Phosphoramidate-Mediated Conversion of Carbonyl Ligands into Isocyanide Ligands: A New Approach to Chiral Isocyanide Ligands

Susan E. Gibson,*[a] Hasim Ibrahim,[a] Corinne Pasquier,[a] Mark A. Peplow,[b] Julia M. Rushton,[a] Jonathan W. Steed,[a] and Surojit Sur[a]

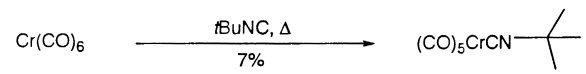
Abstract: Metal isocyanides have been used and studied by organometallic chemists for many years and, as a result, they have a rich and interesting chemistry. The nature of metal-free isocyanides and the methods of making isocyanide complexes, however, has resulted in the vast majority of studies to date being performed with structurally simple isocyanides. We report here a new approach to the synthesis of isocyanide ligands that involves the reaction of a metal carbonyl ligand with the anion of a phosphoramidate. As phosphoramidates can be synthesised in one step from amines, our method means that the structural diversity of readily available amines, particularly chiral amines, can now be incorporated into isocyanide ligands.

Keywords: amines · asymmetric synthesis · carbonyl ligands · iron · isocyanide ligands

Introduction

Isocyanide ligands are known to form complexes with many transition metals.[1] Difficulties associated with the synthesis of isocyanide ligands, however, mean that the vast majority of isocyanide complexes synthesised and studied to date have been complexes of relatively simple aryl and alkyl isocyanides. Complexes of more complicated isocyanides, such as chiral isocyanides, are surprisingly rare, a situation which contrasts sharply of course with the number of complexes bearing chiral phosphine ligands that have been prepared and studied. In this paper we demonstrate how a new method of synthesising isocyanide ligands can be used to generate enantiomerically pure isocyanide complexes in a relatively straightforward manner.

The synthesis of isocyanide complexes is most commonly achieved by direct combination of a metal complex with an isocyanide. In the case of metal–carbonyl complexes, thermolysis or photolysis is used to remove a carbonyl ligand from the parent complex before the free ligand site is occupied by the isocyanide. This approach is generally complicated by multiple substitutions resulting in low yields, as exemplified by the synthesis of the chromium complex **1**,[2] but in some cases, such as those detailed in a recent report on the use of



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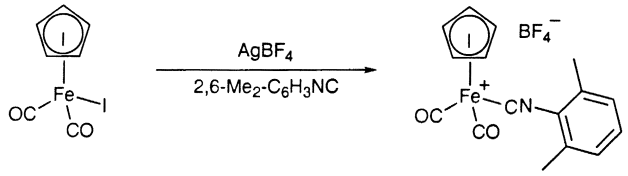
dicarbonyl(isocyanide)chromium(0) linkers for attaching fluoroarenes to solid supports,[3] yields can be very good. Creation of a vacant coordination site may also be achieved by the removal of an iodide ligand with a silver(I) salt as illustrated by the synthesis of iron cation **2**.[4] There are several



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drawbacks to the direct synthesis approaches outlined above which perhaps explain why isocyanides other than simple aryl and alkyl isocyanides have not featured more prominently in organometallic chemistry to date: few free isocyanides are commercially available and the synthesis of other isocyanides

[a] Prof. S. E. Gibson, H. Ibrahim, Dr. C. Pasquier, J. M. Rushton, Dr. J. W. Steed, Dr. S. Sur
Department of Chemistry, King's College London
Strand, London WC2R 2LS (UK)
Fax: (+44) 171-8482810
E-mail: susan.gibson@kcl.ac.uk

[b] M. A. Peplow
Department of Chemistry
Imperial College of Science, Technology and Engineering
South Kensington, London SW7 2AY (UK)

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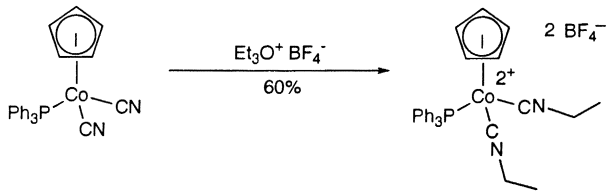
is frequently arduous; some isocyanides are toxic and many are malodorous.

Alternative methods for creating isocyanide ligands have been developed, including alkylation of cyanide ligands and the reaction of phosphinimines with carbonyl ligands. The production of cobalt complex **3** was achieved by a double alkylation reaction.[5] Despite the fact that this approach



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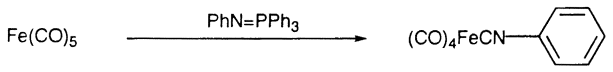
requires the use of KCN to create the necessary cyanide ligands, it continues to find application as indicated by its recent use in the synthesis of a range of alkyl, allyl and propargyl isocyanide complexes by treatment of *trans*-$[FeH(CN)(dppe)_2]$ with suitable electrophiles.[6] The iron isocyanide complex **4** has been synthesised by reaction of



