.

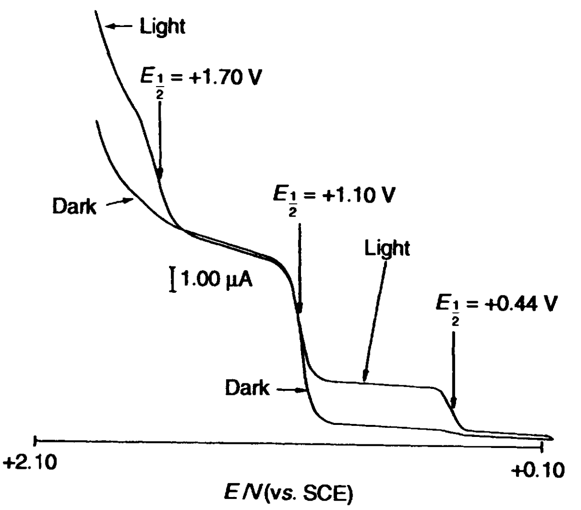

Fig. 4 Photofragmentation voltammogram for the oxidation of **5** measured at a platinum channel electrode using a flow rate of 1.3 × 10^{-3} cm^3 s^{-1}

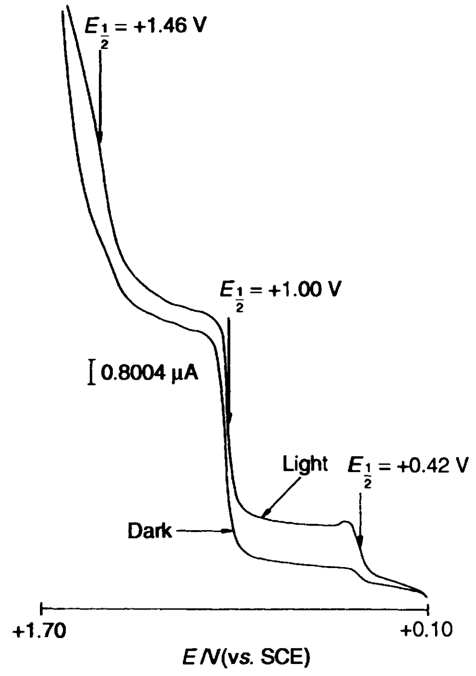

Fig. 5 Photofragmentation voltammogram for the oxidation of **9** measured at a platinum channel electrode using a flow rate of 1.2 × 10^{-3} cm^3 s^{-1}

We suggest that the photofragmentation voltammograms shown in Figs. 2–5 constitute direct evidence for the photofragmentation scheme suggested. In addition none of the figures show voltammetric evidence of any photofragment resulting from the loss of carbon monoxide, and as the sum of the currents due to the pre-wave and to the direct oxidation of the precursor aminocarbene complex is, in all cases, equal (within experimental error) to that observed in the absence of light for the latter process alone we deduce that no other process is important on the PFV timescale.

