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Synthesis and characterisation of the aminocarbene complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{=C(NHR^2)(CH_2R^1)\}]^+BF_4^-$ [R^1 = H, Me or Pr; R^2 = H, Me, Et, $CHMe_2$, CH_2Ph, CH(Me)Ph, $CH_2CH{=}CH_2$ or CH_2CH_2OH]

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A number of secondary aminocarbenes of the type (*RS*)-$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{=C(CH_2R^1)(NHR^2)\}]^+BF_4^-$ were synthesised in very good yield [66–99%, R^1 = H, Me or Pr; R^2 = H, Me, Et, $CHMe_2$, CH_2Ph, CH(Me)Ph, $CH_2CH{=}CH_2$ or CH_2CH_2OH]. The absolute configuration of one of the carbenes was established by a single-crystal X-ray diffraction experiment. The chemistry of the carbene complexes was investigated.

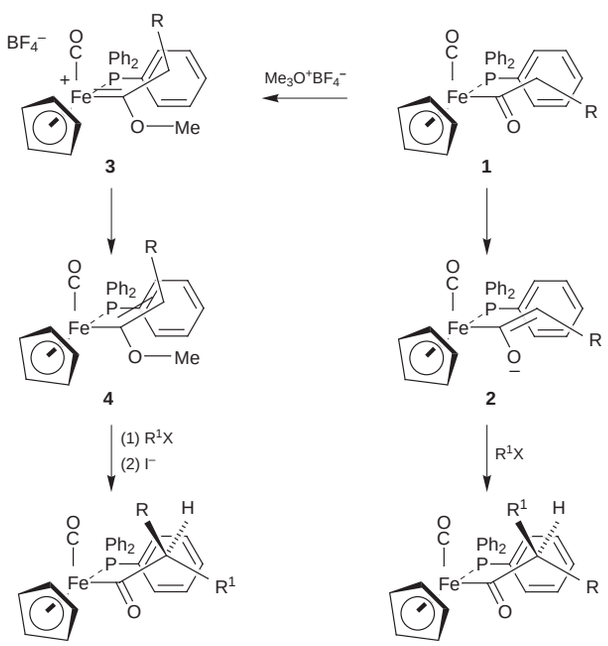
Previously we have established the fragment $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]$ [1–3] as a versatile chiral auxiliary for asymmetric organic synthesis. This iron chiral auxiliary induces high stereoselectivity in the reactions of a wide variety of attached ligands. For example, deprotonation of the acyl ligand in $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2R]$ **1** generates the *E*-enolate (Fe *trans* to R) **2**, which undergoes highly stereoselective alkylation reactions (Scheme 1). These enolate reactions require strong base (butyllithium) and low temperatures (−78 °C). In contrast the derived methoxycarbene salt $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{=C(OMe)(CH_2R)\}]^+BF_4^-$ **3** [4,5] may be deprotonated at ambient temperature with a mild base such as methoxide to generate the corresponding *Z*-enol ether (Fe *cis* to R) **4**. Alkylation of complex **4** is highly stereoselective and demethylation of the thus formed methoxycarbene cation with iodide generates the corresponding elaborated acyl complex (Scheme 1).[6] The two sequences described above are stereocomplementary given the same face selectivity induced by the iron chiral auxiliary but opposite enolate to enol ether geometries.

We were interested in extending this chemistry to the nitrogen series to see if analogous stereoselective reactions could be achieved *via* α-metallated imines or enamines attached to the iron chiral auxiliary $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]$. Achiral α-metallated imines attached to $[Cr(CO)_5]$ have been reported by Hegedus *et al.*[7] We describe here the synthesis and properties of a range of aminocarbene cations of the type $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{=C(NHR^2)(CH_2R^1)\}]^+$. Of particular relevance to the present study is the report by Davison and Reger[8] of the reaction of racemic (*RS*)-$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{=C(Me)(OEt)\}]^+BF_4^-$ with (*S*)-(−)-α-methylbenzylamine yielding a separable mixture of diastereoisomers of (*R*,*S*)-† and (*S*,*S*)-$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{=C(Me)[NHCH(Me)Ph]\}]^+BF_4^-$. Although the absolute configurations at iron for these two diastereoisomers could not be assigned Cotton effect studies were consistent with them being epimeric at iron as expected.

Results and Discussion

Methoxycarbene complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{=C(CH_2R)(OMe)\}]^+BF_4^-$ may be readily prepared by treatment of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)Br]$ with the appropriate lithium acetylide followed by protonation to the corresponding vinylidene complexes[9a] and subsequent addition of methanol.[9b]

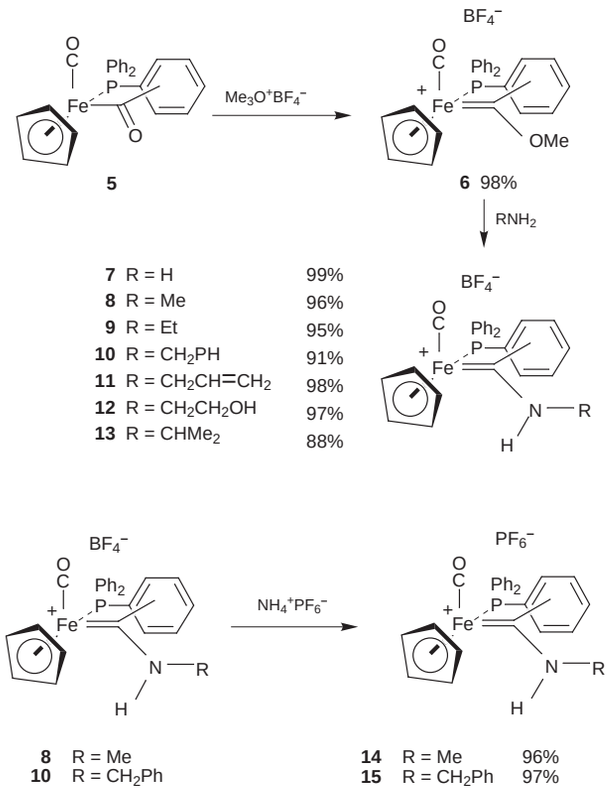
† The configuration at iron is given first followed by the configuration at the α-benzylic centre.



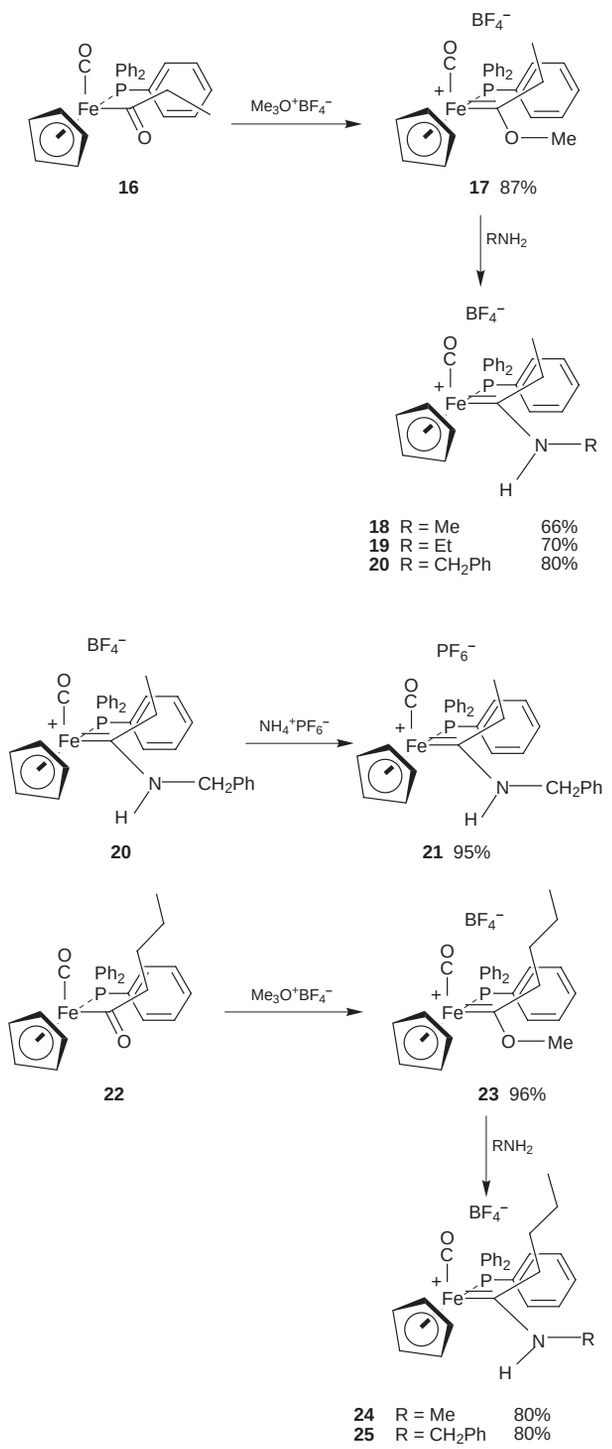
Scheme 1

Alternatively they may be synthesised from the corresponding acyl complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH_2R)]$ by treatment with trimethyloxonium tetrafluoroborate.[10] Thus *O*-methylation of the iron acetyl complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COMe)]$ **5** generated the methoxycarbene derivative $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{=C(Me)(OMe)\}]^+BF_4^-$ **6** in 98% yield (Scheme 2). Treatment of a tetrahydrofuran solution of the methoxycarbene complex **6** at 20 °C with a large excess of ammonia gas or ten molar excess of a range of primary amines generated the corresponding aminocarbene complexes **7**–**13** in high yield (Scheme 2). If a large excess of amine was not employed then the reactions tended to be slower and the yields were lower due to *O*-demethylation of **6** back to **5**. Two of the tetrafluoroborate salts **8** and **10** were converted into their corresponding hexafluorophosphate salts **14** and **15** in excellent yield by treatment with aqueous $NH_4^+PF_6^-$ because of the better solubility of the latter salts in organic solvents.

