Photoinduced configurational instability at iron in the aminocarbene complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)\{=C(NHR^2)(CH_2R^1)\}]^+BF_4^-$

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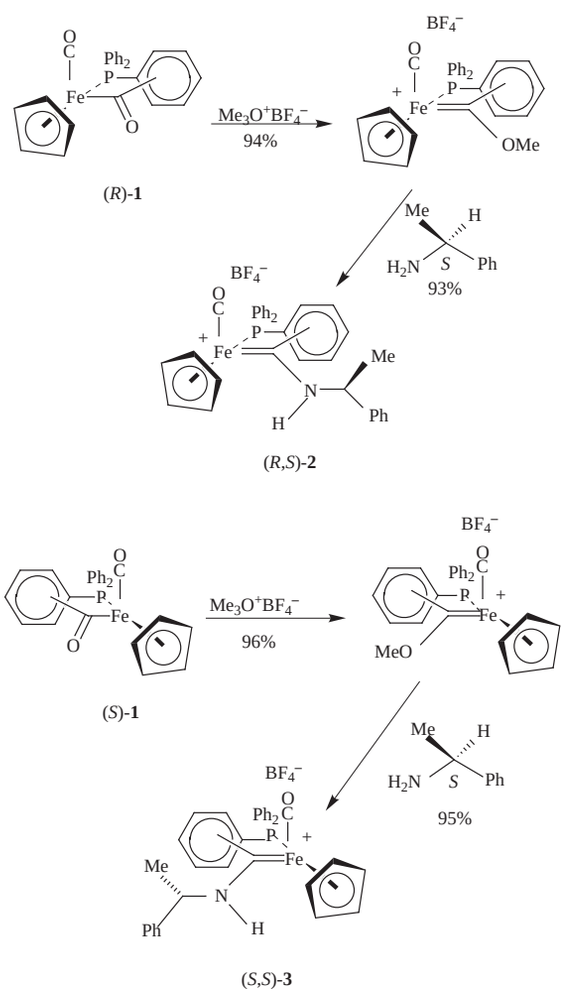
Photoinduced epimerisation of chiral iron aminocarbene complexes of the type $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)\{=C(NHR^2)(CH_2R^1)\}]^+BF_4^-$ [L = PPh_3, P(*p*-tolyl)$_3$; R^1 = H, Me; R^2 = CH_2Ph, CH(Me)Ph] has been observed in 10% H_2O–MeOH, MeOH, EtOH, THF and CH_2Cl_2 at room temperature. Exchange experiments have unambiguously established that reversible phosphine ligand (L) dissociation rather than reversible loss of the carbon monoxide ligand is the only mechanism operating.

Introduction

We have recently described the synthesis of the homochiral aminocarbene complexes (*R*,*S*)-**2** and (*S*,*S*)-**3** by sequential conversion of the enantiomerically pure iron acetyl complexes (*R*)-**1** and (*S*)-**1** to the corresponding methoxycarbene derivatives and treatment with (*S*)-α-methylbenzylamine (Scheme 1).[1] The configurational assignments to (*R*,*S*)-**2** and (*S*,*S*)-**3** were unambiguously established by the X-ray crystal structure of the former complex.



Scheme 1

Davison and Reger[2] have also reported the synthesis of (*R*,*S*)-**2** and (*S*,*S*)-**3** by a similar route from the racemic iron acetyl complex (*RS*)-**1** and (*S*)-α-methylbenzylamine and separation of the resulting diastereoisomers by fractional crystallisation. Furthermore these authors commented that (*R*,*S*)-**2** and (*S*,*S*)-**3** are stable to epimerisation, being unchanged on heating in acetone at reflux. We describe here the photoinduced configurational instability at iron of aminocarbene complexes of the type $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)\{=C(NHR^2)(CH_2R^1)\}]^+BF_4^-$ including (*R*,*S*)-**2** and (*S*,*S*)-**3** and establish a mechanism for this type of epimerisation. Part of this work has been previously communicated.[3]

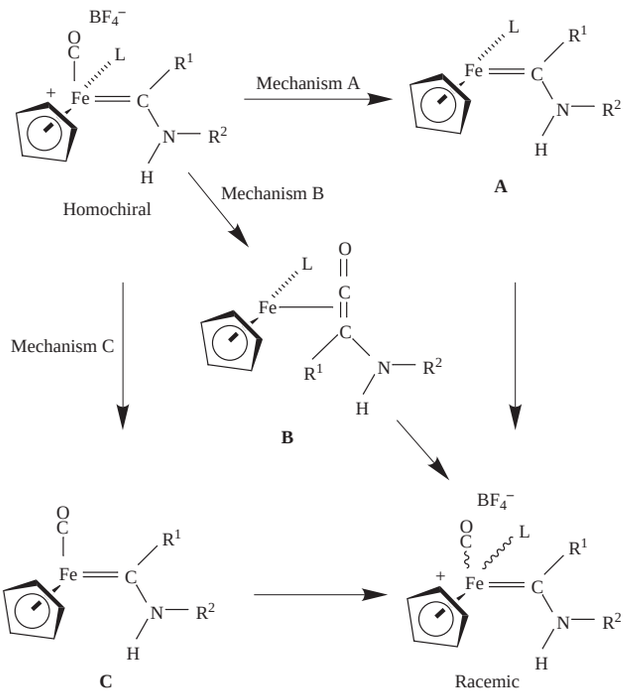
Results and discussion

In the dark in the solid state or in solution (10% H_2O–MeOH, MeOH, EtOH, THF or CH_2Cl_2) at 20 °C the complexes (*R*,*S*)-**2** and (*S*,*S*)-**3** are indefinitely stable to epimerisation. In solution (*R*,*S*)-**2** and (*S*,*S*)-**3** are very air sensitive, decomposing readily to (*S*)-(−)-*N*-(α-methylbenzyl)acetamide and triphenylphosphine oxide. These solutions are, however, indefinitely stable if air is rigorously excluded. In solution (10% H_2O–MeOH, MeOH, EtOH, THF or CH_2Cl_2), however, (*R*,*S*)-**2** and (*S*,*S*)-**3** epimerise under a blanket of nitrogen when exposed to either sunlight or photoirradiation from a standard desk-lamp. The epimerisation process is usually observed to have gone to completion after 72 h of irradiation forming 1:1 mixtures of diastereoisomers **2** and **3**. Since both diastereoisomers had been independently synthesised (Scheme 1) and showed unique cyclopentadienyl hydrogen resonances in their ^{1}H NMR spectra the product mixture compositions were readily established.