Confirmation of the suggested scheme was accomplished

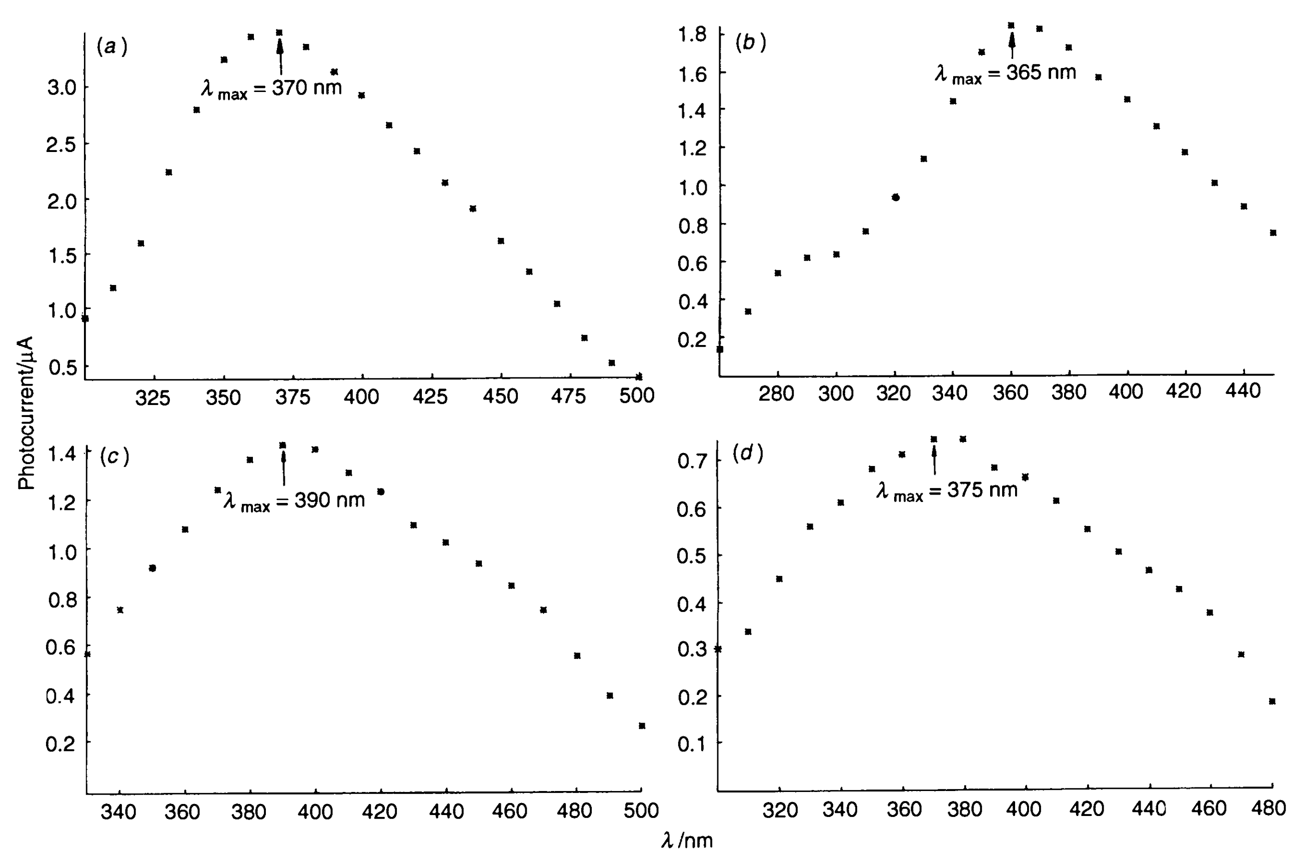

Fig. 6 Action spectra showing how the prewave photocurrent (measured at +0.60 V in all four cases, corresponding to the transport-limited plateau in the irradiated hydrodynamic voltammogram) varies with wavelength for the irradiation of (*a*) **8** measured at a flow rate of 1.8 × 10^{-3} cm^3 s^{-1} and (*b*) **13** measured at a flow rate of 2.0 × 10^{-3} cm^3 s^{-1}, (*c*) **5** measured at a flow rate of 2.3 × 10^{-3} cm^3 s^{-1} and (*d*) **9** measured at a flow rate of 1.2 × 10^{-3} cm^3 s^{-1}. The wavelength corresponding to maximum photocurrent is labelled in each case.

through the measurement of flow rate dependence of the photocurrents in each system. First, however, the photocurrents seen for the pre-wave in each case were optimised by varying the wavelength of the light used to induce the fragmentation. The resulting 'action spectra' are shown in Fig. 6. It can be seen that the optimal wavelengths are 390, 375, 370 and 365 nm for **5**, **9**, **8** and **13** respectively. These values govern the choice of wavelengths used to record Figs. 2–5. Fig. 7 shows UV/VIS spectra recorded for each of the aminocarbene complexes. Comparison with Fig. 6 indicates that the photochemical activity responsible for the dissociative loss of phosphine arises from absorption by the parent compounds in the visible region of the spectrum.