Reaction of methoxycarbene complex **6** with aniline failed to give any of the corresponding aminocarbene complex, exclusively regenerating the acetyl complex **5** with concomitant formation of *N*-methylaniline. This change of reactivity may be



Scheme 2



Scheme 3

attributed to reversible formation of the intermediate generated by addition of the amine to the methoxycarbene in the latter reaction with aniline but not in the former cases with primary aliphatic amines. Consistent with the observation of Davison and Reger,[8] attempted coupling between secondary amines (Me_2NH, Et_2NH or pyrrolidine) and the methoxycarbene **6** proved to be very difficult with the product mixture consisting mostly of the demethylated neutral acetyl complex **5** and recovered methoxycarbene **6**. One aminocarbene complex derived from a secondary amine prepared *via* a different route has been reported.[9b] Although some resonances in the ^1H NMR spectrum of the reaction mixture were consistent with those expected for the product aminocarbene complexes, these never exceeded 10% of the crude reaction mixture which could not be purified.

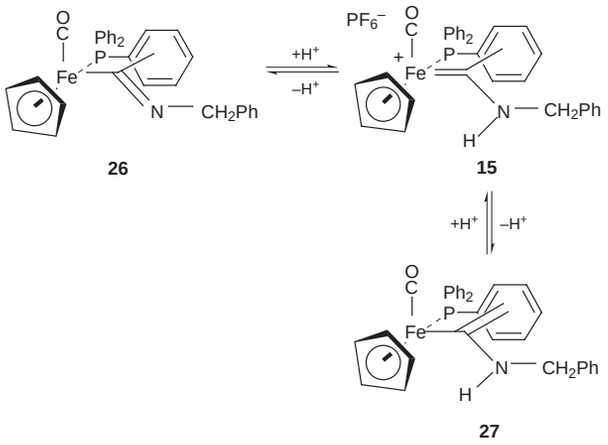
O-Methylation of the propanoyl complex **16** generated the methoxycarbene **17** in 87% yield, which reacted with selected primary amines to generate the corresponding aminocarbene complexes **18**–**20** (Scheme 3). Similar reactions of the pentanoyl complex **22** resulted, *via* the intermediacy of the methoxycarbene **23**, in the formation of the aminocarbenes **24** and **25** (Scheme 3).

For comparison with the known chemistry of the iron acyl and methoxycarbene complexes (Scheme 1), deprotonation–electrophilic trapping experiments were performed on complex **15**. The following deuteriation experiments were readily monitored by ^1H NMR spectroscopy and by mass spectrometry. In deuteriomethanol solution containing a catalytic amount of methoxide complete H/D exchange was observed for the NH and CH_3 protons consistent with expected intermediacy under these equilibrating conditions of **26** and **27** (Scheme 4).

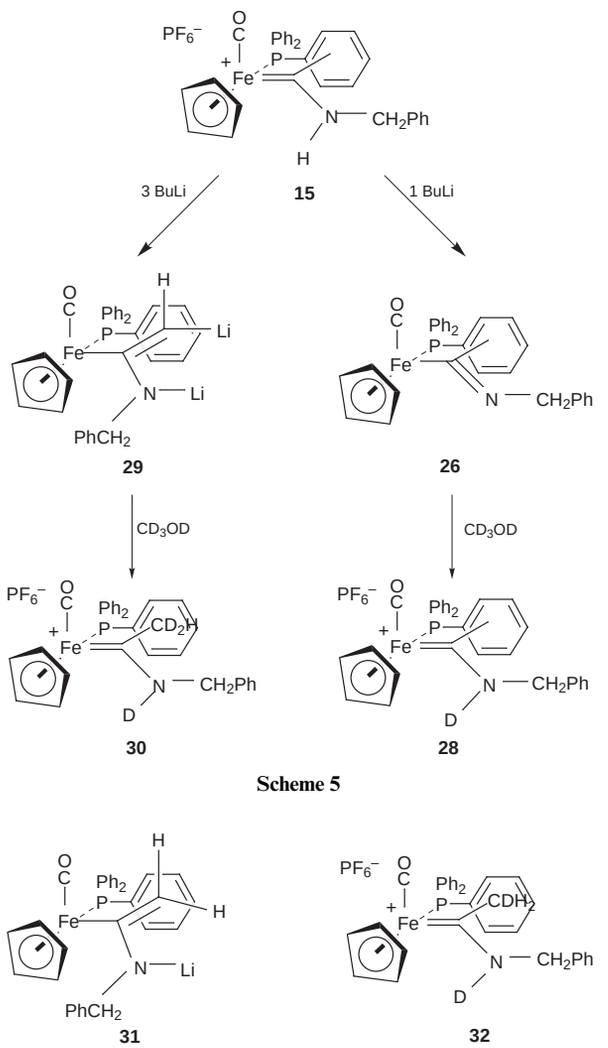
Under kinetically controlled deprotonation conditions treatment of **15** with 1 equivalent of butyllithium followed by quenching with deuteriomethanol led to the exchange of only the NH proton and formation of **28** (Scheme 5). In the presence of greater than 3 equivalents of butyllithium complex **15** generated, after quenching, exclusively the trideuterio derivative **30** (Scheme 5). The formation of **30** is consistent with the intermediacy of the dilithio species **29** for which there is some precedent in organic systems.[11]

Treatment of **15** with 2 equivalents of butyllithium followed by quenching with deuteriomethanol led to a mixture of **28**, **30** and **32** rather than exclusive formation of the monolithio species **31** and hence after quenching to **32**. All attempts to isolate complex **26** were unsuccessful, only complex **15** being recovered in each case. In all of the above experiments attempted quenchings with methyl iodide were completely unsuccessful indicating that the intermediates **26**, **29** and **31** are unreactive towards alkylation. This observation is in direct contrast to the reactions of the enolates **2** and enol ethers **4**.

Very few methods exist for the resolution of the iron chiral auxiliary $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]$[12] and therefore we were interested to see if any chiral recognition could be achieved



Scheme 4

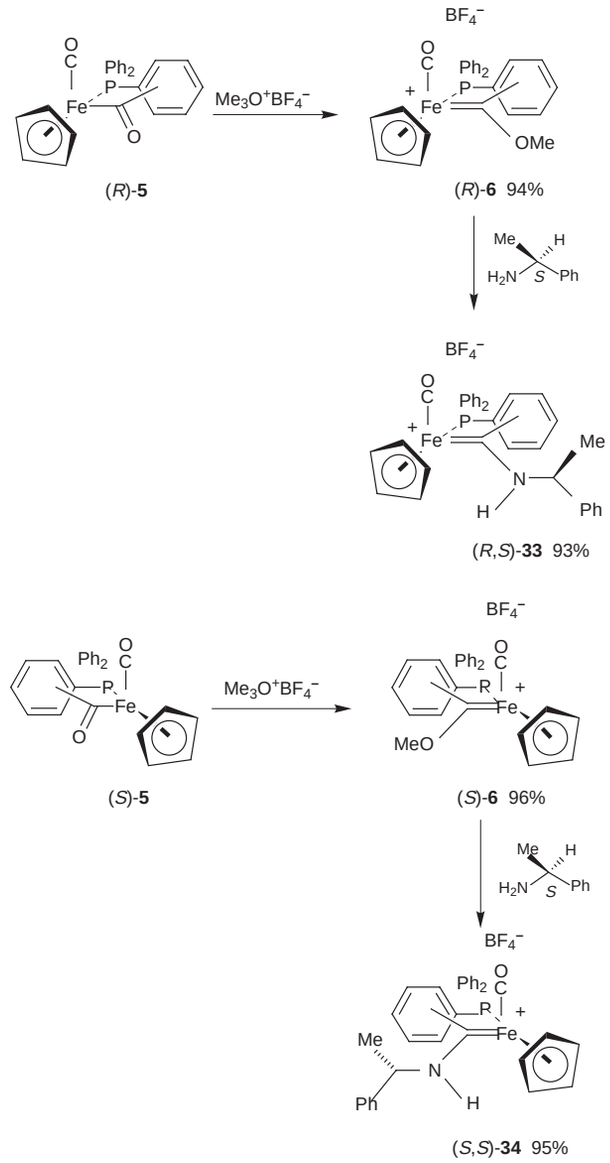


Scheme 5

during the reaction of the methoxycarbene complex **6** and α-methylbenzylamine. Significant chiral recognition would allow the kinetic resolution of racemic **6** with homochiral α-methylbenzylamine. *O*-Methylation of homochiral (*R*)-**5** generated the homochiral methoxycarbene complex (*R*)-**6** (Scheme 6). Treatment of (*R*)-**6** with (*S*)-α-methylbenzylamine generated the corresponding aminocarbene complex (*R*,*S*)-**33** as a single diastereoisomer. Similar treatment of (*S*)-**5** gave *via* (*S*)-**6**[13] the aminocarbene complex epimeric at iron (*S*,*S*)-**34**.

The diastereoisomers (*R*,*S*)-**33** and (*S*,*S*)-**34** were readily distinguishable by NMR spectroscopy and their configurational assignments were confirmed by an X-ray crystal-structure analysis of (*R*,*S*)-**33** which confirmed retention of configuration at both the iron and the α-methylbenzylamine stereogenic centres during the conversion of the methoxycarbenes to the aminocarbenes. Fig. 1 shows the molecular conformation of (*R*,*S*)-**33** present in the crystal structure. Selected bond lengths and torsion angles are given in Table 1. The structure of (*R*,*S*)-**33** shows the normal pseudo-octahedral geometry around iron with the nitrogen of the aminocarbene *anti* to the carbon monoxide ligand. The α-methylbenzyl group is antiperiplanar to the iron auxiliary with the benzylic hydrogen synperiplanar to the aminocarbene methyl group. The conformation adopted in the solid state parallels that of the corresponding methoxycarbene complex[14] and is as expected on steric grounds.