The epimerisation process described above could involve the loss of stereochemical integrity at either or both of the iron or α-methylbenzylamine stereogenic centres. That the epimerisation was occurring exclusively at the iron stereogenic centre was established by completely epimerising (*R*,*S*)-**2** by irradiation for 72 h and decomposing the product mixture in the presence of air. The isolated products were triphenylphosphine oxide and (*S*)-(−)-*N*-(α-methylbenzyl)acetamide (89%) the latter in essentially enantiomerically pure form (>97% ee). For direct comparison purposes authentic samples of *N*-(α-methylbenzyl)acetamide in both enantiomerically pure (*S*)[4] and racemic[5] form were prepared from (*S*)- and (*RS*)-*N*-α-methylbenzylamine respectively and acetic anhydride. Furthermore, when the epimerisation reaction was followed in CD_3OD or 10% D_2O–CD_3OD by ^{1}H NMR spectroscopy the hydrogens at the benzylic positions did not exchange with deuterium, consistent with this position not being epimerised under the

reaction conditions. The epimerisation process has thus been unambiguously established as interconverting (*R*,*S*)-**2** and (*S*,*S*)-**3**.

Three mechanisms were postulated for the above epimerisation process. The first (mechanism A in Scheme 2) involves

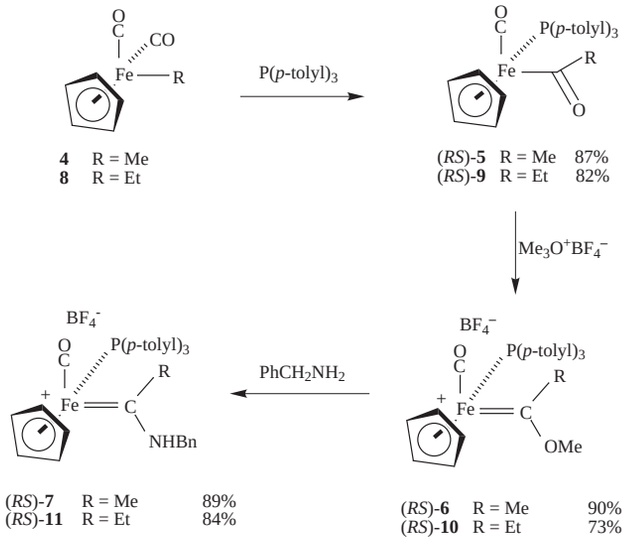


Scheme 2

photochemically promoted reversible loss of the carbon monoxide ligand with epimerisation occurring due to the formation of the coordinatively unsaturated intermediate **A** (Scheme 2). This photoinduced behaviour of dissociation–reassociation of carbon monoxide is well established in the literature.[6] Reversible formation of ketene ligands *via* migration of carbene ligands to carbon monoxide ligands is also becoming an increasingly commonplace reaction.[7–10] Thus the second mechanism considered involves the reversible formation of the ketene intermediate **B** (Scheme 2). The third mechanism envisaged involves photolytically promoted phosphine elimination to give intermediate **C** with subsequent reassociation of the phosphine to form the observed racemate. Photolytically promoted phosphine displacement over carbon monoxide in organometallic complexes has, to the best of our knowledge, not been reported in the literature, although there have been several reports[11–13] of photolytically promoted phosphine displacement reactions in organometallic complexes not containing carbon monoxide ligands.

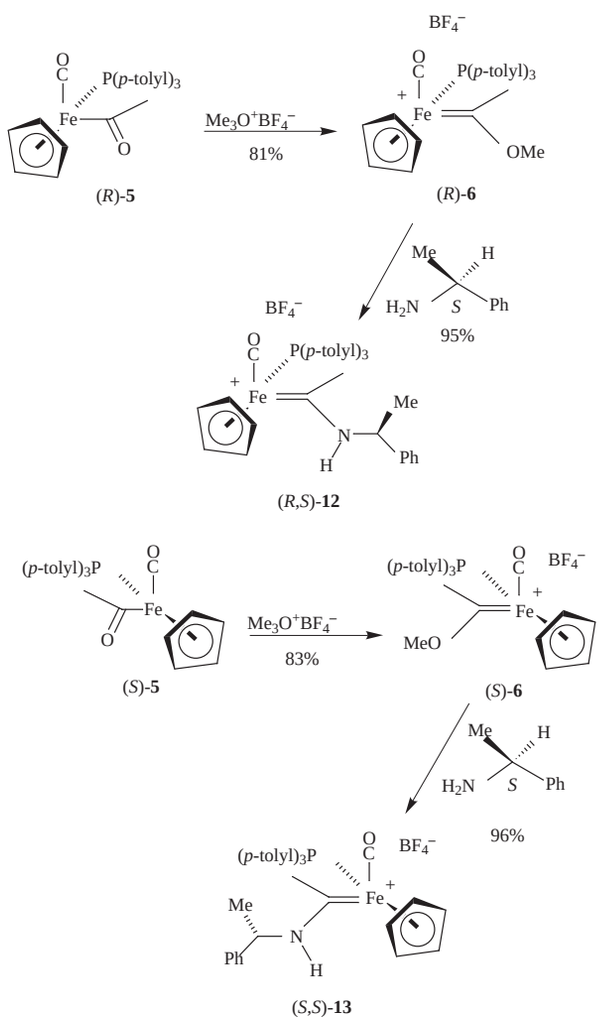
After a number of unproductive attempts to try to establish the apparently more likely mechanisms A and B we turned our attention to mechanism C. If mechanism C is operating then exchange of the phosphine ligand between complexes and free phosphine in solution must be occurring. To establish whether this was indeed the case a series of complexes incorporating the tri(*p*-tolyl)phosphine as ligand analogous to the previously described[14] triphenylphosphine series was prepared.

Thermolysis of the known iron methyl complex [(η^5-C_5H_5)-$Fe(CO)_2Me$][14,15] **4** in the presence of tri(*p*-tolyl)phosphine generated the racemic acetyl complex (*RS*)-**5** in 87% yield (Scheme 3). Racemic (*RS*)-**5** was *O*-methylated to generate the methoxycarbene complex (*RS*)-**6** and was treated with excess benzylamine to form the aminocarbene complex (*RS*)-**7**. An analogous sequence converted the known iron ethyl complex [(η^5-C_5H_5)$Fe(CO)_2Et$][15] **8** *via* the propanoyl complex (*RS*)-**9** and the corresponding methoxycarbene derivative (*RS*)-**10** to the aminocarbene (*RS*)-**11** (Scheme 3).



