Rearrangement of the Phosphonium Methyl Iron Complex $[FeCp(CO)_2CH_2(PEt_2H)]^+$ BPh_4^- by β-Hydrogen Elimination (Cp = Cyclopentadienyl)

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UV photolysis of the title compound yields $FeCp(CO)_2PEt_2Me^+$ by β-elimination from the phosphonium methyl moiety with evidence for an intermediate η^2-phosphinomethanide metal hydride complex.

Elimination of a β-hydrogen atom from metal alkyls is a facile route to the formation of metal–alkene hydride complexes. Pannell proposed the first observation of β-hydrogen elimination from silylmethyl complexes in the photochemical rearrangement of the dimethylsilylmethyl group in $FeCp(CO)_2CH_2SiHMe_2$.[1] In studying a similar rearrangement process, Wrighton *et al.* reported intermediates which contained both η^2-silene and hydride ligands.[2] More recently, Tilley prepared a transition metal stabilized η^2-silene hydride complex prepared *via* β-hydrogen elimination from a silylmethyl ligand.[3] We recently reported the synthesis of an η^1-phosphinomethanide complex (η^1-CH_2PR_2) and its controlled photochemical conversion to the η^2-CH_2PR_2 form.[4] In this communication we report that the precursor for the η^1 complex, $FeCp(CO)_2CH_2PHEt_2^+$ undergoes a photochemical rearrangement which provides the first evidence of hydrogen elimination from a β-phosphonium to form a coordinated η^2-CH_2PR_2 structure.

Room temperature photolysis of a bright yellow CH_2Cl_2 or CD_2Cl_2 solution of phosphonium cation **1** with a tungsten filament lamp provides the rearranged phosphine complex $FeCp(CO)_2PEt_2Me^+$ **3** in quantitative yield by NMR and in 74% isolated yield. When the photolysis is carried out under CO (2 atm) the $^{31}P\{^1H\}$ NMR spectrum shows clean replacement of the single starting material resonance at δ 37.87 with a new resonance at δ 53.17 which is assigned to the product. The ^1H NMR spectrum shows clean formation of product methyl and cyclopentadienyl resonances at δ 1.36 and 4.77, respectively, each clearly coupled to phosphorus. No intermediates are detected by $^{31}P\{^1H\}$ and ^1H NMR under these conditions and no colour change is visible to the eye. In contrast, when the photolysis is carried out in a sealed vessel under vacuum, the photolysis initially yields a bright green solution which persists for several minutes at room temperature. The ^1H NMR spectrum of this solution exhibits an upfield resonance at δ −2.95 in addition to a number of other new peaks. This high field ^1H NMR signal suggests the formation of a metal hydride complex. In addition, a small peak is observed in the ^{31}P NMR at δ 47.39 which may also be assigned to the intermediate phosphametallacyclopropane-hydride complex. These resonances disappear as the green colour of the solution fades and only the signals for **3** remain.

A plausible mechanism for this interconversion is illustrated in Scheme 1. Initial photochemical loss of CO is followed by β-elimination from the β-P^+Et_2H moiety to give the coordinated ylide structure **2a** which, together with **2b** are green.† Ylide insertion into the Fe–H bond with the hydride attacking the carbon followed by CO uptake leads to the yellow coordinated phosphine cation **3**. This mechanism is similar to the mechanism originally proposed by Pannell with the substitution of phosphorus for silicon.

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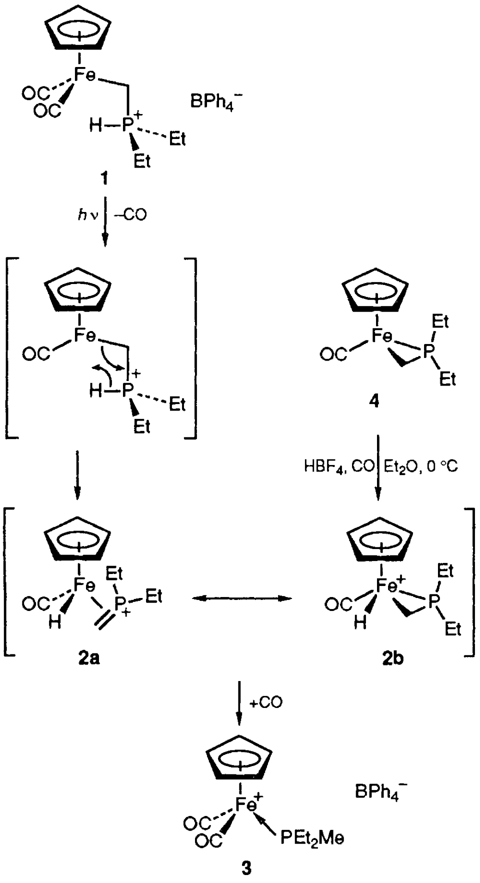
† A referee has made the suggestion that **2** may be a phosphine complex with an agostic methyl–Fe interaction: $Cp(CO)\overline{Fe^+PEt_2CH_2{-}H}$. This alternative structure would also be accessible *via* the proposed β-elimination process. This possibility is consistent with our current data and warrants further investigation.



Scheme 1

In an effort to determine if CO loss was involved in the conversion of **1** to **3**, phosphonium **1** was photolysed in CD_2Cl_2 under ^{13}CO (~230 Torr). Although rapid photosubstitution of CO in the product and starting material are observed, at less than 5% conversion the ^{31}P NMR spectrum of product **3** shows a prominent doublet at δ 53.17 accounting for 52% of the product which arises from coupling to a single ^{13}CO. A smaller amount (36%) of unsubstituted material is present, perhaps due to reaction with the relatively high concentration of ^{12}CO released during the photolysis reaction.[5]‡ The remainder (12%) is doubly labelled material. While not conclusive, this experiment suggests that loss of CO is a significant step in the rearrangement of **1** to **3**.

Further support for the proposed mechanism comes from protonation of the η^2-CH_2PEt_2 complex **4** in CH_2Cl_2 solution with $HBF_4 \cdot OMe_2$ under CO (1 atm) at −78 °C. The phosphine cation **3** is isolated from this reaction in 97% yield. As illustrated in Scheme 1, protonation of **4** at the iron allows entry into the reaction manifold involving the cationic intermediates **2a** and **2b** which are similarly formed upon photolysis of **1**. Reductive elimination as previously described gives the phosphine cation **3**.

It is clear that β-elimination from β-heteroatom substituents are a common reaction step and may have wide synthetic applications towards formation of multiply bonded species.

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‡ With an initial concentration of **1** of 42 mmol dm^{-3}, the concentration of ^{12}CO generated at 5% conversion is 2.1 mmol dm^{-3}. From the data in ref. 5, the concentration of ^{13}CO in solution at 230 Torr is estimated to be 3.5 mmol dm^{-3}. Under the reaction conditions, there was not sufficient time for the gas–liquid equilibrium to be established. Thus, the concentration of ^{12}CO was sufficiently high to give a substantial amount of unlabelled product.