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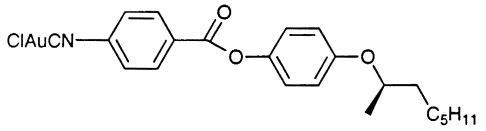
Editorial Board Member:[*] *Sue Gibson, born in 1960, studied Natural Sciences at Cambridge University before undertaking doctoral research work with Professor Stephen Davies at Oxford University. A Research Fellowship awarded by the Royal Society enabled her to study with Professor Albert Eschenmoser at the ETH Zürich, after which she returned to the UK to take up a Lectureship at the University of Warwick in 1985. In 1990 she moved to Imperial College, London, and in 1998, she took up the Daniell Chair of Chemistry at King's College London. Her research interests are dominated by the application of transition metals in organic synthesis. Current projects include the synthesis and application of chiral isonitrile complexes, the use of the Heck reaction to synthesis amino acids embedded in macrocycles, transition metals as linkers in solid-phase chemistry, development of new transition metal catalysts, including immobilised catalysts, the biological and catalytic applications of conformationally constrained amino acids, and the application of chiral base chemistry and tricarbonylchromium(0) complexes of arenes to natural product synthesis and catalyst design.*

[*] Members of the Editorial Board will be introduced to readers with their first manuscript.

pentacarbonyliron(0) with a phosphinimine.[7] This reaction has occasionally been exploited in a similar manner,[8] (see below) although it is of note that phosphinimines are frequently moisture- and/or air-sensitive.[9]

The challenges associated with the present approaches to isocyanide ligand synthesis have led to the vast majority of isocyanide ligands reported to date having very simple structures. The following notable exceptions, however, illustrate the potential interest in more sophisticated isocyanide ligands.

Isocyanides separated from a stereogenic centre by a promesogenic core have been used as monomers to create chiral helical poly(isocyanides). More recently isocyanides of this type have been used as ligands to generate chiral organometallic liquid crystals with helical mesophases.[10] The palladium and gold complexes examined, exemplified by **5**, were synthesised by direct displacement of labile ligands,



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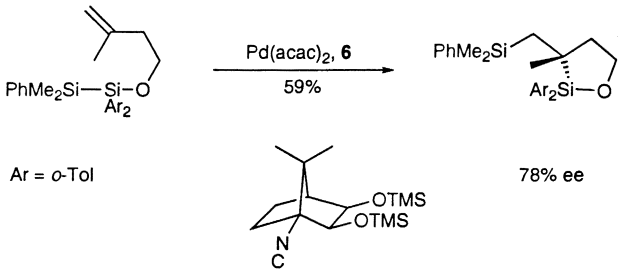
such as benzonitrile and tetrahydrothiophene, from appropriate metal halides by pre-formed isocyanides. To date, the only example of the use of a chiral isocyanide ligand in a catalytic context is provided by the demonstration that a palladium(0) isocyanide complex, formed from pre-formed isocyanide **6** and $Pd(acac)_2$, catalyses an intramolecular bis-silylation of an alkene. This pioneering reaction gave the



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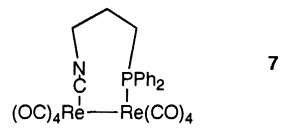
cyclic product in a very encouraging enantiomeric excess.[11] A range of complexes of an isocyanide bearing a pendant phosphine have been prepared.[12a] A typical example is provided by the dirhenium complex **7**, which was prepared



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from the corresponding phosphinimine-phosphine and decacarbonyldirhenium(0). The synthesis and reactivity of com-

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plexes of 2-hydroxyphenyl isocyanide and its derivatives has been reviewed.[12b]

In view of the paucity of studies to date on the synthesis and reactivity of complex isocyanide ligands, we have developed a new synthesis of isocyanide ligands that is designed to provide relatively straightforward access to such ligands. We describe herein 1) our new approach to isocyanide ligands, an outline of which has been published as a preliminary communication,[13] and 2) how our method can be used to generate complexes of structurally interesting isocyanides such as chiral isocyanides.

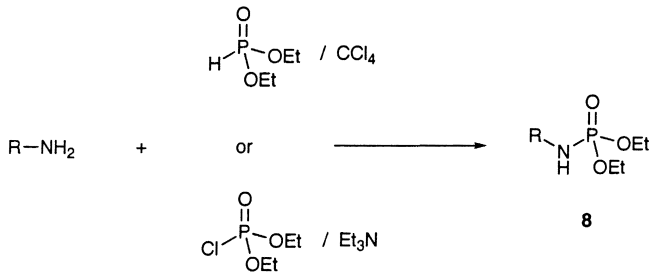
Results and Discussion

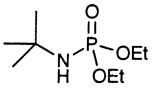
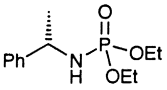
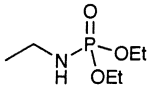
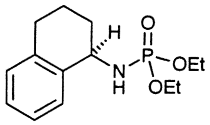
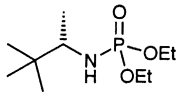
Our interest in tricarbonyl(vinylketene)iron(0) complexes and their nitrogen analogues, tricarbonyl(vinylketenimine)iron(0) complexes, led us to devise a method for the conversion of the former into the latter, central to which were the anions of diethyl *N*-alkylphosphoramidates.[14] We subsequently questioned whether or not this approach to the conversion of carbon–oxygen bonds into carbon–nitrogen bonds could be used to convert metal carbonyls into metal isocyanides. Given that phosphoramidates may be synthesised from the corresponding amines in one step, and that many chiral amines are readily available, it was reasoned that this approach, if successful, should provide access to a wide range of structurally diverse isocyanide ligands.