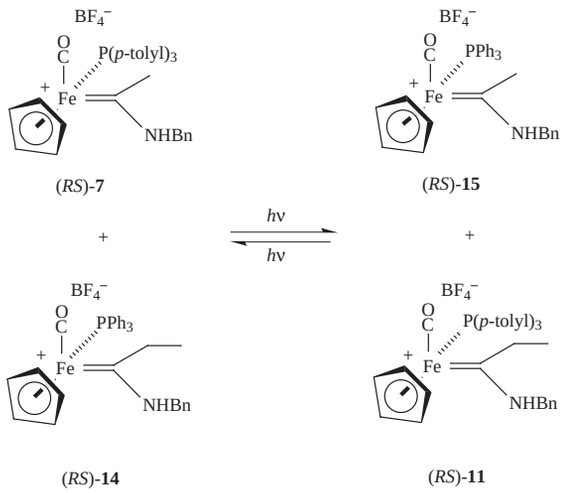
Scheme 3

The racemic acetyl complex (*RS*)-**5** was resolved by the previously reported method[16] involving kinetic resolution of the derived lithium enolate with enantiomerically pure camphor. Enantiomerically pure (*R*)-**5** and (*S*)-**5** were each converted to the corresponding methoxycarbene derivatives (*R*)-**6** and (*S*)-**6** (Scheme 4). Treatment of (*R*)-**6** with (*S*)-α-methylbenzylamine generated the aminocarbene complex (*R*,*S*)-**12** as a single enantiomerically pure diastereoisomer. Similar treatment of (*S*)-**5** with (*S*)-α-methylbenzylamine gave the diastereoisomerically pure epimer (*S*,*S*)-**13** (Scheme 4).



Scheme 4

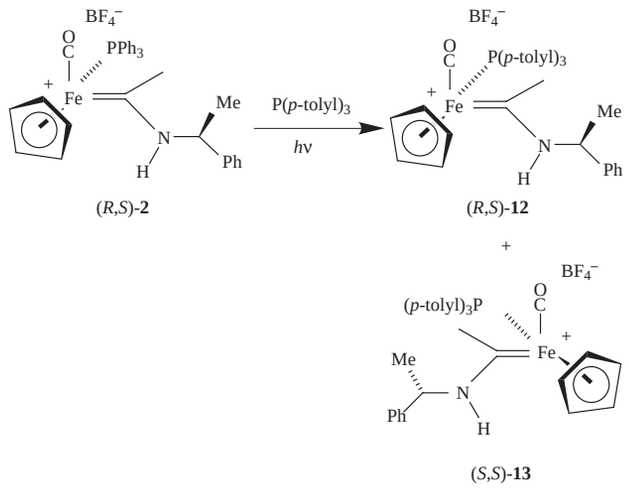
Irradiation of an equimolar mixture of (*RS*)-**7** and (*RS*)-**14** for 72 h led to a mixture of the two starting complexes and (*RS*)-**15** and (*RS*)-**11** in essentially equal amounts (Scheme 5).



Scheme 5

Although this mixture of complexes could not be separated into its individual components by either column chromatography or selective recrystallisation, the ^{1}H NMR spectrum of this mixture showed four cyclopentadienyl doublets in the region of δ 4.5–5.0 which is consistent with those expected for the anticipated aminocarbene complexes. Moreover, the presence of each complex was confirmed when a mixture of these compounds (5 mg of each complex independently synthesised from their respective methoxycarbenes) was examined by ^{1}H NMR spectroscopy and found to have an identical spectrum to the photolysis mixture.

Although the above experiment (Scheme 5) is entirely consistent with the phosphine ligand being labile under the photolytic irradiation conditions it does not preclude the other two mechanisms from occurring as competing processes. To investigate this further a solution of enantiomerically pure (*R*,*S*)-**2** and tri(*p*-tolyl)phosphine (excess) was photolysed, with aliquots of this reaction mixture being examined by ^{1}H NMR spectroscopy at regular time intervals. It was reasoned that if only the phosphine dissociation mechanism (C, Scheme 2) was operating then as the reaction proceeded there should be a steady build up of both (*R*,*S*)-**12** and (*S*,*S*)-**13**. There should be no epimerisation, however, of the enantiomerically pure starting material (*R*,*S*)-**2** early in the reaction, as the amount of tri(*p*-tolyl)phosphine present in the reaction mixture would be far in excess of any triphenylphosphine liberated due to the photolysis. If either of the other mechanisms (A or B, Scheme 2) were operating simultaneously the result would be an increasing amount of epimerisation of (*R*,*S*)-**2** to (*S*,*S*)-**3**. It was also anticipated that as the reaction proceeded over any period in time that the concentration of triphenylphosphine would steadily increase relative to that of the tri(*p*-tolyl) derivative which might result in the later stages in some recoordination of PPh_3 with the overall result of epimerisation of the starting complex to (*S*,*S*)-**3**. In the event, reaction of (*R*,*S*)-**2** and tri(*p*-tolyl)-phosphine showed a steady build up of equal amounts of the two diastereoisomers (*R*,*S*)-**12** and (*S*,*S*)-**13** with no apparent epimerisation of the starting material early in the reaction (Scheme 6). The first traces of epimerised product (<2%) were only observed after about 48 h of reaction time after which the reaction had essentially gone to completion. 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*)-**12** and (*S*,*S*)-**13** in equal amounts is consistent with a dissociative mechanism where phosphine loss precedes phosphine addition. An associative mechanism, involving



Scheme 6

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*)-**13** or to lead to epimerisation and the formation of (*S*,*S*)-**3**. These results unambiguously establish that the sole pathway by which the epimerisation process occurs in the complexes $[(\eta^5\text{-}C_5H_5)\text{-}Fe(CO)(L)\{=C(NHR^2)(CH_2R^1)\}]^+BF_4^-$ is *via* reversible dissociation of the phosphine ligand (L).

Conclusions

We have shown that enantiomerically pure iron aminocarbene complexes of the type $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)\{=C(NHR^2)\text{-}(CH_2R^1)\}]^+BF_4^-$ readily epimerise under photolysis conditions in a number of solvents. Exchange experiments have unambiguously established that reversible phosphine ligand (L) dissociation is the only mechanism operating, *i.e.* upon photolysis these complexes lose the phosphine ligand in preference to the carbon monoxide ligand.[17] This goes against the accepted dogma that complexes containing both phosphine and carbon monoxide ligands preferentially lose the latter on photolysis.[6,17] We are currently investigating the generality of this process.