In order to investigate the possible chiral recognition phenomenon, racemic methoxycarbene complex **6** was treated with racemic α-methylbenzylamine in a variety of solvents. Employing all racemic conditions allows a direct correlation of the



Scheme 6

Table 1 Selected bond distances (Å) and torsion angles (°) for (*R*,*S*)-**33**

Fe(1)–C(1)	1.928(6)	C(1)–N(1)	1.318(7)
C(1)–C(2)	1.513(8)	N(1)–C(3)	1.495(6)
C(1)–N(1)–C(3)–C(4)	−124	C(1)–N(1)–C(3)–C(10)	110
C(2)–C(1)–N(1)–C(3)	−6	Fe(1)–C(1)–N(1)–C(3)	177
N(1)–C(3)–C(4)–C(5)	127		

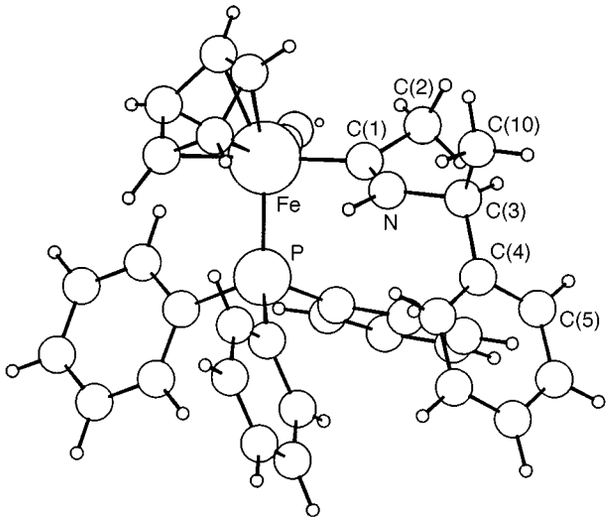


Fig. 1 Crystal structure of (*R*,*S*)-[(η^5-C_5H_5)Fe(CO)(PPh_3){=C(Me)-[NHCH(Me)Ph]}]$^+BF_4^-$ (*R*,*S*)-**33**

ratio of product diastereoisomers with the stereoselectivity factor without the need to consider the complicating effects of mass action. Unfortunately, in a range of solvents (tetrahydrofuran, methanol, ethanol, propan-2-ol, hexane, acetone, ethyl acetate, dibutyl ether, benzene, chloroform and carbon tetrachloride) equimolar mixtures of product diastereoisomers were observed within experimental error. The complete lack of chiral recognition does not allow a kinetic resolution procedure to be effected. However, Davison and Reger[8] have demonstrated the classical resolution procedure by separation of (*R*,*S*)-**33** and (*S*,*S*)-**34** by fractional crystallisation. Photochemical studies on the above aminocarbene complexes have been reported elsewhere.[15]

Experimental

All reactions and purifications were performed under a nitrogen atmosphere using standard vacuum line and Schlenk-tube techniques.[16] All solvents were deoxygenated before use. Tetrahydrofuran (THF) and dichloromethane were distilled from sodium benzophenone and calcium hydride, respectively, under nitrogen. Analytical grade acetone (FSA) was used without purification. 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). Elemental analyses were carried out by the Dyson Perrins Laboratory Analytical Service. Butyllithium (1.5 M in hexane) and methyllithium (1.4 M in diethyl ether) were used as supplied by Aldrich. Infrared spectra were recorded on either a Perkin-Elmer 781 or a Perkin-Elmer 1750 Fourier-transform spectrophotometer in dichloromethane solutions using 1 mm NaCl cells unless otherwise stated. Proton 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. Carbon-13, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker AM250 spectrometer (at 62.90, 235.35 and 125.76 MHz respectively) in $CDCl_3$ solutions. Proton and ^{13}C NMR spectra were referenced to tetramethylsilane using internal solvent peaks. 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: br, broad single; d, doublet; m, multiplet; q, quartet; s, singlet; t, triplet. Mass spectra were recorded on VG Micromass ZAB1F or MM30F instruments using FAB techniques for organometallic compounds. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter in the solvents indicated at 20 °C in a 1 dm cell. Concentrations (*c*) are given in g 100 mL^{-1} and specific rotation in units of 10^{-1} deg cm^2 g^{-1}. The complexes (*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3)(COMe)] (*RS*)-**5**,[17] (*R*)-**5**,[12] (*S*)-**5**,[12] (*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3)(COEt)] (*RS*)-**16**,[18] (*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3)(COBu)] (*RS*)-**22**,[6,19] (*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3){=C(Me)(NHMe)}]$^+BF_4^-$ (*RS*)-**8**,[20] (*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3){=C(Bu)(OMe)}]$^+BF_4^-$ (*RS*)-**23**[20] and (*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3){=C(Bu)(NHCH$_2$-Ph)}]$^+BF_4^-$ (*RS*)-**25**[20] were synthesised by literature procedures. (*S*)-(−)-α-Methylbenzylamine was purchased from Aldrich $[\alpha]_D$ (neat) −39.0, this corresponds to an enantiomeric excess of 95% {lit.,[21a] $[\alpha]_D$ (neat) −40.6}. However with the method of Parker and Taylor[21b] using ^1H NMR with (*R*)-(−)-*O*-acetylmandelic acid [$MeCO_2CH(C_6H_5)CO_2H$] an enantiomeric excess of 99.6% was obtained.

General procedure for the synthesis of the methoxycarbenes

A nitrogen degassed solution of [(η^5-C_5H_5)Fe(CO)(PPh_3)-(COR)] (R = Me, Et or Bu) (30 mL per 1 g of complex) was cannulated into a flask containing trimethyloxonium tetrafluoroborate (1.3 mol equivalents, dried at 60 °C *in vacuo* for 3 h) and the resultant mixture stirred under a nitrogen atmosphere for 8–21 h. During this time the colour of the reaction mixture changed from a deep orange-red to a deep yellow-brown. The reaction mixture was then filtered *via* cannula and concentrated *in vacuo* to yield a yellow-brown oil which was dissolved in a minimum amount of dichloromethane and cannulated dropwise into diethyl ether (40 mL g^{-1}) cooled to 0 °C, forming a bright yellow precipitate. The solvent was removed *via* cannula and the residue washed twice with diethyl ether before being dried *in vacuo*. For analytical analysis the methoxycarbenes were recrystallised from the solvents indicated.

(*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3){=C(Me)(OMe)}]$^+BF_4^-$ (*RS*)-6. Methylation of (*R*,*S*)-**5** (20.0 g, 44.1 mmol) with Me_3O^+-BF_4^- (8.46 g, 57.2 mmol) for 8 h at room temperature afforded (*RS*)-**6** as a yellow solid (23.99 g, 98%) which was crystallised from CH_2Cl_2–Et_2O as yellow microcrystals, m.p. 162–165 °C (decomp.) (lit.,[10a] 164 °C); ν_{max} 1966 (Fe–CO) and 1057 cm^{-1} (BF_4^-); δ_H 2.84 (3 H, s, Fe=CMe), 3.99 (3 H, s, Fe=COMe), 4.92 (5 H, d, J_{PH} 1.2 Hz, C_5H_5), 7.20–7.40 (6 H, m, H_o of PPh_3), 7.43–7.65 (9 H, m, H_m and H_p of PPh_3); δ_C 44.70 (s, Fe=CMe), 65.24 (s, Fe=COMe), 87.75 (s, C_5H_5), 129.12 (d, J_{PC} 11.0, C_m of PPh_3), 131.16 (s, C_p of PPh_3), 132.54 (d, J_{PC} 9.5, C_o of PPh_3), 132.72 (d, J_{PC} 47.4, C_{ipso} of PPh_3), 215.47 (d, J_{PC} 27.4, Fe–CO), 263.19 (d, J_{PC} 21.4 Hz, Fe=C); δ_P 63.13; δ_F −154.49 and −154.54 (1:3); *m*/*z* 469 (M^+, 87), 441 (M − CO, 86), 439 (M − 2Me, 10), 383 (439 − 2CO, 100), 318 (12), 295 (8), 263 (24), 239 (17), 183 (55), 164 (10), 108 (8), 85 (8%).

(*R*)-[(η^5-C_5H_5)Fe(CO)(PPh_3){=C(Me)(OMe)}]$^+BF_4^-$ (*R*)-6. Methylation of (*R*)-**5**[12] (1.42 g, 3.13 mmol) with $Me_3O^+BF_4^-$ (0.60 g, 4.06 mmol) for 12 h at room temperature afforded (*R*)-**6** as a yellow solid (1.64 g, 94%) which was crystallised from CH_2Cl_2–Et_2O as yellow microcrystals, m.p. 162–164 °C (decomp.) (Found: C, 58.19; H, 4.45. $C_{27}H_{26}BF_4FeO_2P$ requires: C, 58.31; H, 4.72%); $[\alpha]_D$ (20 °C, *c* = 3.2, CH_2Cl_2) −257.0.

(*S*)-[(η^5-C_5H_5)Fe(CO)(PPh_3){=C(Me)(OMe)}]$^+BF_4^-$ (*S*)-6. Methylation of (*S*)-**5**[12] (2.00 g, 4.41 mmol) with $Me_3O^+BF_4^-$ (0.85 g, 5.73 mmol) for 12 h at room temperature afforded (*S*)-**6**[11] as a yellow solid (2.35 g, 96%) which was crystallised from CH_2Cl_2–Et_2O as yellow microcrystals, m.p. 162–165 °C (decomp.) (Found: C, 58.07; H, 4.38. $C_{27}H_{26}BF_4FeO_2P$ requires: C, 58.31; H, 4.72%); $[\alpha]_D$ (20 °C, *c* = 2.3, CH_2Cl_2) 257.7.