Five phosphoramidates have been employed in the course of this study and their preparation is summarised at this point. The first method that we used for the synthesis of known phosphoramidates **8a–c** and novel phosphoramidates **8d–e** involved treating the appropriate amine with diethyl phosphite in the presence of carbon tetrachloride.[15, 16, 17] Although this gave satisfactory yields of the required phosphoramidates (Table 1, Method A), we were concerned about the use of environmentally unfriendly carbon tetrachloride. We were therefore pleased to find that a method using diethyl chlorophosphate,[18] (a somewhat more expensive reagent than diethyl phosphite) gave reasonable yields of the phosphoramidates (Table 1, Method B).

The first experiment we carried out to test whether or not metal carbonyls react with anions of phosphoramidates to give metal isocyanides involved the *tert*-butyl phosphoramidate **8a** and the iron carbonyl cation **9**. The carbonyl-containing complex **9** was selected for this study as it is readily synthesised,[19] very stable, and, looking to the future, 16-electron species derived from cations closely related to **9** have been shown to act as Lewis acid catalysts in, for example, the Diels–Alder reaction[20] and the Mukaiyama aldol reaction.[21] Phosphoramidate **8a** was chosen for our initial exploratory experiment, as successful conversion of a carbonyl ligand of **9** to an isocyanide ligand with this phosphoramidate would produce the known complex **10**.[4] Thus phosphoramidate **8a** was dissolved in THF, cooled to −78 °C and treated with one equivalent of *n*-butyllithium (Scheme 1). A stirred suspension of one equivalent of cation **9** in THF was added to this solution, and the resulting mixture was held at −78 °C for four hours. Work up of the product mixture

Table 1. Synthesis of phosphoramidates **8**.



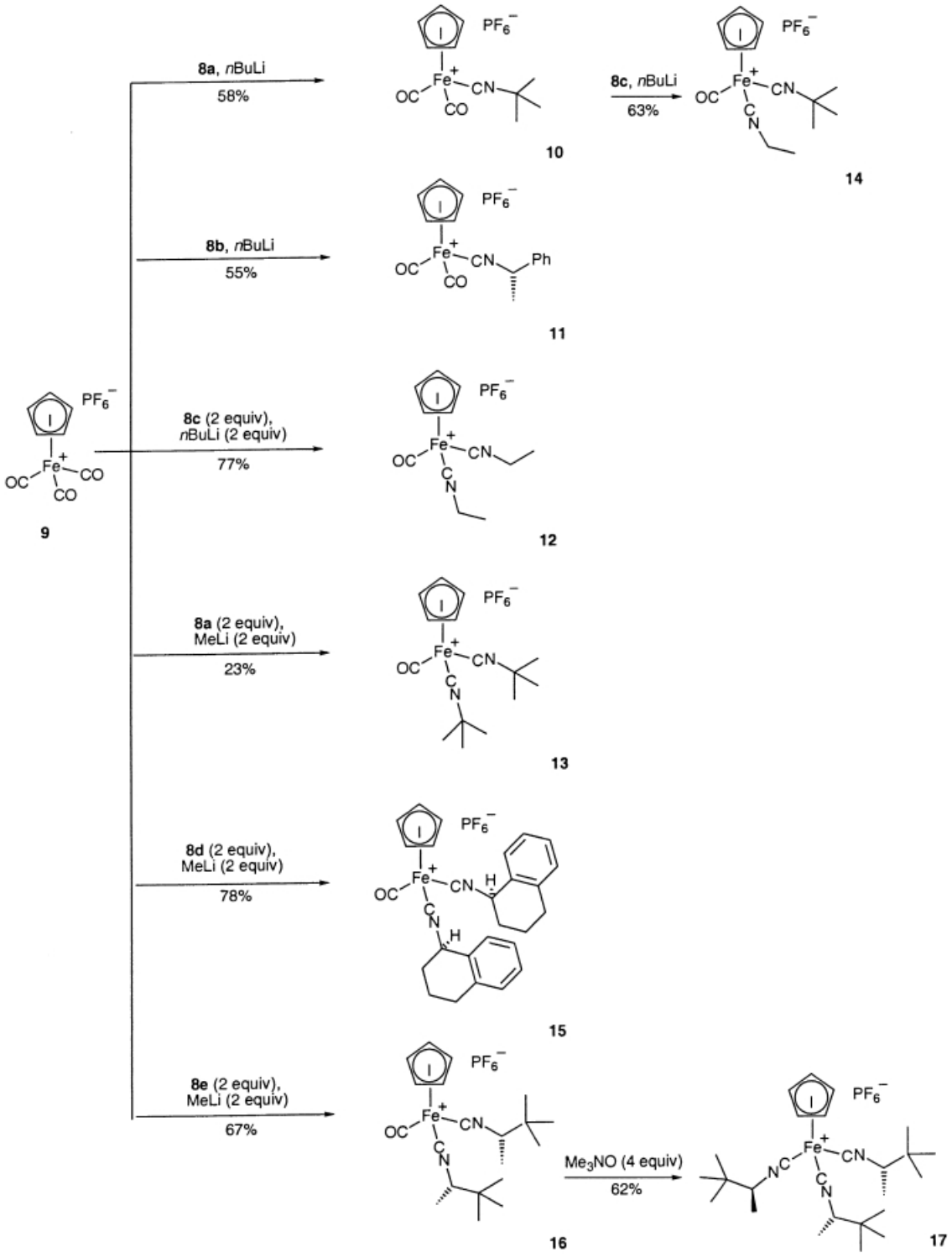
Product	Yield [%] method A[a]	Yield [%] method B[b]
 **8a**	89	
 **8b**	60	86
 **8c**	72	
 **8d**	74	78
 **8e**	59	86