Experimental

All reactions and purifications were performed under a nitrogen atmosphere using standard vacuum line and Schlenk tube techniques.[18] All solvents were deoxygenated before use. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Acetonitrile and dichloromethane were distilled from calcium hydride. Light petroleum for column chromatography refers to the redistilled hydrocarbon fraction boiling at 40–60 °C. Unless otherwise indicated, all commercially available reagents were used as received. Column chromatography was performed on grade I (activated) basic alumina or on silica gel (Merck Kieselgel 60). For organometallic complexes all chromatography was carried out under nitrogen. Elemental analyses were carried out by V. Lamburn of the Dyson Perrins Laboratory. Infrared spectra were recorded on either a Perkin-Elmer 781 or on a Perkin-Elmer 1750 Fourier Transform spectrophotometer in dichloromethane solutions using 1 mm NaCl cells unless otherwise stated. Abbreviations used: s, strong; vs, very strong. NMR spectra were recorded on either a Varian-Gemini 200 (200 MHz) or a Bruker AM500 (500.13 MHz) spectrometer in $CDCl_3$ solutions. Unless otherwise stated ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker AM250 spectrometer (at 62.90, 235.35, 125.76 MHz respectively) in $CDCl_3$ solutions. ^{1}H and ^{13}C NMR spectra were referenced to tetramethylsilane using internal solvent peaks. *J* Values

are given in Hz. The origin of the two peaks observed in the ^{19}F NMR spectra for the BF_4^- salts is a boron isotope shift. In the Experimental section, ^{13}C, ^{19}F and ^{31}P NMR data are described in terms of the proton decoupled (broad band) spectra. Abbreviations used: b, broad signal; d, doublet; m, multiplet; q, quartet; s, singlet; t, triplet. Mass spectra were recorded on V.G. Micromass ZAB1F or MM30F instruments using FAB techniques (DTTDTE matrix) for organometallic compounds. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter in the solvents indicated at 20 °C.

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2Me]$ **4**,[14] $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Et]$ **8**,[15] (*R*,*S*)-$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{=C(Me)(NHCH(Me)Ph)\}]^+BF_4^-$ (*R*,*S*)-**2**[1] and (*S*,*S*)-$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{=C(Me)(NHCH(Me)Ph)\}]^+BF_4^-$ (*S*,*S*)-**3**,[1] were synthesised by literature procedures. (*S*)-(−)-α-Methylbenzylamine was purchased from Aldrich $[a]_D$ (neat) −39.0, this corresponds to an optical purity of 95.0% {lit.,[19a] $[a]_D$ (neat) −40.6}. However, with Parker's method[19b] using ^1H NMR spectroscopy with (*R*)-(−)-*O*-acetylmandelic acid an enantiomeric excess of 99.6% was obtained.

(*RS*)-$[(\eta^5\text{-}C_5H_5)Fe(CO)\{P(p\text{-tolyl})_3\}COMe]$ (*RS*)-5

A nitrogen degassed solution of **4** (1.00 g, 4.64 mmol) and tri-(*p*-tolyl)phosphine (1.00 g, 3.29 mmol) in acetonitrile (25 ml) was heated under reflux for 23.5 h to give a bright red solution. Concentration *in vacuo* followed by chromatography on silica gel (light petroleum–diethyl ether; 4:1) afforded (*RS*)-**5** as an orange solid (1.27 g, 87%). Recrystallisation from diethyl ether–pentane gave red microneedles, mp 157–160 °C (Found: C, 70.29; H, 5.86; P, 6.22. $C_{29}H_{29}FeO_2P$ requires C, 70.17; H, 5.89; P, 6.24%); ν_{max} 1910 (Fe–CO), 1601 (Fe–COMe); δ_H 2.34 (3H, s, Fe–CO*Me*), 2.37 (9H, s, tolyl methyls), 4.42 (5H, s, C_5H_5), 7.17 (6H, d, *J* 7.4, H_{meta} to P), 7.38 (6H, dd, J_{PH} 10.0, J_{HH} 8.2, H_{ortho} to P); δ_C 21.26 (s, tolyl methyls), 51.72 (d, *J* 7.1, Fe–CO*C*H_3), 85.25 (s, *C*$_5H_5$), 128.75 (d, *J* 9.2, C_{meta} to P), 133.31 (d, *J* 9.3, C_{ortho} to P), 133.53 (d, *J* 45.7, C_{ipso} to P), 139.62 (s, C_{ipso} to Me), 220.85 (d, *J* 21.3, Fe–CO), 276.51 (d, *J* 22.1, Fe–*C*OCH_2CH_3); δ_P 70.18; *m*/*z* 497 (M^+ + H, 11), 481 (M − CH_3, 14), 468 (M − CO, 4), 454 (7), 440 (34), 425 (100), 375 (7), 360 (9), 305 (44), 211 (18). This racemate was resolved into its *S* and *R* components using the previously reported method[16] by treatment of the racemic enolate with enantiomerically pure camphor.

(*R*)-$[(\eta^5\text{-}C_5H_5)Fe(CO)\{P(p\text{-tolyl})_3\}COMe]$ (*R*)-**5**, recrystallisation from diethyl ether–pentane gave red microneedles, mp 150–152 °C (Found: C, 70.01; H, 5.99; P, 5.96. $C_{29}H_{29}FeO_2P$ requires C, 70.17; H, 5.89; P, 6.24%); $[a]_D$ (conc. 0.245, benzene) −140.

(*S*)-$[(\eta^5\text{-}C_5H_5)Fe(CO)\{P(p\text{-tolyl})_3\}COMe]$ (*S*)-**5**, recrystallisation from diethyl ether–pentane gave red microneedles, mp 158–160 °C (Found: C, 70.48; H, 5.76; P, 6.12. $C_{29}H_{29}FeO_2P$ requires C, 70.17; H, 5.89; P, 6.24%); $[a]_D$ (conc. 0.19, benzene) +140.5.