We now return to the quantitative mechanistic/kinetic considerations as revealed by the mass transport (flow rate) dependence of the photocurrents seen in Figs. 2–5 due to the oxidation of the iron-containing photofragment inferred, as above, to be $[(\eta^5\text{-}C_5H_5)Fe(CO)(CH_3CN){=}C(NHCH_2Ph)(Bu)]^+$ (**14**, derived from **8** and **13**) or $[(\eta^5\text{-}C_5H_5)Fe(CO)(CH_3CN){=}C(NHMe)Me]^+$ (**15** derived from **5** and **9**). Fig. 8 shows the observed behaviour seen for each complex studied. In all cases the solid line drawn shown is the theoretical behaviour calculated by established procedures[3,4,9,12] for a 'photo-CE' process:

$$CX + CH_3CN \xrightarrow{k} P(Ar)_3 + Y$$

$$EY - e^- \rightleftharpoons Y^+$$

where X is any of **5**, **9**, **8** or **13**. Y is either **14** (when X = **8** and **13**) or **15** (when X = **5** and **9**). The overall fate of the iron containing photofragment has been inferred to be the dication, Y^+, on the basis of the measured chemical and electrochemical reversibility of the photochemical prewave as demonstrated by mass transport corrected Tafel analysis[13] (*ca.* 60 mV/decade in all four cases).

Experiments such as those shown in Fig. 8 were repeated for various concentrations of each of the four complexes in the range 10^{-4} to 10^{-3} mol dm^{-3}. Different light intensities from 0 to 39 mW cm^{-2} were also examined. For all experiments excellent agreements with the theoretical model proposed above were found confirming further our inference of a 'photo-CE' mechanism. The best-fit rate constant, *k*, deduced for all four species showed no systematic dependence on concentration which is again consistent with the proposed mechanistic scheme. At the maximum light intensity used (39 mW cm^{-2}), the mean values for the rate constant *k* were found to be 0.068 (+/−0.008) s^{-1} (**8**), 0.066 (+/−0.002) s^{-1} (**13**), 0.055 (+/−0.007) s^{-1} (**5**) and 0.075 (+/−0.004) s^{-1} (**9**). For all species the rate constant, *k*, was found to display a linear dependence on the light intensity used as shown in Fig. 9 which again confirms our choice of mechanism. The mean rate constants quoted were used to estimate the quantum yields (at the wavelengths corresponding to maximum photocurrent) for photofragmentation of 0.06_5 (**8**), 0.07 (**13**), 0.09 (**5**) and 0.11 (**8**). These values are rather similar to those measured for the loss of phosphines from derivatives of molybdenum hexacarbonyl.[14]

Conclusions

We have conclusively demonstrated with photofragmentation voltammetry that the primary process upon photolysis of four different aminocarbenes is loss of the phosphine ligand and not the carbonyl ligand. This corroborates our previous findings