[a] Amine (or hydrochloride salt)/diethyl phosphite/CCl_4. [b] Amine/Et_3N/diethyl chlorophosphate.

produced light yellow crystals that were identified as the dicarbonyl isonitrile complex **10** by comparison of their ^{1}H NMR and IR spectra with literature values.[4] Cation **10** was generated in an acceptable 58% yield on a 1.0 mmol scale, thus indicating that the phosphoramidate-mediated conversion of carbonyl ligands to isocyanide ligands is indeed feasible.

Having established that a phosphoramidate anion may be used to convert a metal carbonyl ligand into an isocyanide ligand, we turned our attention to the creation of a chiral isocyanide ligand by this approach. Pleasingly, reaction of cation **9** with the anion of phosphoramidate **8b**, derived from commercially available (*S*)-α-methylbenzylamine, gave the novel complex **11** containing a chiral isocyanide ligand (Scheme 1).

Aware that many of the best chiral environments created by phosphine ligands around metal centres are generated by two phosphine ligands or diphosphines, we wished to determine whether or not our carbonyl–isocyanide conversion method could be used to introduce two isocyanide ligands. Initially we attempted to introduce achiral ethyl and *tert*-butyl groups in order to determine to what extent steric bulk affected the



Scheme 1.

creation of two isocyanide ligands. Reaction of two equivalents of the anions of phosphoramidates **8c** and **8a** with cation **9** gave the novel diisocyanide cation **12** and the known diisocyanide cation **13**[4] in 77% and 23% yield, respectively (Scheme 1). Interestingly the *tert*-butylisocyanide containing cation **10** reacted with the anion of phosphoramidate **8c** to give the novel mixed diisocyanide cation **14** in 63% yield. From these experiments it was predicted that it should be possible to create two isocyanide ligands at the iron centre by using phosphoramidates derived from primary amines attached to dialkyl- or alkyl/aryl-substituted carbon atoms. Indeed reaction of cation **9** with two equivalents of anions derived from phosphoramidates **8d** and **8e** gave the novel diisocyanide complexes **15** and **16** in good yield (Scheme 1). The X-ray crystal structure of complex **16** revealed the expected "piano stool" geometry (Figure 1). The Fe–CNR bond lengths of

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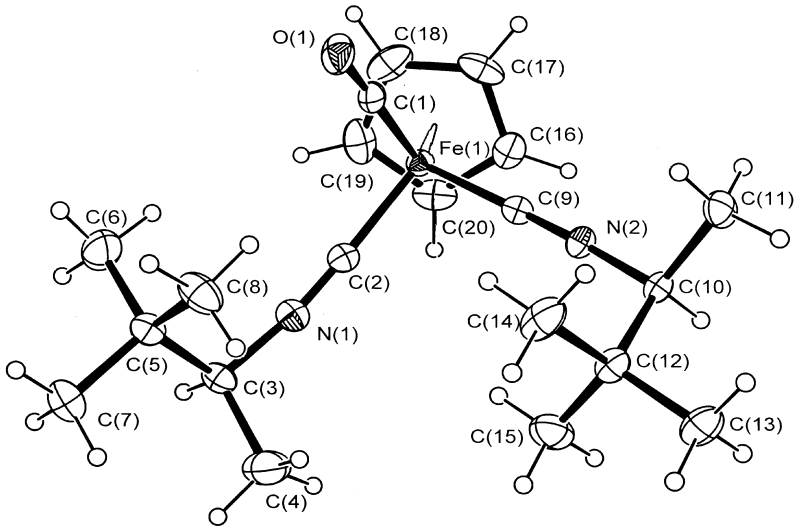

Figure 1. ORTEP view of the cationic part of carbonylcyclopentadienyldi[(*S*)-1,2,2-trimethylpropylisocyanide]iron(II) hexafluorophosphate, **16**. Ellipsoids at the 50% probability level.

1.855(4) Å (av) are similar to other unhindered isonitrile complexes (e.g., $[Fe(CO)_3(CN\textit{t}Bu)_2]$ 1.865 Å av,[22] $[Fe_2Cp_2(CO)_3(CNCH_2CHMe_2)]$ 1.846 Å,[23] and $[FeCp(CO)_2(CNMe)][BF_4]$ 1.900 Å[24]) indicating an absence of strain at the metal centre. The C-N-C angles are essentially linear and the C–N bond lengths are consistent with a triple-bond description. Interestingly, the bulky CHMe*t*Bu substituents are interlocked in such a way as to render the static complex chiral (Figure 1). This is necessary in order to avoid unfavourable steric interactions between the substituents and augurs well for the design of chirality at the metal centre.

Having established that iron cations containing one and two chiral isocyanide ligands may be created by using phosphoramidate anions, we were interested to determine whether or not the third carbonyl ligand of the tricarbonyl cation **9** could be replaced with a chiral isocyanide ligand. Attempts to treat cation **9** with three equivalents of phosphoramidate anions were unsuccessful. Reaction of cation **16**, however, with trimethylamine-*N*-oxide led to decarbonylation and the isolation of the triisocyanide complex **17** in 62% yield (theoretical maximum 67%) (Scheme 1).