(*RS*)-$[(\eta^5\text{-}C_5H_5)Fe(CO)\{P(p\text{-tolyl})_3\}COEt]$ (*RS*)-9

A nitrogen degassed solution of **8** (0.10 g, 0.49 mmol) and tri-(*p*-tolyl)phosphine (0.16 g, 0.54 mmol) in acetonitrile (10 ml) was heated under reflux for 18.5 h to give a bright red solution. Concentration *in vacuo* followed by chromatography on silica gel (light petroleum–diethyl ether; 4:1) afforded (*RS*)-**9** as an orange solid (0.25 g, 82%). Recrystallisation from diethyl ether–pentane gave red globular crystals, mp 161–164 °C (Found: C, 70.70; H, 6.15; P, 6.02. $C_{30}H_{31}FeO_2P$ requires C, 70.60; H, 6.13; P, 6.07%); ν_{max} 1909 (Fe–CO), 1602 (Fe–COEt); δ_H 0.62 (3H, t, *J* 6.7, Fe–$COCH_2CH_3$), 2.36 (9H, s, tolyl methyls), 2.53–2.64 (1H, m, Fe–$COCH_2CH_3$), 2.75–2.84 (1H, m, Fe–$COCH_2CH_3$), 4.40 (5H, s, C_5H_5), 7.15 (6H, d, *J* 6.7, H_{meta} to P), 7.38 (6H, dd, J_{PH} 9.8, J_{HH} 7.8, H_{ortho} to P); δ_C 9.61 (s, Fe–$COCH_2CH_3$), 21.22 (s, tolyl methyls), 58.80 (d, *J* 7.2, Fe–$COCH_2CH_3$), 85.10 (s, C_5H_5), 128.68 (d, *J* 9.5, C_{meta} to P), 133.31 (d, *J* 9.7, C_{ortho} to P), 133.33 (d, *J* 45.7, C_{ipso} to P), 139.54 (s, C_{ipso} to Me), 220.85 (d, *J* 30.9, Fe–CO), 277.26 (d, *J* 31.2, Fe–*C*OCH_2CH_3); δ_P 70.23; *m*/*z* 511 (M^+ + H, 15), 482 (M − CO, 14), 481 (M − CH_2CH_3, 38), 454 (7), 425 (100), 360 (11), 305 (46), 211 (15).

Synthesis of methoxycarbenes

(*RS*)-$[(\eta^5\text{-}C_5H_5)Fe(CO)\{P(p\text{-tolyl})_3\}\{=C(Me)(OMe)\}]^+BF_4^-$ (*RS*)-6. A solution of (*RS*)-**5** (1.00 g, 2.01 mmol) in dichloromethane (25 ml) was cannulated into a round bottomed flask containing trimethyloxonium tetrafluoroborate[20] (0.39 g, 2.62 mmol, dried at 60 °C *in vacuo* for 3 h) and the resultant mixture stirred at room temperature for 17 h. The mixture was then cannulated through filter paper, concentrated to 5 ml and added dropwise to diethyl ether (100 ml) cooled to 0 °C. The resultant yellow precipitate was washed with diethyl ether (3 × 20 ml) and dried *in vacuo* to give (*RS*)-**6** as a yellow solid (1.21 g, 90%). Recrystallisation from CH_2Cl_2–Et_2O gave yellow microneedles, mp 181–184 °C (dec) (Found: C, 59.93; H, 5.46; P, 5.36. $C_{30}H_{32}BF_4FeO_2P$ requires C, 60.23; H, 5.40; P, 5.18%); ν_{max} 1978 (CO) and 1055 (BF_4^-); δ_H 2.42 (9H, s, tolyl methyls), 2.81 (3H, s, Fe=C–*Me*), 4.02 (3H, s, Fe=C–O*Me*), 4.87 (5H, d, J_{PH} 1.3, C_5H_5), 7.10–7.20 [6H, m, P(tolyl)$_3$], 7.25–7.35 [6H, m, P(tolyl)$_3$]; δ_C 21.30 (s, tolyl methyls), 45.96 (s, Fe=C–*Me*), 65.42 (s, Fe=C–O*Me*), 87.80 (s, C_5H_5), 129.72 (d, J_{PC} 49.5, C_{ipso} to P), 129.76 (d, *J* 9.7, C_{meta} to Me), 132.72 (d, J_{PC} 9.0, C_{ortho} to P), 141.80 (s, C_{ipso} to P), 215.72 (d, J_{PC} 27.8, Fe–CO), 268.93 (d, J_{PC} 21.4, Fe=C); δ_P 60.31; δ_F −154.80 and −154.85 (1:3); *m*/*z* 511 (M^+, 98), 483 (M − CO, 90), 497 (11), 457 (16), 425 (100), 360 (12), 337 (76), 321 (10), 305 (65), 245 (15), 213 (42), 197 (12), 179 (33), 121 (17).

(*R*)-$[(\eta^5\text{-}C_5H_5)Fe(CO)\{P(p\text{-tolyl})_3\}\{=C(Me)(OMe)\}]^+BF_4^-$ (*R*)-6. Methylation of (*R*)-**5** (0.57 g, 1.15 mmol) with $Me_3O^+BF_4^-$ (0.21 g, 1.38 mmol) in CH_2Cl_2 (15 ml) for 19 h afforded after work-up (*R*)-**6** as a bright yellow solid (0.56 g, 81%). Recrystallisation from CH_2Cl_2–Et_2O gave yellow microneedles, mp 183–185 °C (dec) (Found: C, 60.27; H, 5.38; P, 5.03. $C_{30}H_{32}BF_4FePO_2$ requires C, 60.23; H, 5.40; P, 5.18%); $[a]_D$ −221.3 (conc. 0.155, CH_2Cl_2).

(*S*)-$[(\eta^5\text{-}C_5H_5)Fe(CO)\{P(p\text{-tolyl})_3\}\{=C(Me)(OMe)\}]^+BF_4^-$ (*S*)-6. Methylation of (*S*)-**5** (0.65 g, 1.31 mmol) with $Me_3O^+BF_4^-$ (0.25 g, 1.38 mmol) in CH_2Cl_2 (15 ml) for 19 h afforded after work-up (*S*)-**6** as a bright yellow solid (0.65 g, 83%). Recrystallisation from CH_2Cl_2–Et_2O gave yellow microneedles, mp 184–185 °C (dec) (Found: C, 60.51; H, 5.52; P, 5.08. $C_{30}H_{32}BF_4FePO_2$ requires C, 60.23; H, 5.40; P, 5.18%); $[a]_D$ +221.8 (conc. 0.275, CH_2Cl_2).

(*RS*)-$[(\eta^5\text{-}C_5H_5)Fe(CO)\{P(p\text{-tolyl})_3\}\{=C(Et)(OMe)\}]^+BF_4^-$ (*RS*)-10. Methylation of (*RS*)-**9** (1.10 g, 2.16 mmol) with $Me_3O^+BF_4^-$ (0.42 g, 2.80 mmol) in CH_2Cl_2 (25 ml) for 18 h afforded after work-up (*RS*)-**10** as an inseparable mixture with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{P(p\text{-tolyl})_3\}]^+BF_4^-$ (7:1) (1.32 g, 73%). Microanalytical data could therefore not be obtained. ν_{max} 1964 (CO) and 1054 (BF_4^-); δ_H 1.14 (3H, t, *J* 7.4, Fe=C–CH_2CH_3), 2.42 (9H, s, tolyl methyls), 2.65–2.73 (2H, m, Fe=C–CH_2CH_3), 4.27 (3H, s, Fe=C–O*Me*), 4.87 (5H, d, J_{PH} 1.3, C_5H_5), 7.10–7.20 [6H, m, P(tolyl)$_3$], 7.25–7.35 [6H, m, P(tolyl)$_3$]; δ_C 10.29 (s, Fe=C–CH_2CH_3), 21.30 (s, tolyl methyls), 49.52 (s, Fe=C–CH_2CH_3), 65.82 (s, Fe=C–O*Me*), 87.36 (s, C_5H_5), 129.83 (d, J_{PC} 9.8, C_{meta}), 130.83 (d, J_{PC} 43.2, C_{ipso} to P), 132.71 (d, J_{PC} 9.5, C_{ortho} to P), 141.93 (s, C_{ipso} to Me), 215.72 (d, J_{PC} 27.8, Fe–CO), 268.93 (d, J_{PC} 21.4, Fe=C); δ_P 59.30; δ_F −154.98 and −159.03 (1:3); *m*/*z* 525 (M^+, 49), 497 (M − CO, 53), 481 (30), 457 (13), 425 (100), 360 (8), 337 (42), 305 (42), 305 (54), 211 (32), 193 (14), 193 (14), 121 (15).