(*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3){=C(Et)(OMe)}]$^+BF_4^-$ (*RS*)-17. Methylation of (*RS*)-**16** (5.0 g, 10.7 mmol) with $Me_3O^+BF_4^-$ (2.04 g, 13.9 mmol) for 21 h at room temperature afforded (*RS*)-**17** as a yellow solid (5.29 g, 87%) which was

crystallised from CH_2Cl_2–Et_2O as yellow microcrystals, m.p. 169–172 °C (decomp.) (Found: C, 58.70; H, 4.86. $C_{28}H_{28}BF_4FeO_2P$ requires: C, 58.98; H, 4.95%); ν_{max} 1966 (Fe–CO) and 1052 cm^{-1} (BF_4^-); δ_H 1.16 (3 H, d, *J* 7.6, Fe=CCH$_2$*Me*), 2.76 (2 H, q, *J* 7.6, Fe=CC*H*$_2$Me), 4.25 (3 H, s, Fe=COMe), 4.89 (5 H, d, J_{PH} 1.4 Hz, C_5H_5), 7.20–7.40 (6 H, m, H_o of PPh_3), 7.45–7.60 (9 H, m, H_m and H_p of PPh_3); δ_C 10.17 (s, Fe=CCH$_2$*Me*), 49.75 (s, Fe=CCH$_2$Me), 65.84 (s, Fe=CO*Me*), 87.31 (s, C_5H_5), 129.15 (d, J_{PC} 9.9, C_m of PPh_3), 131.41 (s, C_p of PPh_3), 132.75 (d, J_{PC} 10.4, C_o of PPh_3), 132.84 (d, J_{PC} 47.3, C_{ipso} of PPh_3), 216.26 (d, J_{PC} 26.8, Fe–CO), 257.91 (d, J_{PC} 21.1 Hz, Fe=C); δ_P 62.28; δ_F −154.69 and −154.75 (1:3); *m*/*z* 483 (M^+, 100), 455 (*M* − CO, 86), 439 (*M* − Me − Et, 14), 383 (*M* − Me − Et, 100), 318 (18), 295 (38), 263 (36), 239 (19), 221 (16), 193 (38), 183 (65), 161 (24), 121 (31), 103 (12), 85 (25%).

General procedure for the synthesis of the aminocarbenes

The amine (10 mol equivalents) was injected dropwise into a solution of the methoxycarbene in THF (20 mL g^{-1}) under a nitrogen atmosphere and the resultant red-orange solution stirred at the specified temperatures for the times indicated. The reaction mixture was then concentrated *in vacuo* to yield a red oil which was dissolved in a minimum amount of dichloromethane and cannulated dropwise into diethyl ether (40 mL g^{-1}) cooled to 0 °C forming a bright yellow precipitate. The solvent was removed *via* cannula and the residue washed twice with diethyl ether before being dried *in vacuo*. For analytical analysis the aminocarbenes were recrystallised from the solvents indicated.

(*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3){=C(Me)(NH_2)}]$^+BF_4^-$ (*RS*)-7. Reaction of (*RS*)-**6** (0.91 g, 1.64 mmol) with gaseous NH_3 for 1.5 h at room temperature afforded (*RS*)-**7** as a yellow solid (0.87 g, 99%) which was crystallised from CH_2Cl_2–Et_2O as yellow microneedles, m.p. 93–97 °C (decomp.) (Found: C, 57.89; H, 4.85; N, 2.62; P, 5.57. $C_{26}H_{25}BF_4FeNOP\cdot0.67\ C_2H_{10}O$ requires: C, 57.87; H, 4.86; N, 2.53; P, 5.60%); ν_{max} 1958 (Fe–CO) and 1098 cm^{-1} (BF_4^-); δ_H 2.40 (3 H, s, Fe=CMe), 4.76 (5 H, d, J_{PH} 1.2 Hz, C_5H_5), 7.30–7.33 (6 H, m, H_o of PPh_3), 7.50–7.53 (9 H, m, H_m and H_p of PPh_3), 9.26 (1 H, br s, NH_2), 9.37 (1 H, br s, NH_2); δ_C 43.75 (s, Fe=C*Me*), 85.65 (s, C_5H_5), 129.16 (d, J_{PC} 10.2, C_m of PPh_3), 131.17 (s, C_p of PPh_3), 132.78 (d, J_{PC} 9.4, C_o of PPh_3), 133.03 (d, J_{PC} 44.7, C_{ipso} of PPh_3), 217.38 (d, J_{PC} 28.1, Fe–CO), 273.89 (d, J_{PC} 19.4 Hz, Fe=C); δ_P 66.46; δ_F −153.06 and −153.11 (1:3); *m*/*z* 454 (M^+, 100), 426 (*M* − CO, 58), 383 (24), 295 (30), 263 (42), 183 (35), 164 (82), 121 (18), 85 (18%).

(*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3){=C(Me)(NHEt)}]$^+BF_4^-$ (*RS*)-9. Reaction of (*RS*)-**6** (1.00 g, 1.80 mmol) with gaseous ethylamine for 2 h at room temperature afforded (*RS*)-**9** as a yellow solid (0.97 g, 95%) which was crystallised from CH_2Cl_2–Et_2O as red-brown-yellow microcrystals, m.p. 184–187 °C (decomp.) (Found: C, 58.86; H, 5.09; N, 2.34; P, 5.57. $C_{28}H_{29}BF_4FeNOP$ requires: C, 59.09; H, 5.14; N, 2.46; P, 5.44%); ν_{max} 1954 (Fe–CO) and 1056 cm^{-1} (BF_4^-); δ_H 0.93 (3 H, t, *J* 7.1, NCH$_2$C*H*$_3$), 2.39 (3 H, s, Fe=CMe), 3.45 (2 H, m, NC*H*$_2$CH$_3$), 4.77 (5 H, d, J_{PH} 1.1 Hz, C_5H_5), 7.20–7.30 (6 H, m, H_o of PPh_3), 7.40–7.50 (9 H, m, H_m and H_p of PPh_3), 9.57 (1 H, br s, N*H*Et); δ_C 13.20 (s, NCH$_2$*C*H$_3$), 36.92 (s, Fe=C*Me*), 44.88 (s, N*C*H$_2$CH$_3$), 85.33 (s, C_5H_5), 129.05 (d, J_{PC} 9.8, C_m of PPh_3), 131.01 (s, C_p of PPh_3), 132.69 (d, J_{PC} 9.2, C_o of PPh_3), 133.19 (d, J_{PC} 45.1, C_{ipso} of PPh_3), 217.66 (d, J_{PC} 28.8, Fe–CO), 263.69 (d, J_{PC} 21.0 Hz, Fe=C); δ_P 67.65; δ_F −153.80 and −153.85 (1:3); *m*/*z* 482 (M^+, 73), 454 (*M* − CO, 28), 383 (9), 318 (10), 295 (8), 263 (14), 192 (100%).

(*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3){=C(Me)(NHMe)}]$^+PF_6^-$ (*RS*)-14. A saturated solution of NH_4PF_6 in water (150 mL) was added dropwise to a solution of (*RS*)-**8** (1.01 g, 1.78 mmol) in acetone (40 mL) at room temperature under a nitrogen atmosphere. This resulted in the immediate precipitation of a bright yellow solid which was filtered off and washed with water, ethanol and diethyl ether to afford pure (*RS*)-**14** (1.07 g, 96%) which was crystallised from CH_2Cl_2–Et_2O as red-brown yellow-brown plates, m.p. 172–174 °C (decomp.) (Found: C, 53.49; H, 4.38; N, 2.20. $C_{28}H_{29}F_6FeNOP_2$ requires: C, 53.61; H, 4.66; N, 2.23%); ν_{max} 1957 (Fe–CO) and 847 cm^{-1} (PF_6^-); $\delta_H(CD_3COCD_3)$ 1.04 (3 H, t, *J* 7.3, NCH$_2$C*H*$_3$), 2.62 (3 H, s, Fe=CMe), 3.52 (1 H, dq, *J* 13.2, 7.0, NC*H*$_2$CH$_3$), 3.59 (1 H, dq, *J* 13.3, 7.1, NC*H*$_2$CH$_3$), 4.98 (5 H, s, C_5H_5), 7.38 (6 H, dd, J_{PH} 10.3, J_{HH} 7.3 Hz, H_o of PPh_3), 7.56–7.63 (9 H, m, H_m and H_p of PPh_3), 9.79 (1 H, br s, N*H*Et); $\delta_C(CD_3COCD_3)$ 13.60 (s, NCH$_2$*C*H$_3$), 37.52 (s, Fe=C*Me*), 49.57 (s, N*C*H$_2$CH$_3$), 86.46 (s, C_5H_5), 129.99 (d, J_{PC} 9.9, C_m of PPh_3), 131.94 (s, C_p of PPh_3), 133.79 (d, J_{PC} 9.9, C_o of PPh_3), 133.37 (d, J_{PC} 45.5, C_{ipso} of PPh_3), 218.67 (d, J_{PC} 29.3, Fe–CO), 266.67 (d, J_{PC} 22.1 Hz, Fe=C); $\delta_P(CD_3COCD_3)$ 73.12, −142.92 (septet, J_{PF} 708.5 Hz, PF_6^-); $\delta_F(CD_3COCD_3)$ −67.48 (d, J_{PF} 708.5 Hz, PF_6^-); *m*/*z* 482 (M^+, 65), 454 (*M* − CO, 34), 383 (10), 318 (10), 263 (14), 192 (100), 183 (20), 121 (18), 70 (20%).