Conclusion

We have demonstrated that phosphoramidates, which are easy to synthesise from amines, may be used to convert carbonyl ligands into isocyanide ligands. As a wide variety of amines are readily available, particularly chiral amines, this new approach to isocyanide ligands provides access to a wide range of structurally diverse isocyanide ligands.

Experimental Section

General: All reactions were performed under an inert atmosphere of dry nitrogen by using standard vacuum line and Schlenk tube techniques.[25] THF was distilled over sodium/benzophenone. The concentration of alkyllithium reagents was determined by titration against diphenylacetic acid in THF.[26] Melting points were recorded in open capillaries on a Büchi 510 melting point apparatus, and are uncorrected. IR spectra were recorded on a Perkin–Elmer 1600 FT IR spectrometer and in $CHCl_3$ unless otherwise stated. NMR spectra were recorded at room temperature on JEOL GSX270, Bruker AM360 and Bruker DRX400 instruments in $CDCl_3$ unless otherwise stated. Chemical shifts are reported in ppm relative to residual undeuterated solvent as the reference and *J* values are reported in Hz. Mass spectra were recorded on JEOL AX505W, VG Micromass 7070E and Kratos MS890MS mass spectrometers, and all elemental analyses were performed by the North London University microanalytical services. Flash column chromatography was performed over Merck silica gel 60 (230–400 mesh).

Synthesis of phosphoramidates by using method A

Diethyl *N*-*tert*-butylphosphoramidate (8a):[15] *tert*-Butylamine (17.9 mL, 170.7 mmol) was added to a cooled solution of diethyl phosphite (10.0 mL, 77.6 mmol) in petroleum ether (200 mL) and CCl_4 (120 mL), and the reaction mixture stirred for 24 h at room temperature. The reaction mixture was washed with aq. HCl (2 M, 2 × 100 mL), the organic fraction was dried over $MgSO_4$, and the solvent removed in vacuo to afford **8a** as a colourless oil (14.5 g, 89%). IR: $\tilde{\nu}$ = 3398 (N–H stretch), 1266 cm^{-1} (P=O); ^1H NMR (400 MHz): δ = 4.00 (quin, J = 7.2 Hz, 4H; OCH_2), 1.31 (dt, J = 1.2, 7.2 Hz, 6H; OCH_2CH_3), 1.26 (s, 9H; *t*Bu); CI-MS: *m*/*z* (%): 227 (20) $[M+NH_4]^+$, 210 (100) $[M+H]^+$.

Diethyl *N*-[(*S*)-α-methylbenzyl]phosphoramidate (8b):[16, 17] (*S*)-α-Methylbenzylamine (8.52 mL, 66.1 mmol), was added to a cooled solution of diethyl phosphite (7.10 mL, 55.1 mmol) in petroleum ether (150 mL) and CCl_4 (100 mL), and the reaction mixture stirred for 24 h at room temperature. The solution was washed with HCl (2 M, 2 × 50 mL), the organic fraction collected and dried over $MgSO_4$, and the solvent removed in vacuo to afford **8b** as a white solid (8.40 g, 60%). $[\alpha]_D^{32} = -51.3$ (c = 0.87 in CH_2Cl_2); m.p. 42–43 °C; IR: $\tilde{\nu}$ = 3383 (N–H stretch), 1602 (N–H bend), 1234 cm^{-1} (P=O); ^1H NMR (270 MHz): δ = 7.34–7.30 (m, 5H; Ph), 4.32–4.29 (m, 1H; CH), 4.09–3.64 (m, 4H; OCH_2), 3.19 (br s, 1H; NH), 1.47 (dd, J = 0.9, 6.9 Hz, 3H; $CHCH_3$), 1.30 (dt, J = 0.9, 6.9 Hz, 3H; OCH_2CH_3), 1.09 (dt, J = 0.9, 6.9 Hz, 3H; OCH_2CH_3); ^{13}C NMR (100.6 MHz): δ = 145.6 (s, *ipso*-Ph), 129.1 (s, *o*-Ph), 127.9 (s, *p*-Ph), 126.3 (s, *m*-Ph), 62.7 (d, J = 5 Hz, OCH_2), 62.6 (d, J = 5 Hz, OCH_2), 51.9 (s, *C*H), 25.6 (s, $CHCH_3$), 16.7 (d, J = 8 Hz, OCH_2CH_3), 16.4 (d, J = 8 Hz, OCH_2CH_3); EI-MS: *m*/*z* (%): 257 (25) $[M]^+$, 242 (100) $[M-Me]^+$, 228 (10) $[M-CH_2CH_3]^+$, 120 (25) $[PhCH(Me)NH]^+$, 105 (30) $[PhCHMe]^+$.