Synthesis of aminocarbenes

(*RS*)-$[(\eta^5\text{-}C_5H_5)Fe(CO)\{P(p\text{-tolyl})_3\}\{=C(Me)(NHCH_2Ph)\}]^+BF_4^-$ (*RS*)-7. Benzylamine (1.73 ml, 15.9 mmol) was added dropwise into a solution of (*RS*)-**6** (0.95 g, 1.59 mmol) in THF (30 ml) forming a red–orange solution which was stirred for 2 h at room temperature. The reaction mixture was then concen-

trated *in vacuo*, dissolved in dichloromethane (5 ml) and added dropwise to diethyl ether (50 ml) cooled to 0 °C, forming a bright yellow precipitate. The solvent was then cannulated off, the residue was washed twice with diethyl ether (15 ml) and then dried *in vacuo* to give (*RS*)-**7** as a yellow solid (1.07 g, 89%). Recrystallisation from CH_2Cl_2–Et_2O gave yellow microneedles, mp 119–121 °C (Found: C, 63.92; H, 5.62; N, 2.20; P, 4.59. $C_{36}H_{37}BF_4FeNOP$ requires C, 63.92; H, 5.54; N, 2.08; P, 4.60%); ν_{max} 1956 (CO) and 1057 (BF_4^-); δ_H 2.39 (9H, s, tolyl methyls), 2.44 (3H, s, Fe=C−*Me*), 4.65 (1H, dd, *J* 13.9, 6.9, N−C*H*$_2$Ph), 4.73 (1H, dd, *J* 13.9, 2.1, N−C*H*$_2$Ph), 4.80 (5H, d, J_{PH} 1.3, C_5H_5), 6.97 (6H, dd, J_{PH} 10.4, J_{HH} 7.1, H_{ortho} to P), 7.03 (2H, d, *J* 7.2, H_{ortho}, Ph), 7.16 (6H, d, *J* 7.1, H_{meta} to P), 7.21–7.27 (3H, m, H_{meta} and H_{para}, Ph), 9.94 (b s, N−H); δ_C 21.28 (s, tolyl methyls), 37.96 (s, Fe=C−*Me*), 53.61 (s, N−*C*H$_2$), 85.47 (s, C_5H_5), 127.94 (s, C_{para}, Ph), 128.82 (s, C_{meta}, Ph), 128.86 (s, C_{ortho}, Ph), 129.75 (d, J_{PC} 10.6, C_{meta} to P), 129.95 (d, J_{PC} 50.9, C_{ipso} to P), 132.61 (d, J_{PC} 9.6, C_{ortho} to P), 134.93 (s, C_{ipso}, Ph), 141.38 (s, C_{ipso} to Me), 217.93 (d, J_{PC} 22.1, Fe−CO), 266.25 (d, J_{PC} 22.3, Fe=C); δ_P 65.07; δ_F −153.54 and −153.59 (1:3); *m*/*z* 586 (M^+, 46), 558 (M − CO, 15), 425 (10), 360 (8), 305 (17), 254 (100), 211 (16), 91 (15).

(*RS*)-[(η^5-C_5H_5)Fe(CO){P(*p*-tolyl)$_3$}{=C(Et)(NHCH$_2$Ph)}]$^+$-BF_4^- (*RS*)-11. Reaction of (*RS*)-**10** (0.87 g, 1.42 mmol) with benzylamine (1.55 ml, 14.2 mmol) at room temperature for 2 h afforded (*RS*)-**11** as a yellow solid (0.82 g, 84%). Recrystallisation from CH_2Cl_2–Et_2O gave yellow microneedles, mp 187–190 °C (dec) (Found: C, 64.69; H, 5.30; N, 1.77; P, 4.52. $C_{37}H_{39}BF_4FeNOP$ requires C, 64.69; H, 5.72; N, 2.04; P, 4.51%); ν_{max} 1952 (CO) and 1056 (BF_4^-); δ_H 1.09 (3H, *J* 7.2, Fe=C−CH$_2$C*H*$_3$), 2.10–2.20 (1H, m, Fe=C−C*H*$_2$CH$_3$), 2.38 (9H, s, tolyl methyls), 2.72–2.80 (1H, m, Fe=C−C*H*$_2$CH$_3$), 4.47–4.53 (1H, m, N−C*H*$_2$Ph), 4.80–4.86 (1H, m, N−C*H*$_2$Ph), 4.86 (5H, s, C_5H_5), 6.94 (6H, dd, J_{PH} 10.5, J_{HH} 7.2, H_{ortho} to P), 7.15 (6H, d, *J* 6.9, H_{meta} to P), 7.14–7.40 (5H, m, H_{ortho}, H_{meta} and H_{para}, Ph), 10.03 (s, N−H); δ_C 9.28 (s, Fe=C−CH$_2$*C*H$_3$), 21.30 (s, tolyl methyls), 41.83 (s, Fe=C−*C*H$_2$CH$_3$), 52.95 (s, N−*C*H$_2$Ph), 85.34 (s, C_5H_5), 127.76 (s, C_{para}, Ph), 128.72 (s, C_{meta} and C_{ortho}, Ph), 129.68 (d, J_{PC} 10.1, C_{meta} to P), 129.70 (d, J_{PC} 47.8, C_{ipso} to P), 132.61 (d, J_{PC} 10.0, C_{ortho} to P), 135.40 (s, C_{ipso}, Ph), 141.31 (s, C_{ipso} to Me), 218.15 (d, J_{PC} 22.1, Fe−CO), 269.89 (d, J_{PC} 23.3, Fe=C); δ_P 64.99; δ_F −153.35 and −153.40 (1:3); *m*/*z* 600 (M^+, 54), 572 (M − CO, 15), 481 (572 − CH_2Ph, 13), 425 (22), 360 (8), 337 (9), 305 (27), 268 (100), 211 (19), 91 (24).