(*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3){=C(Me)(NHCH$_2$Ph)}]$^+BF_4^-$ (*RS*)-10. Reaction of (*RS*)-**6** (24.27 g, 44.0 mmol) with benzylamine (42.6 mL, 0.43 mol) at 0 °C for 2 h afforded (*RS*)-**10** as a yellow solid (25.12 g, 91%). Recrystallisation from CH_2Cl_2–EtOH gave yellow microneedles, m.p. 199–201 °C (decomp.) [lit.,[9b] 203 °C (decomp.)] (Found: C, 63.08; H, 4.92; N, 2.23; P, 4.96. $C_{33}H_{31}BF_4FeNOP$ requires: C, 62.79; H, 4.95; N, 2.22; P, 4.91%); ν_{max} 1960 (Fe–CO) and 1062 cm^{-1} (BF_4^-); $\delta_H(CDCl_3)$ 2.40 (3 H, s, Fe=CMe), 4.66 (1 H, dd, *J* 14.4, 6.8, NC*H*$_2$Ph), 4.76 (1 H, dd, *J* 14.4, 5.5, NC*H*$_2$Ph), 4.90 (5 H, d, J_{PH} 1.6, C_5H_5), 7.02 (2 H, br d, *J* 7.0, H_o of Ph), 7.11 (6 H, dd, J_{PH} 10.9, J_{HH} 7.7, H_o of PPh_3), 7.20–7.29 (3 H, m, H_m and H_p of Ph), 7.40 (6 H, td, *J* 7.4, 2.0, H_m of PPh_3), 7.48 (3 H, td, *J* 7.9, 2.0 Hz, H_p of PPh_3), 10.14 (1 H, br s, N*H*CH$_2$Ph); $\delta_H(CD_3COCD_3)$ 2.67 (3 H, s, Fe=C*Me*), 4.74 (1 H, d, *J* 13.2, NC*H*$_2$Ph), 4.82 (1 H, d, *J* 13.3, NC*H*$_2$Ph), 5.02 (5 H, d, J_{PH} 0.9, C_5H_5), 7.20 (2 H, dd, *J* 7.5, 2.1, H_o of Ph), 7.30 (6 H, dd, J_{PH} 10.7, J_{HH} 7.8, H_o of PPh_3), 7.35–7.40 (3 H, m, H_m and H_p of Ph), 7.50 (6 H, td, *J* 7.7, 2.0, H_m of PPh_3), 7.58 (3 H, td, *J* 7.2, 1.8 Hz, H_p of PPh_3), 10.32 (1 H, br s, N*H*CH$_2$Ph); $\delta_C(CD_3COCD_3)$ 37.47 (s, Fe=C*Me*), 52.49 (s, N*C*H$_2$Ph), 85.57 (s, C_5H_5), 127.69 (s, C_p of Ph), 127.89 (s, C_m of Ph), 128.76 (s, C_o of Ph), 128.91 (d, J_{PC} 9.2, C_m of PPh_3), 130.83 (s, C_p of PPh_3), 132.53 (d, J_{PC} 9.7, C_o of PPh_3), 133.25 (d, J_{PC} 44.4, C_{ipso} of PPh_3), 135.45 (s, C_{ipso} of Ph), 217.85 (d, J_{PC} 28.8, Fe–CO), 265.44 (d, J_{PC} 23.9 Hz, Fe=C); $\delta_P(CD_3COCD_3)$ 67.31; $\delta_F(CD_3COCD_3)$ −153.42 and −153.48 (1:3); *m*/*z* 544 (M^+, 37), 516 (*M* − CO, 7), 383 (7), 295 (9), 254 (38), 152 (47), 135 (42), 103 (34), 85 (95), 59 (70), 47 (100%).

(*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3){=C(Me)(NHCH$_2$Ph)}]$^+PF_6^-$ (*RS*)-15. A saturated solution of NH_4PF_6 in water (150 mL) was added dropwise to a solution of (*RS*)-**10** (1.00 g, 1.58 mmol) in acetone (200 mL) at room temperature under a nitrogen atmosphere. This resulted in the immediate precipitation of a bright yellow solid which was filtered off, washed with water, ethanol and diethyl ether to afford pure (*RS*)-**15** (1.06 g, 97%). Recrystallisation from CH_2Cl_2–acetone gave yellow microneedles, m.p. 190–192 °C (Found: C, 57.34; H, 4.32; N, 2.06. $C_{33}H_{31}F_6FeNOP_2$ requires: C, 57.49; H, 4.54; N, 2.03%); ν_{max} 1959 (Fe–CO) and 841 cm^{-1} (PF_6^-); $\delta_H(CD_3COCD_3)$ 2.69 (3 H, d, *J* 3.0, Fe=CMe), 4.73 (1 H, dd, *J* 14.8, 3.8, NHC*H*$_2$Ph), 4.83 (1 H, dd, *J* 14.8, 5.3, NHC*H*$_2$Ph), 5.02 (5 H, d, J_{PH} 1.5, C_5H_5), 7.20 (2 H, dd, *J* 7.6, 2.0, H_o of Ph), 7.30 (6 H, dd, J_{PH} 10.8, J_{HH} 7.7, H_o of PPh_3), 7.35–7.42 (3 H, m, H_m and H_p of Ph), 7.50 (6 H, td, *J* 7.9, 2.3, H_m of PPh_3), 7.60 (3 H, tq, *J* 7.8, 1.9 Hz, H_p of PPh_3), 10.26 (1 H, br s, N*H*CH$_2$Ph); $\delta_C(CD_3COCD_3)$ 38.29 (s, Fe=C*Me*), 54.14 (s, N*C*H$_2$Ph), 86.36 (s, C_5H_5), 129.00 (s, C_p of Ph), 129.19 (s, C_m of Ph), 129.88 (s, C_o of Ph), 129.91 (d, J_{PC}

8.3, C_m of PPh_3), 131.90 (s, C_p of PPh_3), 133.50 (d, J_{PC} 9.6, C_o of PPh_3), 133.67 (d, J_{PC} 31.4, C_{ipso} of PPh_3), 134.17 (s, C_{ipso} of Ph), 218.85 (d, J_{PC} 30.8, Fe–CO), 271.44 (d, J_{PC} 23.1 Hz, Fe=C); $\delta_P(CD_3COCD_3)$ 67.49 (s, PPh_3), −147.12 (septet, J_{PF} 706.5 Hz, PF_6^-); $\delta_F(CD_3COCD_3)$ −69.18 (d, J_{PF} 707.7 Hz, PF_6^-); *m*/*z* 544 (M^+, 85), 516 (M − CO, 13), 383 (14), 279 (19), 254 (100), 212 (14), 183 (20), 91 (20), 85 (24), 59 (18), 47 (27%).

(*RS*)-[(η⁵-C_5H_5)Fe(CO)(PPh_3){=C(Me)($NHCH_2CH$=CH_2)}]⁺BF_4^- (*RS*)-11. Reaction of (*RS*)-**6** (0.50 g, 0.90 mmol) with allylamine (1.18 g, 20 mmol) at room temperature for 2 h afforded (*RS*)-**11** as a yellow solid (0.51 g, 98%). Recrystallisation from CH_2Cl_2–EtO_2 gave red microneedles, m.p. 174–177 °C (Found: C, 59.77; H, 4.86; N, 1.97; P, 5.18. $C_{29}H_{29}BF_4FeNOP$ requires: C, 59.93; H, 5.03; N, 2.41; P, 5.33%); ν_{max} 1955 (Fe–CO) and 1055 cm^{-1} (BF_4^-); δ_H 2.37 (3 H, s, Fe=CMe), 4.00–4.10 (2 H, m, NCH_2CH=CH_2), 4.78 (5 H, s, C_5H_5), 5.08 (1 H, d, *J* 12.5, NCH_2CH=CH_2), 5.11 (1 H, d, *J* 4.5 Hz, NCH_2CH=CH_2), 5.43–5.52 (1 H, m, NCH_2CH=CH_2), 7.24–7.27 (6 H, m, H_o of PPh_3), 7.48–7.50 (9 H, m, H_m and H_p of PPh_3), 9.78 (1 H, br s, N*H*CH_2CH=CH_2); δ_C 37.46 (s, Fe=C*Me*), 52.44 (s, N*C*H_2CH=CH_2), 85.58 (s, C_5H_5), 119.95 (s, NCH_2CH=*C*H_2), 129.14 (d, J_{PC} 9.5, C_m of PPh_3), 130.67 (s, NCH_2*C*H=CH_2), 131.09 (s, C_p of PPh_3), 132.80 (d, J_{PC} 9.5, C_o of PPh_3), 133.26 (d, J_{PC} 45.7, C_{ipso} of PPh_3), 217.80 (d, J_{PC} 29.0, Fe–CO), 265.96 (d, J_{PC} 22.6 Hz, Fe=C); δ_P 67.05; δ_F −153.77 and −153.83 (1:3); *m*/*z* 494 (M^+, 100), 466 (M − CO, 22), 458 (9), 383 (20), 310 (12), 295 (18), 263 (30), 239 (11), 227 (17), 204 (87), 183 (37), 162 (20), 121 (18%).

(*RS*)-[(η⁵-C_5H_5)Fe(CO)(PPh_3){=C(Me)($NHCH_2CH_2OH$)}]⁺BF_4^- (*RS*)-12. Reaction of (*RS*)-**6** (1.80 g, 3.24 mmol) with aminoethanol (1.95 mL, 32.4 mmol) at room temperature for 15 min afforded (*RS*)-**12** as an orange solid (2.08 g, 97%). Recrystallisation from CH_2Cl_2–EtO_2 gave orange microneedles, m.p. 139–141 °C (Found: C, 59.64; H, 5.18; N, 2.23; P, 5.05. $C_{28}H_{29}BF_4FeNO_2P$ requires: C, 59.52; H, 5.00; N, 2.39; P, 5.29%); ν_{max} 1940 (Fe–CO) and 1057 cm^{-1} (BF_4^-); δ_H 2.46 (3 H, s, Fe=CMe), 2.81 (1 H, t, *J* 5.5, NCH_2CH_2OH), 3.42–3.58 (3 H, m, NCH_2CH_2OH), 4.77 (5 H, d, J_{PH} 1.0, C_5H_5), 7.28 (6 H, dd, J_{PH} 10.9, J_{HH} 7.5, H_o of PPh_3), 7.50 (6 H, td, *J* 6.9, 1.9, H_m of PPh_3), 7.55 (3 H, td, *J* 7.5, 2.0 Hz, H_p of PPh_3), 9.35 (1 H, br s, N*H*CH_2CH_2OH); δ_C 38.11 (s, Fe=C*Me*), 52.10 (s, N*C*H_2-CH_2OH), 59.83 (s, NCH_2*C*H_2OH), 85.97 (s, C_5H_5), 129.68 (d, J_{PC} 9.6 Hz, C_m of PPh_3), 131.70 (s, C_p of PPh_3), 133.37 (d, J_{PC} 10.0, C_o of PPh_3), 133.74 (d, J_{PC} 53.9, C_{ipso} of PPh_3), 218.25 (d, J_{PC} 28.4, Fe–CO), 267.64 (d, J_{PC} 22.1 Hz, Fe=C); δ_P 69.52; δ_F −153.54 and −153.58 (1:3); *m*/*z* 498 (M^+, 71), 470 (M − CO, 8), 383 (13), 318 (6), 295 (35), 263 (25), 208 (100), 183 (22), 142 (13%).