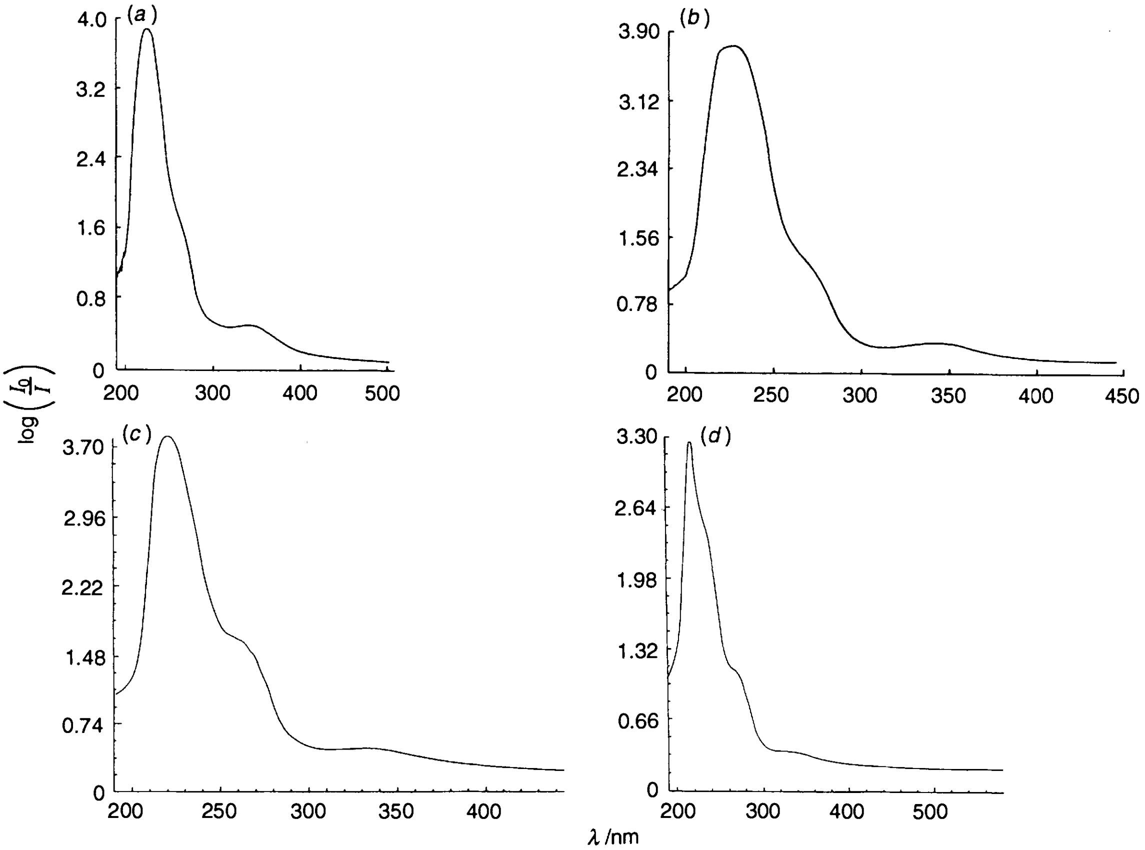

Fig. 7 UV/VIS spectra measured for (*a*) **8** where the extinction coefficient at a wavelength of 370 nm (corresponding to maximum photocurrent) is 3.8×10^3 dm^3 mol^{-1} cm^{-1}, (*b*) **13** where the extinction coefficient at a wavelength of 365 nm (corresponding to maximum photocurrent) is 3.5×10^3 dm^3 mol^{-1} cm^{-1}, (*c*) **5** where the extinction coefficient at a wavelength of 390 nm (corresponding to maximum photocurrent) is 2.2×10^3 dm^3 mol^{-1} cm^{-1}, and (*d*) **9** where the extinction coefficient at a wavelength of 375 nm (corresponding to maximum photocurrent) is 2.5×10^3 dm^3 mol^{-1} cm^{-1}