Diethyl *N*-ethylphosphoramidate (8c):[17] Ethylamine hydrochloride (8.15 g, 100 mmol), K_2CO_3 (27.6 g, 200 mmol), $KHCO_3$ (20.0 g, 200 mmol) and $n Bu_4NBr$ (1.61 g, 5 mmol) were added to a cooled solution of diethyl phosphite (12.9 mL, 100 mmol) in CH_2Cl_2 (40 mL) and CCl_4 (60 mL), and the reaction mixture stirred for 24 h at room temperature. The solution was filtered, and the solvents removed in vacuo to afford **8c** as a pale yellow oil (13.1 g, 72%); IR: $\tilde{\nu}$ = 3362 (N–H stretch), 1267 cm^{-1} (P=O); ^1H NMR (400 MHz): δ = 3.97 (quin, J = 7.2 Hz, 4H; OCH_2), 2.86 (t, J = 4.6 Hz, 2H; NCH_2), 1.24 (dt, J = 7.2, 0.7 Hz, 6H; OCH_2CH_3), 1.06 (dt, J = 7.2, 1.2 Hz, 3H; NCH_2CH_3); CI-MS: *m*/*z* (%): 199 (30) $[M+NH_4]^+$, 182 (100) $[M+H]^+$.

Diethyl *N*-[*(R)*-1,2,3,4-tetrahydro-1-naphthyl]phosphoramidate (8d): *(R)*-1,2,3,4-Tetrahydro-1-naphthylamine (818 mg, 5.5 mmol) was added to a cooled solution of diethyl phosphite (0.6 mL, 5.2 mmol) in hexane (10 mL) and CCl_4 (10 mL), and the reaction mixture stirred for 24 h at room temperature. The solution was filtered, and the solvents removed in vacuo to afford **8d** as a yellow solid (1.084 g, 74%); $[\alpha]_D^{20} = +25.5$ (c = 0.87 in CH_2Cl_2); m.p. 61–62 °C; IR: $\tilde{\nu}$ = 3362 (N–H stretch), 1267 cm^{-1} (P=O); ^1H NMR (400 MHz): δ = 7.47–6.98 (m, 4H; Ph), 4.28 (m, 1H; CH), 4.08 (m, 4H; OCH_2), 2.69 (m, 3H), 2.01 (m, 1H; NH), 1.85–1.68 (m, 3H), 1.34 (m, 6H; OCH_2CH_3); ^{13}C NMR (400 MHz): δ = 138.8 (Ar), 137.5 (Ar), 129.4 (Ar), 129.0 (Ar), 127.5 (Ar), 126.5 (Ar), 62.8 (CH_2O), 62.0 (CH_2O), 50.4

(CH), 33.0, 29.5, 20.2, 16.7 (CH_3,CH_2); MS: *m*/*z* (%): 283 (89) $[M]^+$, 254 (68) $[M-Et]^+$, 154 (98) $[M-naphthyl]^+$, 146 (100) $[M-2EtO-PO]^+$; elemental analysis calcd (%) for $C_{14}H_{22}NO_3P$ (283.29): C 59.30, H 7.80, N 4.94; found: C 59.4, H 7.8, N 4.9.

Diethyl *N*-[*(S)*-1,2,2-trimethylpropyl]phosphoramidate (8e): *(S)*-1,2,2-Trimethylpropylamine (556 mg, 5.5 mmol) was added to a cooled solution of diethyl phosphite (0.64 mL, 5.0 mmol) in hexane (10 mL) and CCl_4 (10 mL), and the reaction mixture stirred for 24 h at room temperature. The solution was washed with HCl (2 M, 2 × 50 mL), the organic fraction was collected and dried over $MgSO_4$, and the solvent removed in vacuo to afford **8e** as a white solid. Crystallisation from hexane afforded white crystals (0.696 g, 59%); $[\alpha]_D^{20} = +27.7$ (c = 0.87, CH_2Cl_2); m.p. 42–43 °C; IR: $\tilde{\nu} = 3368$ (N–H stretch), 1267 cm^{-1} (P=O); ^1H NMR (400 MHz): $\delta =$ 3.97 (m, 4H; OCH_2), 2.86 (m, 1H; CH), 2.23 (t, $J = 9.7$ Hz, 1H; NH), 1.24 (dt, $J = 7.2$, 0.9 Hz, 6H; OCH_2CH_3), 1.06 (d, $J = 6.6$ Hz, 3H; CH_3-CH), 0.82 (s, 9H; $C(CH_3)_3$); ^{13}C NMR (400 MHz): $\delta = 62.6$ (OCH_2), 56.7 (CH), 35.0 ($C(CH_3)_3$), 26.5 ($C(CH_3)_3$), 18.7 (CH_3CH), 16.7 (CH_3CH_2); CI-MS: *m*/*z* (%): 255 (11) $[M+NH_4]^+$, 238 (100) $[M+H]^+$; elemental analysis calcd (%) for $C_{10}H_{24}NO_3P$ (237.27): C 50.62, H 10.10, N 5.90; found: C 50.6, H 10.2, N 5.8.

Synthesis of phosphoramidates by using method B

Diethyl *N*-[(*S*)-α-methylbenzyl]phosphoramidate (8b):
Dry dichloromethane (15 mL) was added to (*S*)-α-methylbenzylamine (0.61 g, 5 mmol) and dry triethylamine (2.09 mL, 15 mmol), and the solution was cooled to −10 °C in an ice/sodium chloride bath. Diethyl chlorophosphate (0.76 mL, 5.25 mmol) was added dropwise, and the solution was left in the cooling bath to reach room temperature overnight. After 14 h, the precipitate was filtered off and washed with diethyl ether. The solvents were removed in vacuo and the residue purified by chromatography (SiO_2; diethyl ether/hexane/triethylamine 80:17:3) to give **8b** as a white solid (1.10 g, 86%). Data corresponded with those obtained from **8b** generated by using method A.