(*RS*)-[(η⁵-C_5H_5)Fe(CO)(PPh_3){=C(Me)($NHCHMe_2$)}]⁺BF_4^- (*RS*)-13. Reaction of (*RS*)-**6** (1.11 g, 2.00 mmol) with isopropylamine (1.18 g, 20 mmol) at room temperature for 2 h afforded (*RS*)-**13** as a yellow solid (1.02 g, 88%). Recrystallisation from CH_2Cl_2–EtOH gave yellow microcrystals, m.p. 213–214 °C (decomp.) (Found: C, 59.81; H, 5.58; N, 2.29; P, 5.15. $C_{29}H_{31}BF_4FeNOP$ requires: C, 59.73; H, 5.35; N, 2.40; P, 5.31%); ν_{max} 1964 (Fe–CO) and 1058 cm^{-1} (BF_4^-); δ_H 0.97 (3 H, d, *J* 6.5, CH*Me*$_2$), 1.23 (3 H, d, *J* 6.5, CH*Me*$_2$), 2.53 (3 H, s, Fe=CMe), 3.96 (1 H, octet, NHC*H*Me_2), 4.80 (5 H, s, C_5H_5), 7.19–7.27 (6 H, m, H_o of PPh_3), 7.48–7.53 (9 H, m, H_m and H_p of PPh_3), 9.22 (1 H, br s, N*H*$CHMe_2$); δ_C 20.67 (s, NHCH*Me*$_2$), 21.21 (s, NHCH*Me*$_2$), 37.38 (s, Fe=C*Me*), 52.51 (s, NH*C*HMe_2), 85.40 (s, C_5H_5), 129.25 (d, J_{PC} 9.8, C_m of PPh_3), 131.18 (s, C_p of PPh_3), 132.74 (d, J_{PC} 9.7, C_o of PPh_3), 133.07 (d, J_{PC} 44.8 Hz, C_{ipso} of PPh_3), 217.54 (d, J_{PC} 28.8, Fe–CO), 262.48 (d, J_{PC} 21.8 Hz, Fe=C); δ_P 68.32; δ_F −152.73 and −152.79 (1:3); *m*/*z* 496 (M^+, 35), 468 (M − CO, 15), 383 (6), 318 (10), 294 (9), 206 (100), 183 (27), 164 (20), 121 (21), 84 (25), 56 (9%).

(*R*,*S*)-[(η⁵-C_5H_5)Fe(CO)(PPh_3){=C(Me)[NHCH(Me)Ph]}]⁺-BF_4^- (*R*,*S*)-33. Reaction of (*R*)-**6** (0.40 g, 0.72 mmol) with (*S*)-α-methylbenzylamine (0.93 mL, 7.19 mmol) at room temperature for 2 h afforded (*R*,*S*)-**33** as a yellow solid (0.43 g, 93%). Recrystallisation from CH_2Cl_2–EtOH gave orange microneedles, m.p. 194–196 °C (decomp.) [lit.,[8] 195 °C (decomp.)] (Found: C, 63.51; H, 5.16; N, 2.16; P, 5.00. $C_{34}H_{33}BF_4FeNOP$ requires: C, 63.29; H, 5.15; N, 2.17; P, 4.80%); $[\alpha]_D$ (20 °C, *c* = 3.00, CH_2Cl_2) −16.3; ν_{max} 1965 (Fe–CO) and 1058 cm^{-1} (BF_4^-); $\delta_H(CD_3COCD_3)$ 1.60 [3 H, d, *J* 6.8 Hz, NHCH(*Me*)Ph], 2.64 (3 H, Fe=CMe), 5.01 (5 H, d, J_{PH} 1.3, C_5H_5), 5.27 [1 H, quintet, *J* 6.8 Hz, NHC*H*(Me)Ph], 7.17–7.63 (20 H, m, PPh_3 and Ph), 9.98 [1 H, br s, N*H*CH(Me)Ph]; $\delta_H(CDCl_3)$ 1.54 [3 H, d, *J* 6.8, NHCH(*Me*)Ph], 2.52 (3 H, s, Fe=C*Me*), 4.84 (5 H, d, J_{PH} 1.3 Hz, C_5H_5), 5.00 [1 H, quintet, *J* 6.8, NHC*H*-(Me)Ph], 6.89–7.53 (20 H, m, PPh_3 and Ph), 9.46 [1 H, br s, N*H*CH(Me)Ph]; $\delta_C(CDCl_3)$ 22.11 [s, NHCH(*Me*)Ph], 39.12 (s, Fe=C*Me*), 60.64 [s, NH*C*H(Me)Ph], 85.60 (s, C_5H_5), 126.72 (s, C_m of Ph), 128.1 (s, C_p of Ph), 129.1 (s, C_o of Ph), 129.25 (d, J_{PC} 9.8 Hz, C_m of PPh_3), 131.18 (s, C_p of PPh_3), 132.74 (d, J_{PC} 9.7, C_o of PPh_3), 133.17 (d, J_{PC} 44.8, C_{ipso} of PPh_3), 140.38 (s, C_{ipso} of Ph), 217.53 (d, J_{PC} 29.8, Fe–CO), 267.03 (d, J_{PC} 21.9 Hz, Fe=C); $\delta_P(CDCl_3)$ 68.84; $\delta_F(CDCl_3)$ −153.07 and −153.13 (1:3); *m*/*z* 558 (M^+, 71), 530 (M − CO, 92), 383 (8), 268 (100), 239 (9), 226 (14), 203 (13), 183 (32), 162 (20), 146 (13), 121 (20), 105 (49%).

(*S*,*S*)-[(η⁵-C_5H_5)Fe(CO)(PPh_3){=C(Me)[NHCH(Me)Ph]}]⁺-BF_4^- (*S*,*S*)-34. Reaction of (*S*)-**6** (0.40 g, 0.72 mmol) with (*S*)-α-methylbenzylamine (0.93 mL, 7.19 mmol) at room temperature for 2 h afforded (*S*,*S*)-**34** as a yellow solid (0.46 g, 95%). Recrystallisation from CH_2Cl_2–EtOH gave yellow plates, m.p. 194–196 °C (decomp.) [lit.,[8] m.p. 186 °C (decomp.)] (Found: C, 63.42; H, 5.18; N, 2.08; P, 5.03. $C_{34}H_{33}BF_4FeNOP$ requires: C, 63.29; H, 5.15; N, 22.17; P, 4.80%); $[\alpha]_D$ (20 °C, *c* = 1.005, CH_2Cl_2) 154.6; ν_{max} 1965 (Fe–CO) and 1062 cm^{-1} (BF_4^-); $\delta_H(CD_3COCD_3)$ 1.41 [3 H, d, *J* 6.8, NHCH(*Me*)Ph], 2.72 (3 H, Fe=CMe), 4.97 (5 H, d, J_{PH} 1.4, C_5H_5), 5.32 [1 H, quintet, *J* 6.8 Hz, NHC*H*(Me)Ph], 7.29–7.61 (20 H, m, PPh_3 and Ph), 9.90 [1 H, br s, N*H*CH(Me)Ph]; $\delta_H(CDCl_3)$ 1.40 [3 H, d, *J* 6.9, NHCH(*Me*)Ph], 2.48 (3 H, s, Fe=CMe), 4.76 (5 H, d, J_{PH} 1.3, C_5H_5), 4.79 [1 H, quintet, *J* 6.9 Hz, NHC*H*(Me)Ph], 7.18–7.53 (20 H, m, PPh_3 and Ph), 9.68 [1 H, br s, N*H*CH(Me)Ph]; δ_C 21.61 [s, NHCH(*Me*)Ph], 38.83 (s, Fe=C*Me*), 60.65 [s, NH*C*H(Me)Ph], 85.30 (s, C_5H_5), 126.51 (s, C_m of Ph), 128.1 (s, C_p of Ph), 129.1 (s, C_o of Ph), 129.25 (d, J_{PC} 9.8, C_m of PPh_3), 131.18 (s, C_p of PPh_3), 132.74 (d, J_{PC} 9.7 Hz, C_o of PPh_3), 133.08 (d, J_{PC} 44.8, C_{ipso} of PPh_3), 140.60 (s, C_{ipso} of Ph), 217.33 (d, J_{PC} 29.8, Fe–CO), 267.93 (d, J_{PC} 21.9 Hz, Fe=C); $\delta_P(CDCl_3)$ 68.85; $\delta_F(CDCl_3)$ −153.07 and −153.13 (1:3); *m*/*z* 558 (M^+, 60), 530 (M − CO, 13), 383 (8), 268 (100), 239 (9), 226 (12), 183 (19), 163 (19), 105 (20), 89 (23), 77 (35), 59 (85%).