(*R*,*S*)-[(η^5-C_5H_5)Fe(CO){P(*p*-tolyl)$_3$}{=C(Me)(NHCH(Me)-Ph)}]$^+$$BF_4^-$ (*R*,*S*)-12. Reaction of (*R*)-**6** (0.40 g, 0.67 mmol) with (*S*)-α-methylbenzylamine (0.86 ml, 6.69 mmol) at room temperature for 2 h afforded (*R*,*S*)-**12** as a yellow solid (0.47 g, 95%). Recrystallisation from CH_2Cl_2–Et_2O gave yellow–brown microneedles, mp 180–185 °C (Found: C, 64.79; H, 5.61; N, 1.82. $C_{37}H_{39}BF_4FeNOP$ requires C, 64.65; H, 5.72; N, 2.04%); $[\alpha]_D$ +14.2 (conc. 0.99, CH_2Cl_2); ν_{max} 1957 (CO) and 1055 (BF_4^-); δ_H 1.49 [3H, d, *J* 6.3, N−CH(*Me*)Ph], 2.40 (9H, s, tolyl methyls), 2.55 (3H, s, Fe=C−*Me*), 4.78 (5H, s, C_5H_5), 5.02 [1H, b q, *J* 6.3, N−C*H*(Me)Ph], 6.91 (2H, d, *J* 7.1, H_{ortho}, Ph), 6.95 (6H, dd, J_{PH} 10.2, J_{HH} 7.9, H_{ortho} to P), 7.18–7.26 [9H, m, H_{meta} to P, H_{meta} (Ph) and H_{para} (Ph)], 9.28 (s, N−H); δ_C 21.17 (s, tolyl methyls), 21.89 [s, N−CH(*Me*)Ph], 38.80 (s, Fe=C−*Me*), 6.07 [s, N−*C*H(Me)Ph], 85.25 (s, C_5H_5), 126.44 (s, C_{meta}, Ph), 127.88 (s, C_{para}, Ph), 128.89 (s, C_{ortho}, Ph), 129.77 (b s, C_{ipso} to P), 129.78 (d, J_{PC} 8.1, C_{meta} to P), 132.52 (d, J_{PC} 7.3, C_{ortho} to P), 140.19 (s, C_{ipso}, Ph), 141.52 (s, C_{ipso} to Me), 217.32 (d, J_{PC} 29.6, Fe−CO), 268.14 (d, J_{PC} 24.9, Fe=C); δ_P 66.36; δ_F −153.36 and −153.42 (1:3); *m*/*z* 600 (M^+, 44), 572 (M − CO, 20), 337 (20), 305 (30), 268 (100), 226 (18), 211 (19), 105 (19).

(*S*,*S*)-[(η^5-C_5H_5)Fe(CO){P(*p*-tolyl)$_3$}{=C(Me)(NHCH(Me)-Ph)}]$^+$$BF_4^-$ (*S*,*S*)-13. Reaction of (*S*)-**6** (0.45 g, 0.75 mmol) with (*S*)-α-methylbenzylamine (0.97 ml, 7.53 mmol) at room temperature for 2 h afforded (*S*,*S*)-**13** as a yellow solid (0.51 g, 96%). Recrystallisation from CH_2Cl_2–Et_2O gave yellow microneedles, mp 180–185 °C (dec) (Found: C, 64.32; H, 5.79; N, 1.75; P, 4.49. $C_{37}H_{39}BF_4FeNOP$ requires C, 64.65; H, 5.72; N, 2.04; P, 4.51%); $[\alpha]_D$ +106.9 (conc. 0.304, CH_2Cl_2); ν_{max} 1959 (CO) and 1056 (BF_4^-); δ_H 1.38 [3H, d, *J* 6.8, N−CH(*Me*)Ph], 2.39 (9H, s, tolyl methyls), 2.54 (3H, s, Fe=C−*Me*), 4.70 (5H, s, C_5H_5), 4.88 [1H, b q, *J* 6.3, N−C*H*(Me)Ph], 7.04 (6H, dd, J_{PH} 10.5, J_{HH} 8.1, H_{ortho} to P), 7.22 (6H, b d, *J* 7.4, H_{meta} to P), 7.27 (2H, b d, *J* 7.1, H_{ortho}, Ph), 7.30 (1H, t, *J* 7.3, H_{para}, Ph), 7.37 (2H, t, *J* 7.5, H_{meta}, Ph); δ_C 21.29 (s, tolyl methyls), 21.49 [s, N−CH(*Me*)Ph], 38.61 (s, Fe=C−*Me*), 60.18 [s, N−*C*H(Me)Ph], 85.25 (s, C_5H_5), 126.45 (s, C_{meta}, Ph), 127.19 (s, C_{para}, Ph), 129.32 (s, C_{ortho}, Ph), 129.65 (d, J_{PC} 10.1, C_{meta} to P), 130.20 (b s, C_{ipso} to P), 132.67 (d, J_{PC} 10.0, C_{ortho} to P), 140.52 (s, C_{ipso}, Ph), 141.52 (s, C_{ipso} to Me), 217.45 (d, J_{PC} 28.5, Fe−CO), 268.32 (d, J_{PC} 25.0, Fe=C); δ_P 65.70; δ_F −152.83 and −152.88 (1:3); *m*/*z* 600 (M^+, 38), 572 (M − CO, 16), 305 (24), 268 (100), 211 (18), 105 (24).