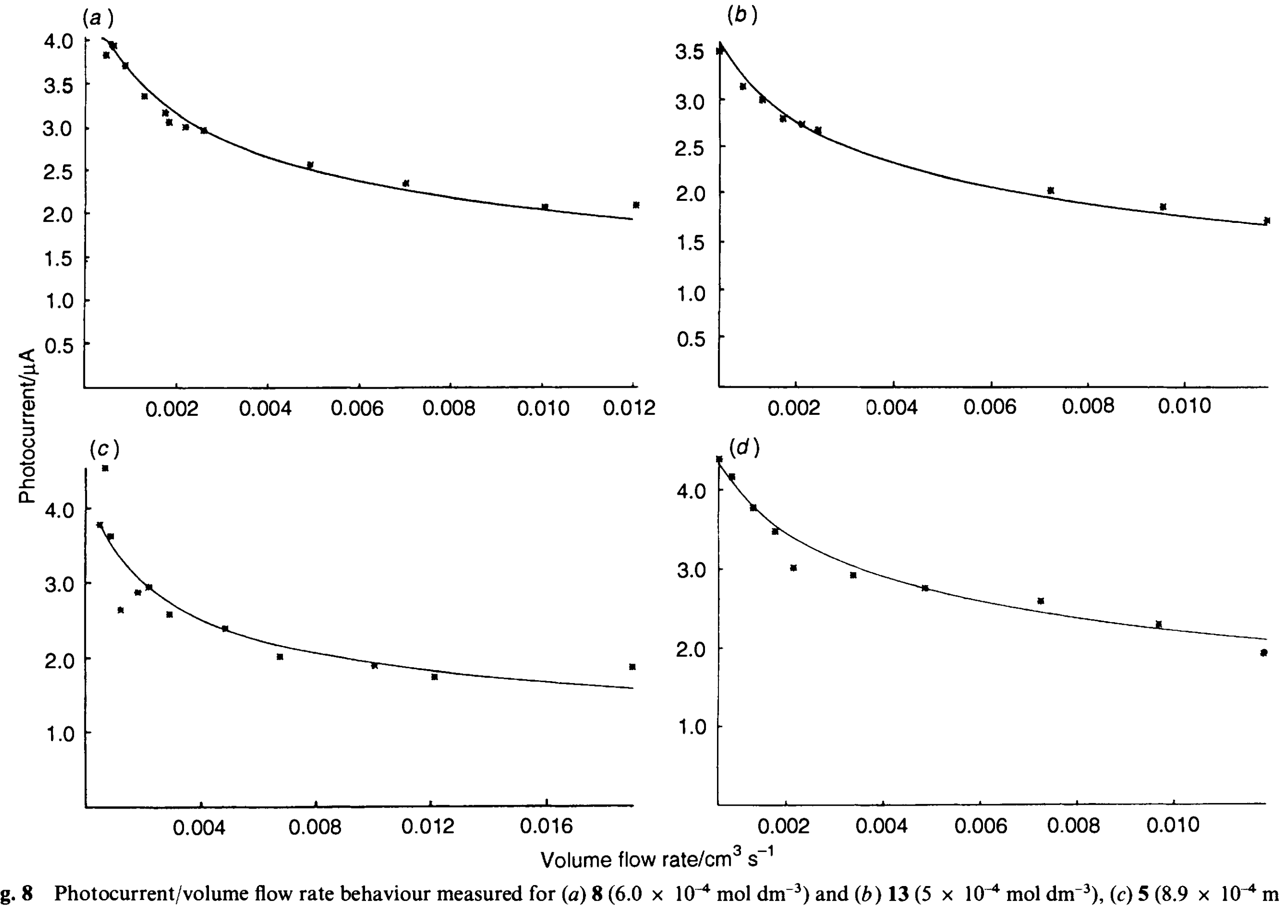

Fig. 8 Photocurrent/volume flow rate behaviour measured for (*a*) **8** (6.0×10^{-4} mol dm^{-3}) and (*b*) **13** (5×10^{-4} mol dm^{-3}), (*c*) **5** (8.9×10^{-4} mol dm^{-3}) and (*d*) **9** (7.1×10^{-4} mol dm^{-3}) using a platinum channel electrode and a light intensity of 39 mW cm^{-2}. The solid lines depicted are those calculated using standard theory[3,4,9,12] with rate constant of (*a*) 0.075 s^{-1} and (*b*) 0.065 s^{-1}, (*c*) 0.05 s^{-1} and (*d*) 0.08 s^{-1}.