Diethyl *N*-[*(R)*-1,2,3,4-tetrahydro-1-naphthyl]phosphoramidate (8d): Dry dichloromethane (15 mL) was added to (*R*)-1,2,3,4-tetrahydronaphthylamine (740 mg, 5 mmol) and dry triethylamine (2.09 mL, 15 mmol), and the solution was cooled to −10 °C in an ice/sodium chloride bath. Diethyl chlorophosphate (0.76 mL, 5.25 mmol) was added dropwise and the solution left in the cooling bath to reach room temperature overnight. After 14 h, the precipitate was filtered off and washed with diethyl ether. The solvents were removed in vacuo, and the residue was purified by chromatography (SiO_2; diethyl ether/hexane/triethylamine 80:17:3) to give **8d** as a white solid (1.11 g, 78%). Data corresponded with those obtained from **8d** generated by using method A.

Diethyl *N*-[*(S)*-1,2,2-trimethylpropyl]phosphoramidate (8e): Dry dichloromethane (15 mL) was added to (*S*)-1,2,2-trimethylpropylamine (510 mg, 5 mmol) and dry triethylamine (2.09 mL, 15 mmol), and the solution was cooled to −10 °C in an ice/sodium chloride bath. Diethyl chlorophosphate (0.76 mL, 5.25 mmol) was added dropwise, and the solution left in the cooling bath to reach room temperature overnight. After 14 h, the precipitate was filtered off and washed with diethyl ether. The solvents were removed in vacuo, and the residue purified by chromatography (SiO_2; diethyl ether/hexane/triethylamine 80:17:3) to give **8e** as a white solid (1.02 g, 86%). Data corresponded with those obtained from **8e** generated by using method A.

Synthesis of iron the tricarbonyl substrate

Tricarbonylcyclopentadienyliron(II) hexafluorophosphate (9):[18] A solution of dicarbonylcyclopentadienyliron(II) dimer (4.0 g, 11.3 mmol) in THF (200 mL) was added to 2% Na/Hg, and the mixture was allowed to stir at room temperature for 24 h. The supernatent liquid was carefully transferred into a Schlenk flask and the solution cooled to −78 °C. Ethyl chloroformate (10.0 mL, 104 mmol) was added dropwise, and the reaction mixture was stirred for 1 h at −78 °C and slowly warmed to room temperature. Solvent was removed in vacuo, and the resultant solid triturated with petroleum ether (4 × 40 mL) to yield a yellow solution. HCl gas was then bubbled through the solution for a period of 20 minutes at room temperature; this resulted in the precipitation of a yellow solid. This was dissolved in MeOH (40 mL) and added to NH_4PF_6 (3.7 g, 22.7 mmol). After stirring at room temperature for 1 h, the solvent was evaporated and the orange solid was crystallised from acetone/diethyl ether (6.24 g, 81%). M.p. >250 °C (decomp); IR: $\tilde{\nu} = 2124$, 2074 (C≡O) cm^{-1}; ^1H NMR (270 MHz): $\delta = 6.12$ (s, 5H; Cp); ^{13}C NMR (100.6 MHz): $\delta = 203.2$ (CO), 90.8 (Cp); FAB-MS: *m*/*z* (%): 205 (100) $[M]^+$, 177 (10) $[M-CO]^+$, 140 (5) $[M-Cp]^+$.

Synthesis of monoisocyanide cyclopentadienyliron dicarbonyl complexes

(*tert*-Butylisocyanide)dicarbonylcyclopentadienyliron(II) hexafluorophosphate (10):[4] A solution of **8a** (209 mg, 1.00 mmol) in THF (10 mL) was cooled to −78 °C and *n*BuLi (0.63 mL, 1.00 mmol of 1.6 M solution in diethyl ether) was added to it. The reaction mixture was allowed to warm to room temperature before recooling to −78 °C. A suspension of **9** (350 mg, 1.00 mmol) in degassed THF (30 mL) was added through a cannula to the reaction mixture. The mixture was then stirred at −78 °C for 4 h and the solvent removed in vacuo. The dark brown residue was purified by chromatography (SiO_2; acetone/petroleum ether 1:1) to afford a yellow solid. Crystallisation (acetone/dichloromethane) afforded **10** as cubic yellow crystals (235 mg, 58%). M.p. 154–155 °C; IR: $\tilde{\nu} = 2206$ (C≡N), 2081, 2040 cm^{-1} (C≡O); ^1H NMR (270 MHz): $\delta = 5.38$ (s, 5H; Cp), 1.60 (s, 9H; CMe_3); ^{13}C NMR (100.6 MHz) $\delta = 205.8$ (CO), 87.0 (Cp), 61.1 (CMe_3), 29.4 (CMe_3); FAB-MS: *m*/*z* (%): 260 (100) $[M]^+$, 204 (30) $[M-2CO]^+$.