(*RS*,*SR*)- and (*RR*,*SS*)-[(η⁵-C_5H_5)Fe(CO)(PPh_3){=C(Me)-[NHCH(Me)Ph]}]⁺BF_4^- (*RS*,*SR*)-33 and (*RR*,*SS*)-34. A solution of (±)-α-methylbenzylamine (4.85 g, 40 mmol) in THF (20 mL) was added to (*RS*)-**6** (1.11 g, 2.0 mmol) and the reaction mixture was stirred for 2 h at 0 °C under nitrogen. The yellow precipitate that had formed in the reaction mixture was filtered off, washed with THF, and dried *in vacuo*. The precipitate [0.77 g, 60%, (*RS*,*SR*):(*RR*,*SS*) = 92:8] was recrystallised twice from CH_2Cl_2–EtOH to give yellow needles (*RS*,*SR*) (0.66 g, 51%). The filtrate and washings were combined and concentrated *in vacuo*. The residual oil was distilled at 60–65 °C under vacuum to give (±)-α-methylbenzylamine as a colourless oil (2.30 g, 47%) and a yellow residue which was left overnight to crystallise. Filtration followed by washing with benzene gave a yellow solid which consisted (^{1}H NMR spectroscopy) of (*RS*,*SR*):(*RR*,*SS*) in a ratio of 15:85. Column chromatography on alumina (5% MeOH–CH_2Cl_2) followed by two crystallisations

from CH_2Cl_2–benzene gave the (*RR*,*SS*) diastereoisomers as yellow needles (0.139 g, 11%).

(*R*,*S*)- and (*S*,*S*)-[(η^5-C_5H_5)Fe(CO)(PPh_3){=C(Me)[NHCH(Me)Ph]$^+BF_4^-$ (*R*,*S*)-33 and (*S*,*S*)-34. A solution of (*S*)-(−)-α-methylbenzylamine (5.69 g, 47 mmol) in THF (47 mL) was added to (*RS*)-**6** (2.64 g, 4.7 mmol) and the reaction mixture was stirred for 2.75 h at 0 °C. The red reaction mixture was concentrated to about 30 mL and was then stirred for a further 1.5 h during which time a precipitate formed. The yellow precipitate was filtered off, washed with THF and dried *in vacuo*. The precipitate (1.14 g, 1.77 mmol, 38%) was shown to consist of a mixture of diastereoisomers of (*R*,*S*):(*S*,*S*) in the ratio of 93:7. This solid was recrystallised from EtOH (150 mL) to give pure (*R*,*S*)-**33** as yellow needles (0.95 g, 1.48 mmol, 31%). The filtrate and washings were combined and concentrated *in vacuo*. The residual oil was distilled at 60–65 °C *in vacuo* to give (*S*)-(−)-α-methylbenzylamine as a colourless oil {4.32 g, 76%, $[\alpha]_D$ (neat) −39.4°}. The resultant residue was dissolved in a minimum amount of benzene and left to crystallise over 3 d. Filtration followed by washing with benzene gave a mixture of (*R*,*S*):(*S*,*S*) in the ratio of 22:78. Two recrystallisations from EtOH gave pure (*S*,*S*)-**34** as yellow plates (0.44 g, 0.68 mmol, 15%).

Coupling reactions with secondary amines and amino acid derivatives

Attempted coupling reactions of (*RS*)-**6** with Me_2NH, Et_2NH, pyrrolidine, glycine, glycine methyl ester, and glycine *tert*-butyl ester under the standard reaction conditions afforded mostly unreacted starting material and demethylated (*RS*)-**5**.

(*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3){=C(Et)(NHMe)}]$^+BF_4^-$ (*RS*)-18. Reaction of (*RS*)-**17** (1.32 g, 2.37 mmol) with aqueous $MeNH_2$ (40%, 1.86 mL, 23.7 mmol) for 2 h at 0 °C afforded (*RS*)-**18** as a yellow solid (0.89 g, 66%) which was crystallised from CH_2Cl_2–Et_2O as yellow rods (hemisolvate), m.p. 185–189 °C (decomp.) (Found: C, 59.27; H, 5.45; N, 2.31. $C_{28}H_{29}BF_4FeNOP\cdot0.5C_4H_{10}O$ requires: C, 59.44; H, 5.66; N, 2.31%); ν_{max} 1953 (Fe–CO) and 1056 cm^{-1} (BF_4^-); δ_H 1.01 (3 H, t, *J* 7.4 Hz, Fe=CCH_2CH_3), 2.18–2.29 (2 H, m, Fe=CCH_2CH$_3$), 3.03 (3 H, s, NH*Me*), 4.82 (5 H, s, C_5H_5), 7.31–7.36 (6 H, m, H_o of PPh_3), 7.50–7.55 (9 H, m, H_m and H_p of PPh_3), 9.84 (1 H, br s, N*H*Me); δ_C 10.15 (s, Fe=CCH$_2$*C*H$_3$), 36.65 (s, NH*Me*), 41.39 (s, Fe=C*C*H$_2$CH$_3$), 85.68 (s, C_5H_5), 129.19 (d, J_{PC} 9.5, C_m of PPh_3), 131.12 (s, C_p of PPh_3), 132.95 (d, J_{PC} 8.8, C_o of PPh_3), 133.31 (d, J_{PC} 46.0, C_{ipso} of PPh_3), 218.47 (d, J_{PC} 30.2, Fe–CO), 268.48 (d, J_{PC} 20.1 Hz, Fe=C); δ_P 66.20; δ_F −154.00 and −154.05 (1:3); *m*/*z* 482 (M^+, 100), 454 (*M* − CO, 27), 383 (13), 318 (9), 295 (46), 263 (23), 220 (9), 192 (98), 183 (27), 85 (29), 70 (34%). The yield of this reaction could not be improved by using gaseous methylamine.

(*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3){=C(Et)(NHEt)}]$^+BF_4^-$ (*RS*)-19. Reaction of (*RS*)-**17** (1.00 g, 1.80 mmol) with gaseous ethylamine for 2 h at 0 °C afforded (*RS*)-**19** as a yellow foam (0.73 g, 70%) which could not be crystallised from a number of solvents. Microanalytical data could not be obtained as this product contained 5% of [(η^5-C_5H_5)Fe(CO)$_2$(PPh_3)]$^+BF_4^-$ which could not be separated from the product either by chromatography or selective crystallisation; ν_{max} 1954 (Fe–CO) and 1057 cm^{-1} (BF_4^-); δ_H 0.85 (3 H, t, *J* 7.1, NCH$_2$CH_3), 1.08 (3 H, t, *J* 7.6 Hz, Fe=CCH$_2$CH_3), 2.37–2.56 (2 H, m, Fe=CCH_2CH$_3$), 3.42–3.51 (2 H, m, NCH_2CH$_3$), 4.82 (5 H, s, C_5H_5), 7.15–7.65 (15 H, m, PPh_3), 9.61 (1 H, br s, N*H*Et); δ_C 11.14 (s, Fe=CCH$_2$*C*H$_3$), 13.95 (s, NCH$_2$*C*H$_3$), 41.31 (s, Fe=C*C*H$_2$CH$_3$), 44.62 (s, N*C*H$_2$CH$_3$), 85.34 (s, C_5H_5), 129.11 (d, J_{PC} 9.6, C_m of PPh_3), 131.10 (s, C_p of PPh_3), 132.76 (d, J_{PC} 8.9, C_o of PPh_3), 133.00 (d, J_{PC} 50.5, C_{ipso} of PPh_3), 218.12 (d, J_{PC} 28.5, Fe=CO), 267.04 (d, J_{PC} 23.2 Hz, Fe=C); δ_P 67.19; δ_F −153.57 and −153.63 (1:3); *m*/*z* 496 (M^+, 73), 468 (*M* − CO, 21), 383 (12), 318 (10), 295 (10), 279 (32), 263 (13), 206 (100), 183 (17), 129 (40), 84 (27%).

(*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3){=C(Et)(NHCH$_2$Ph)}]$^+BF_4^-$ (*RS*)-20. Reaction of (*RS*)-**17** (7.29 g, 0.13 mol) with benzylamine (14.2 mL, 0.13 mol) at 0 °C for 2 h afforded (*RS*)-**20** as a yellow solid (6.73 g, 80%). Recrystallisation from CH_2Cl_2–EtOH gave yellow microneedles, m.p. 197–199 °C (decomp.) (Found: C, 63.15; H, 4.91; N, 2.05; P, 4.74. $C_{34}H_{33}BF_4FeNOP$ requires: C, 63.15; H, 5.16; N, 2.17; P, 4.80%); ν_{max} 1957 (Fe–CO) and 1068 cm^{-1} (BF_4^-); δ_H 1.09 (3 H, t, *J* 7.6, Fe=CCH$_2$CH_3), 2.41–2.06 (1 H, m, Fe=CCH_2CH$_3$), 2.71–2.74 (1 H, m, Fe=CCH_2CH$_3$), 4.40 (1 H, dd, *J* 14.2, 7.4, NCH_2Ph), 4.84 (1 H, dd, *J* 14.2, 4.5, NCH_2Ph), 4.90 (5 H, d, J_{PH} 1.6, C_5H_5), 6.95 (2 H, d, *J* 7.3, H_o of Ph), 7.08 (6 H, dd, J_{PH} 10.1, J_{HH} 7.5, H_o of PPh_3), 7.09 (3 H, br d, *J* 8.1, H_m of PPh_3), 7.15 (2 H, br t, *J* 7.5, H_m of Ph), 7.21 (1 H, t, *J* 7.5, H_p of Ph), 7.38 (6 H, br t, *J* 7.4, H_m of PPh_3), 7.47 (3 H, br t, *J* 7.9 Hz, H_p of PPh_3), 10.19 (1 H, br s, N*H*CH$_2$Ph); δ_C 10.94 (s, Fe=CCH$_2$*C*H$_3$), 41.68 (s, Fe=C*C*H$_2$CH$_3$), 52.08 (s, N*C*H$_2$Ph), 85.74 (s, C_5H_5), 128.32 (s, C_p of Ph), 128.69 (s, C_m of Ph), 129.49 (s, C_o of Ph), 129.59 (d, J_{PC} 9.7, C_m of PPh_3), 131.59 (s, C_p of PPh_3), 133.26 (d, J_{PC} 9.7, C_o of PPh_3), 133.47 (d, J_{PC} 45.6, C_{ipso} of PPh_3), 136.75 (s, C_{ipso} of Ph), 218.40 (d, J_{PC} 29.8, Fe–CO), 268.45 (d, J_{PC} 23.9 Hz, Fe=C); δ_P 67.33; δ_F −153.01 and −153.06 (1:3); *m*/*z* 558 (M^+, 74), 530 (*M* − CO, 7), 383 (11), 318 (8), 295 (10), 268 (100), 212 (17), 183 (20), 91 (30), 85 (22), 47 (17%).

