Photolabilisation of the Triphenylphosphine Ligand in the Aminocarbene Complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\text{=}C(NHCH_2Ph)Me]^+BF_4^-$

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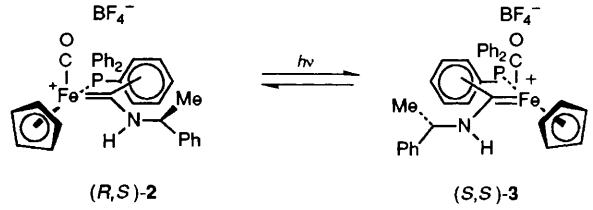
Photolysis of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\text{=}C(NHCH_2Ph)Me]^+BF_4^-$ and related aminocarbene complexes leads to exclusive loss of the phosphine ligand rather than the carbon monoxide ligand.

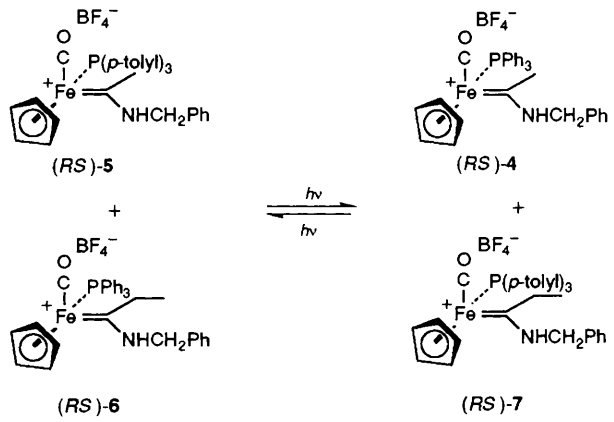
The fragment $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]$ has been established as a powerful chiral auxiliary for asymmetric synthesis imparting high stereoselectivities during reactions of attached acyl derived enolates[1–3] and enol ethers.[4–6] In order to extend the scope of this iron chiral auxiliary we have embarked on a study of the corresponding nitrogen analogues. We describe here an investigation of the configurational stability of the iron stereogenic centre in $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\text{=}C(NHCH_2Ph)Me]^+BF_4^-$ and related aminocarbene complexes.

Following Davison and Reger's procedure,[7] sequential treatment of racemic (*RS*)-$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe]$ **1** with trimethyloxonium tetrafluoroborate, to generate the corresponding methoxycarbene, and (*S*)-α-methylbenzylamine generated a 1:1 mixture of the aminocarbene diastereoisomers (*R,S*)-**2**† and (*S,S*)-**3**. Starting from homochiral (*R*)-**1** and (*S*)-**1** led to the formation of diastereoisomerically pure (*R,S*)-**2** and (*S,S*)-**3** with a single crystal X-ray analysis of (*R,S*)-**2** unambiguously confirming the assigned absolute configurations.[8] Similar coupling of (*RS*)-**1** with benzylamine gave (*RS*)-**4**. All other aminocarbenes described herein were prepared in analogous fashion from the appropriate combinations of iron acyls and amines. The overall yields for these preparations were in the range 75–90% and all compounds were fully characterised.

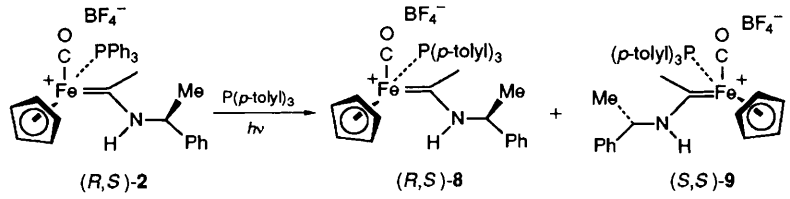
In the absence of light and air solutions [MeOH–H_2O, MeOH, EtOH, tetrahydrofuran (THF), CH_2Cl_2] of (*R,S*)-**2** and (*S,S*)-**3** are indefinitely stable at 20 °C. Upon irradiation (sunlight or standard desk lamp) under nitrogen (*R,S*)-**2** and



† The descriptor for the absolute configuration at iron is given first followed by that for the α-methylbenzyl moiety.



Scheme 1



Scheme 2

(*S,S*)-**3** interconvert slowly giving after *ca.* 72 h a 1 : 1 mixture. This epimerisation process could involve loss of stereochemical integrity at either the iron or α-methylbenzyl stereogenic centre. Converting (*S*)-α-methylbenzylamine [> 97% enantiomeric excess (e.e.)] to (*R,S*)-**2**, photoepimerising it to a 1 : 1 mixture with (*S,S*)-**3** and decomplexing this mixture by exposure to air gave (*S*)-(−)-*N*-(α-methylbenzyl)acetamide (89% yield, >97% e.e.),[9] which unambiguously establishes epimerisation at the iron stereogenic centre.

Irradiation of an equimolar mixture of (*RS*)-**5** and (*RS*)-**6** gave after 72 h an essentially equimolar mixture of four compounds, the starting complexes together with (*RS*)-**4** and (*RS*)-**7** for each of which authentic samples were synthesised as described above (Scheme 1).

The above exchange experiment is consistent with one mechanism of epimerisation being photolabilisation of the phosphine ligand: other mechanisms such as reversible carbon monoxide loss are not precluded however. It was reasoned that if photolabilisation of the phosphine ligand was the only epimerisation mechanism operating then irradiation of (*R,S*)-**2** in the presence of an excess of tri(*p*-tolyl)phosphine should lead to the formation only of (*R,S*)-**8** and (*S,S*)-**9**. All other mechanisms would lead to the formation of (*S,S*)-**3**. In the event, on irradiation of (*R,S*)-**2** in the presence of an excess of tri(*p*-tolyl)phosphine a steady build up of equal amounts of (*R,S*)-**8** and (*S,S*)-**9** was observed with these being essentially the only products (>98%) (Scheme 2).

Qualitatively the rate of epimerisation is unaffected by the concentration of free phosphine and this coupled with the immediate formation from (*R,S*)-**2** of (*R,S*)-**8** and (*S,S*)-**9** in equal amounts is consistent with a dissociative mechanism where phosphine loss preceeds phosphine addition. An associative mechanism, involving phosphine coordination (presumably with the cyclopentadienyl changing from η^5 to η^3) prior to phosphine loss, would have been expected to proceed *via* inversion to (*S,S*)-**9** or to lead to epimerisation and the formation of (*S,S*)-**3**.

In conclusion we have demonstrated that on irradation of aminocarbenes of the type $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)=C(NHCH_2Ph)Me]^+BF_4^-$ the primary photoreaction is loss of the triphenylphosphine ligand. This goes against the accepted dogma that complexes containing both phosphine and carbon monoxide ligands preferentially lose the latter on photolysis, although a few examples of photosubstitutions of phosphines in carbonyl containing complexes have been reported.[10] We are currently investigating the generality of this process.

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