Air decomposition of (*R*,*S*)-[(η^5-C_5H_5)Fe(CO)(PPh$_3$)-{=C(Me)(NHCH(Me)Ph)}]$^+$$BF_4^-$ (*R*,*S*)-2. A solution of (*R*,*S*)-**2** (129 mg, 0.20 mmol) in 10% H_2O–MeOH (20 ml) was stirred exposed to air and sunlight for 88 h. The resulting brown suspension was filtered through alumina and the filtrate concentrated *in vacuo*. Column chromatography on alumina (CH_2Cl_2) gave in order of increasing polarity (i) (*S*)-(−)-(α-methylbenzyl)acetamide (25 mg, 77%) which was recrystallised from CH_2Cl_2–hexane to give colourless plates, mp 99–100 °C (lit.,[4] mp 104 °C); $[\alpha]_D$ −164.8 (conc. 0.85, EtOH, 19 °C) {lit.,[4] $[\alpha]_D$ −168.1 (conc. 2.117, EtOH, 17 °C)} which corresponds to an enantiomeric excess of 98%. The NMR data were consistent with those obtained from an authentic sample synthesised by the reaction of (*S*)-α-methylbenzylamine with acetic anhydride {ν_{max}($CHCl_3$) 3442 (NH), 1667 (CO); δ_H 1.50 (3H, d, *J* 6.8, CH*Me*), 1.99 (3H, s, CO*Me*), 5.13 [1H, q, *J* 6.8, C*H*(Me)Ph], 5.86 (1H, b s, N−H), 7.23–7.40 (5H, m, Ph); δ_C 21.7 and 23.1 (2 Me), 48.7 [s, *C*H(Me)(Ph)], 126.32 (C_{meta}), 127 (C_{para}), 128.71 (C_{ortho}), 143.62 (C_{ipso}), 169.7 (CO)}; and (ii) triphenylphosphine oxide (57 mg, 100%) which crystallised from CH_2Cl_2–hexane as prisms, mp 152–153 °C (lit.,[21] mp 154–155 °C).

Air decomposition of (*RS*,*SR*)- and (*RR*,*SS*)-[(η^5-C_5H_5)-Fe(CO)(PPh$_3$){=C(Me)(NHCH(Me)Ph)}]$^+$$BF_4^-$ (*RS*,*SR*)-2 and (*RR*,*SS*)-3. A solution of (*RS*,*SR*)-**2** and (*RR*,*SS*)-**3** (128 mg, 0.20 mmol) in 10% H_2O–MeOH (20 ml) was stirred exposed to air and sunlight for 88 h. The resulting brown suspension was filtered through alumina and the filtrate concentrated *in vacuo*. Column chromatography on alumina (CH_2Cl_2) gave in order of increasing polarity (i) (±)-(α-methylbenzyl)acetamide (23 mg, 74%) which was recrystallised from CH_2Cl_2–hexane to give colourless plates, mp 72–73 °C (lit.,[5] mp 75 °C); and (ii) triphenylphosphine oxide (57 mg, 100%) which crystallised from CH_2Cl_2–hexane as prisms, mp 152–153 °C (lit.,[21] mp 154–155 °C).

Epimerisation followed by air decomposition of (*R*,*S*)-[(η^5-C_5H_5)Fe(CO)(PPh$_3$){=C(Me)(NHCH(Me)Ph)}]$^+$$BF_4^-$ (*R*,*S*)-2. A solution of (*R*,*S*)-**2** (0.19 g, 0.30 mmol) in 10% H_2O–MeOH (20 ml) was stirred under a nitrogen blanket for 72 h at room temperature while being exposed to sunlight. The reaction mixture was worked up in the usual manner and examined by ^{1}H NMR spectroscopy which showed it to be a mixture of (*R*,*S*)-**2** and (*S*,*S*)-**3**. The residue was then redissolved in the same solvent mixture and stirred for 72 h while being open to air. Work-up in the same way as described above gave two fractions (i) (*S*)-(−)-(α-methylbenzyl)acetamide (25 mg, 77%) which was recrystallised from CH_2Cl_2–hexane to give colourless plates, mp 99–100 °C (lit.,[4] mp 104 °C); $[\alpha]_D$ −163.8 (conc. 0.85, EtOH, 19 °C) [lit.,[4] $[\alpha]_D$ −168.1 (conc. 2.117, EtOH, 17 °C)], which corresponds to an enantiomeric excess of 97%; and (ii) triphenylphosphine oxide (57 mg, 100%) which crystallised from CH_2Cl_2–hexane as prisms, mp 152–153 °C (lit.,[21] mp 154–155 °C).

Cross-over experiments

Reaction of (*RS*)-[(η^5-C_5H_5)Fe(CO){P(*p*-tolyl)$_3$}{=C(Me)(NHCH$_2$Ph)}]$^+$BF$_4^-$ (*RS*)-7 and (*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh$_3$){=C(Et)(NHCH$_2$Ph)}]$^+$BF$_4^-$ (*RS*)-14 with photoirradiation. A nitrogen degassed solution of (*RS*)-**7** (50 mg, 72.9 μmol) and (*RS*)-**14** (50 mg, 75.0 μmol) in 10% H_2O–MeOH (12 ml) was stirred under a nitrogen atmosphere while being irradiated with a desk lamp for 48 h. The reaction mixture was concentrated *in vacuo* and the residue was examined by ^{1}H NMR spectroscopy which showed it to contain in addition to (*RS*)-**7** and (*RS*)-**14**, (*RS*)-**11** and (*RS*)-**15** in roughly equal amounts. Although this mixture of carbene complexes could not be separated into its various components by chromatography the ^{1}H NMR spectrum of the mixture showed four cyclopentadienyl doublets consistent with those expected for the predicted complexes. This was confirmed when a mixture of the above four complexes (5 mg of each) was examined by ^{1}H NMR spectroscopy and found to have an identical spectrum to the photolysis mixture.

Reaction of (*R*,*S*)-[(η^5-C_5H_5)Fe(CO)(PPh$_3$){=C(Me)(NHCH(Me)Ph)}]$^+$BF$_4^-$ (*R*,*S*)-2 with tri(*p*-tolyl)phosphine with photoirradiation. A nitrogen degassed solution of (*R*,*S*)-**2** (0.11 g, 0.16 mmol) and tri(*p*-tolyl)phosphine (0.50 g, 1.64 mmol) in 10% H_2O–MeOH (10 ml) was stirred under a nitrogen atmosphere while being irradiated with a desk lamp for 48 h. Aliquots from the reaction mixture were examined by ^{1}H NMR spectroscopy (initially every 30 min and then every 6 h) which showed it to contain in addition to (*R*,*S*)-**2**, (*R*,*S*)-**12** and (*S*,*S*)-**13** in roughly equal amounts. There was no sign of any epimerised starting material (*S*,*S*)-**3**. Although this mixture of carbene complexes could not be separated into its various components by chromatographic techniques, the ^{1}H NMR spectrum of the mixture showed three cyclopentadienyl doublets consistent with those expected for the predicted complexes. This was confirmed when a mixture containing 5 mg of each of the above three complexes was examined by ^{1}H NMR spectroscopy and found to have an identical spectrum to the photolysis mixture. Similarly a mixture consisting of the above three complexes and the epimerised starting complex (*S*,*S*)-**3** (5 mg each) was examined by ^{1}H NMR spectroscopy showing four distinct cyclopentadienyl doublets. After 48 h the reaction was essentially complete and a very small amount of the epimerised isomer of the starting complex (*S*,*S*)-**3** (<2% of the mixture) was observed in the ^{1}H NMR spectrum.

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