(*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3){=C(Et)(NHCH$_2$Ph)}]$^+PF_6^-$ (*RS*)-21. A saturated solution of NH_4PF_6 in water (80 mL) was added dropwise to a solution of (*RS*)-**20** (1.00 g, 1.55 mmol) in acetone (120 mL) at room temperature under a nitrogen atmosphere. This resulted in the immediate precipitation of a bright yellow solid which was filtered off, washed with water, ethanol and diethyl ether to afford pure (*RS*)-**21** (1.04 g, 95%). Recrystallisation from CH_2Cl_2–acetone gave yellow microneedles, m.p. 186–188 °C (Found: C, 58.29; H, 4.72; N, 2.06. $C_{34}H_{33}F_6FeNOP_2$ requires: C, 58.05; H, 4.73; N, 1.99%); ν_{max} 1958 (Fe–CO) and 842 cm^{-1} (PF_6^-); δ_H(CD_3COCD_3) 1.21 (3 H, t, *J* 7.7, Fe=CCH$_2$CH_3), 2.36–2.42 (1 H, m, Fe=CCH_2CH$_3$), 3.02–3.07 (1 H, m, Fe=CCH_2CH$_3$), 4.69 (1 H, dd, *J* 14.7, 4.4, NHCH_2Ph), 4.87 (1 H, dd, *J* 14.7, 6.7, NHCH_2Ph), 5.12 (5 H, d, J_{PH} 1.4, C_5H_5), 7.07 (2 H, dd, *J* 7.7, 2.1, H_o of Ph), 7.25 (6 H, dd, J_{PH} 10.1, J_{HH} 7.7, H_o of PPh_3), 7.31–7.36 (3 H, m, H_m and H_p of Ph), 7.48 (6 H, tq, *J* 7.5, 2.1, H_m of PPh_3), 7.58 (3 H, tq, *J* 7.6, 1.9 Hz, H_p of PPh_3), 10.11 (1 H, br s, N*H*CH$_2$Ph); δ_C(CD_3COCD_3) 11.35 (s, Fe=CCH$_2$*C*H$_3$), 43.14 (s, Fe=C*C*H$_2$CH$_3$), 53.82 (s, N*C*H$_2$Ph), 86.42 (s, C_5H_5), 128.99 (s, C_p of Ph), 129.25 (s, C_m of Ph), 129.95 (s, C_o of Ph), 129.98 (d, J_{PC} 9.2, C_m of PPh_3), 132.00 (s, C_p of PPh_3), 133.70 (d, J_{PC} 9.6, C_o of PPh_3), 133.91 (d, J_{PC} 43.3, C_{ipso} of PPh_3), 136.25 (s, C_{ipso} of Ph), 218.86 (d, J_{PC} 29.1, Fe–CO), 273.03 (d, J_{PC} 23.3 Hz, Fe=C); δ_P(CD_3COCD_3) 67.70 (s, PPh_3), −147.11 (septet, J_{PF} 708.7 Hz, PF_6^-); δ_F(CD_3COCD_3) −69.13 (d, J_{PF} 707.8 Hz, PF_6^-); *m*/*z* 558 (M^+, 87), 530 (*M* − CO, 7), 383 (10), 295 (10), 268 (100), 212 (15), 183 (25), 121 (10), 91 (27), 59 (13%).

(*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3){=C(CH$_2$CH$_2$CH$_2$CH$_3$)(NHMe)}]$^+BF_4^-$ (*RS*)-24. Reaction of (*RS*)-**23** (1.18 g, 1.97 mmol) with gaseous methylamine at 0 °C for 2 h afforded (*RS*)-**24** as a yellow foam (0.88 g, 80%). Microanalytical data could not be obtained for this product which was isolated as a mixture with [(η^5-C_5H_5)Fe(CO)$_2$(PPh_3)]BF_4^- (10%). This impurity could not be removed by column chromatography or selective recrystallisation; ν_{max} 1964 (Fe–CO) and 1054 cm^{-1} (BF_4^-); δ_H 0.88 (3 H, t, *J* 7.1 Hz, Fe=CCH$_2$CH$_2$CH$_2$CH_3), 1.10–2.50 (6 H, m, Fe=CCH_2CH_2CH_2CH$_3$), 3.00 (3 H, s, NMe), 4.79 (5 H, s, C_5H_5), 7.19–7.82 (15 H, m, PPh_3), 10.19 (1 H, br s, N*H*Me);

δ_C 13.46 (s, Fe=$CCH_2CH_2CH_2CH_3$), 22.66 (s, Fe=CCH_2CH_2-CH_2CH_3), 27.75 (s, Fe=$CCH_2CH_2CH_2CH_3$), 36.12 (s, NMe), 48.05 (s, Fe=$CCH_2CH_2CH_2CH_3$), 85.33 (s, C_5H_5), 129.04 (d, J_{PC} 9.8, C_m of PPh_3), 131.06 (s, C_p of PPh_3), 133.82 (d, J_{PC} 9.8, C_o of PPh_3), 133.11 (d, J_{PC} 46.3, C_{ipso} of PPh_3), 218.28 (d, J_{PC} 28.5, Fe–CO), 267.94 (d, J_{PC} 23.5 Hz, Fe=C); δ_P 66.25; δ_F −153.85 and −153.90 (1:3); *m*/*z* 510 (M^+, 44), 482 (M − CO, 18), 220 (100), 183 (20), 129 (72), 98 (40%).

Deuteriation studies of (*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3){=C(Me)-($NHCH_2Ph$)}]$^+PF_6^-$ (*RS*)-15

Method (a). Treatment of a nitrogen degassed solution of **15** (50 mg) in CD_3OD with NaOMe (20 mol %) at room temperature for 3 d afforded by ^{1}H NMR analysis (*RS*)-[(η^5-C_5H_5)-Fe(CO)(PPh_3){=C(CD_3)($NDCH_2Ph$)}]$^+PF_6^-$.

Method (b). Treatment of a solution of (*RS*)-**15** (100 mg) in THF (10 mL) with BuLi (1 mol equivalent) at −78 °C for 30 min followed by quenching with CD_3OD and concentration *in vacuo* afforded by ^{1}H NMR analysis (*RS*)-[(η^5-C_5H_5)Fe(CO)-(PPh_3){=C(Me)($NDCH_2Ph$)}]$^+PF_6^-$ (*RS*)-**28**.

Method (c). Treatment of a solution of (*RS*)-**15** (100 mg) in THF (10 mL) with BuLi (3 or more mol equivalents) at −78 °C for 3 h followed by quenching with either CD_3OD or D_2O and filtration through dry Celite afforded (*RS*)-[(η^5-C_5H_5)-Fe(CO)(PPh_3){=C(CD_2H)($NDCH_2Ph$)}]$^+PF_6^-$ (*RS*)-**30** which was recrystallised from CH_2Cl_2–hexane as yellow microneedles, m.p. 197–199 °C (decomp.) (Found: C, 57.40; H, 4.80; N, 2.03. $C_{33}H_{28}BD_3F_4FeNOP$ requires: C, 57.24; H, 4.95; N, 2.02%); ν_{max} 1958 (Fe–CO) and 841 cm^{-1} (PF_6^-); δ_H(CD_2Cl_2) 2.69 (1 H, br s, Fe=CD_2H), 4.53 (1 H, dd, *J* 14.6, 4.8, $NHCH_2Ph$), 4.58 (1 H, dd, *J* 14.4, 5.9, $NHCH_2Ph$), 4.77 (5 H, s, C_5H_5), 7.00 (2 H, br d, *J* 7.3, H_o of Ph), 7.10 (6 H, dd, J_{PH} 10.8, J_{HH} 7.7, H_o of PPh_3), 7.30–7.38 (3 H, m, H_m and H_p of Ph), 7.41 (6 H, td, *J* 7.6, 1.9, H_m of PPh_3), 7.51 (3 H, tq, *J* 7.5, 1.7 Hz, H_p of PPh_3); *m*/*z* 547 (M^+, 68), 519 (M − CO, 10), 383 (18), 338 (17), 318 (11), 295 (31), 279 (32), 263 (37), 256 (100), 212 (35), 183 (25), 161 (30), 148 (13), 133 (15), 121 (17), 103 (24), 91 (41%).

Crystal structure determination of (*R*,*S*)-33

$C_{34}H_{33}BF_4FeNOP$, M = 589.42, orthorhombic, $P22_12_1$ (no. 18), a = 10.603(1), b = 11.894(1), c = 24.779(3) Å (from least squares fitting of setting angles for 25 reflections $20.1 \leqslant \theta \leqslant 32.9°$), U = 3125 Å^3, Z = 4, D_x = 1.253 g cm^{-3}, Cu-Kα radiation, orange needles 0.2 × 0.2 × 0.1 mm, μ = 11.99 cm^{-1}. 7271 Reflections measured, 5759 unique (R_{merge} = 0.03, Friedel pairs were not merged) of which 2978 were observed ($I \geqslant 3\sigma I$). At convergence R = 0.038, R' = 0.031 for 399 parameters. CCDC reference number 186/949.

Acknowledgements

We thank the EPSRC for a ROPA award.

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Received 3rd *February* 1998; *Paper* 8/00927I