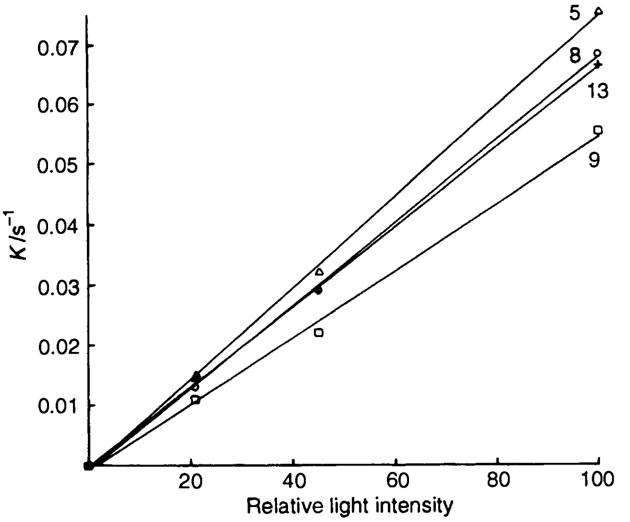

Fig. 9 The mean first order rate constants for the photofragmentation of **8**, **13**, **5** and **9** depend linearly on the light intensity used to induce fragmentation. This is consistent with the mechanism proposed.

that the epimerisation of homochiral aminocarbenes under photolytic conditions is due to phosphine loss and not carbonyl loss. These results are contrary to the accepted dogma that has hitherto pervaded the literature.

Acknowledgements

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References

1 (*a*) S. G. Davies, M. R. Metzler, K. Yanada and R. Yanada, *J. Chem. Soc., Chem. Commun.* 1993, 658; (*b*) S. G. Davies, M. R. Metzler, K. Yanada and R. Yanada, submitted for publication.
2 R. G. Compton, R. Barghout, J. C. Eklund, A. C. Fisher, S. G. Davies and M. R. Metzler, *J. Chem. Soc., Perkin Trans. 2*, 1993, 39.
3 R. G. Compton, R. Barghout, J. C. Eklund and A. C. Fisher, *Electroanalysis*, in the press.
4 R. G. Compton, R. Barghout, J. C. Eklund, A. C. Fisher, A. M. Bond and R. Colton, *J. Phys. Chem.*, 1993, **97**, 1661.
5 S. G. Davies, M. R. Metzler, W. C. Watkins, R. G. Compton, J. Booth and J. C. Eklund, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1005.
6 D. F. Shriver, *The Manipulation of Air-Sensitive Compounds*, McGraw-Hill, New York, 1969.
7 (*a*) G. J. Baird, S. G. Davies, R. H. Jones, K. Prout and P. Warner, *J. Chem. Soc., Chem. Commun.*, 1984, 745; (*b*) S. Abbott, G. J. Baird, S. G. Davies, I. M. Dorder-Hedgecock, T. R. Maberly, J. C. Walker and P. Warner, *J. Organomet. Chem.*, 1985, **289**, C13.
8 S. G. Davies, A. J. Edwards, M. R. Metzler, K. Yanada and R. Yanada, submited for publication.
9 R. G. Compton, R. G. Wellington, A. C. Fisher, D. Bethell and P. Lederer, *J. Phys. Chem.*, 1991, **95**, 4749.
10 G. Schiavon, S. Zecchin, G. Cogoni and G. Bontempelli, *J. Electroanal. Chem.*, 1973, **48**, 425.
11 A. Leiva, L. Rivera and B. Loeb, *Polyhedron*, 1991, **10**, 347.
12 A. C. Fisher, B. A. Coles, R. G. Compton, D. Bethell and S. Tripathi, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 3603.
13 W. J. Albery, *Electrode Kinetics*, Clarendon Press, Oxford, 1975.
14 D. J. Darensbourg and M. A. Murphy, *J. Am. Chem. Soc.*, 1978, **100**, 463.

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