Dicarbonylcyclopentadienyl[(*S*)-α-methylbenzylisocyanide)iron(II) hexafluorophosphate (11): A solution of **8b** (257 mg, 1.00 mmol) in THF (10 mL) was cooled to −78 °C and *n*BuLi (0.63 mL, 1.00 mmol of 1.6 M solution in diethyl ether) was added to it. The reaction mixture was allowed to warm to room temperature before recooling to −78 °C. A suspension of **9** (350 mg, 1.00 mmol) in degassed THF (30 mL) was added through a cannula to the reaction mixture. The mixture was then stirred at −78 °C for 6 h and solvent removed in vacuo. The dark brown residue was purified by chromatography (SiO_2; acetone/petroleum ether 1:2) to yield an orange oil. Crystallisation (dichloromethane/diethyl ether 1:1) afforded **11** as yellow crystals (250 mg, 55%). $[\alpha]_D^{29} = -2.26$ (*c* = 1.55 in CH_2Cl_2); M.p. 62–63 °C; IR: $\tilde{\nu} = 2214$ (C≡N), 2082, 2041 cm^{-1} (C≡O); ^1H NMR (270 MHz): $\delta = 7.48$ (m, 5H; Ph), 5.81 (s, 5H; Cp), 5.54 (q, $J = 6.8$ Hz, 1H; C*H*Me), 1.81 (d, $J =$ 6.8 Hz, 3H; Me); ^{13}C NMR (100.6 MHz): $\delta = 206.3$ (CO), 137.8 (*ipso*-Ph), 129.8 (*o*-/*m*-Ph), 129.4 (*p*-Ph), 126.0 (*o*-/*m*-Ph), 87.8 (Cp), 59.2 (*C*HMe), 23.9 (Me); FAB-MS: *m*/*z* (%): 308 (100) $[M]^+$, 280 (5) $[M-CO]^+$, 252 (15) $[M-2CO]^+$, 204 (20) $[FpCNH]^+$; HRMS calcd for $C_{16}H_{14}NF_6FeO_2P$: 308.0374; found: 308.0358.

Synthesis of diisocyanide cyclopentadienyliron dicarbonyl complexes

Carbonylcyclopentadienyldi(ethylisocyanide)iron(II) hexafluorophosphate (12): Phosphoramidate **8c** (362 mg, 2.00 mmol) was dissolved in THF (10 mL), the solution degassed and cooled to −78 °C. *n*BuLi (1.6 M in hexane, 1.25 mL, 2.00 mmol) was added dropwise, and the mixture allowed to warm to room temperature before recooling to −78 °C. A suspension of **9** (350 mg, 1.00 mmol) in degassed THF (20 mL) was cooled to −78 °C and added through a cannula to the phosphoramidate anion solution. The mixture was stirred at −78 °C for 6 h, and solvent removed in vacuo. The dark brown residue was dissolved in acetone, and preadsorbed onto silica gel before purification by column chromatography (SiO_2; acetone/light petroleum 1:2) to afford **12** as a yellow oil (310 mg, 77%). IR: $\tilde{\nu} = 2218$, 2191 (C≡N), 2021 cm^{-1} (C≡O); ^1H NMR (270 MHz): $\delta = 5.32$ (s, 5H; Cp), 3.91 (q, $J = 7.2$ Hz, 4H; CH_2), 1.42 (t, $J = 7.2$ Hz, 6H; Me); ^{13}C NMR (100.6 MHz): $\delta = 213.8$ (CO), 86.2 (Cp), 42.0 (NCH_2), 15.5 (Me).

Di(*tert*-butylisocyanide)carbonylcyclopentadienyliron(II) hexafluorophosphate (13):[4] Phosphoramidate **8a** (500 mg, 2.39 mmol) was dissolved in THF (10 mL), and the solution degassed and cooled to −78 °C. MeLi (1.35 M in hexane, 1.81 mL, 2.44 mmol) was added dropwise, and the mixture allowed to warm to room temperature before recooling to −78 °C. A suspension of **9** (400 mg, 1.14 mmol) in degassed THF (40 mL) was cooled to −78 °C and added through a cannula to the phosphoramidate anion solution. The mixture was stirred at −78 °C for 5 h, and then allowed to warm to room temperature for a further 19 h, before solvent was removed in vacuo. The dark brown residue was dissolved in acetone and preadsorbed onto silica gel before purification by column chromatography (SiO_2; acetone/petroleum ether 1:2). The product was crystallised from dichloromethane to afford **13** as yellow crystals (120 mg, 23%). M.p. 123–125 °C; IR: $\tilde{\nu} = 2197$, 2171 (C≡N), 2021 cm^{-1} (C≡O); ^1H NMR (300 MHz): $\delta = 5.24$ (s, 5H; Cp), 1.45 (s, 18H; 2 CMe_3); ^{13}C NMR (75.4 MHz): $\delta = 206.5$ (CO), 86.4 (Cp), 61.5 (CMe_3), 30.7 (CMe_3); FAB-MS: *m*/*z* (%): 315 (100) $[M]^+$, 287 (25) $[M-CO]^+$, 259 (5) $[MH^+-CMe_3]^+$, 231 (5) $[MH^+-CO-CMe_3]^+$, 148 (15) $[CpFeCNH]^+$; elemental analysis calcd (%) for

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$C_{16}H_{23}N_2F_6FeOP$ (477.97): C 41.76, H 5.04 N 6.09; found: C 41.58, H 5.02, N 5.89.

(*tert*-Butylisocyanide)carbonylcyclopentadienyl(ethylisocyanide)iron(II) hexafluorophosphate 14: Diethyl *N*-ethylphosphoramidate **8c** (92 mg, 0.51 mmol) was dissolved in THF (10 mL), and the solution was degassed and cooled to −78 °C. *n*BuLi (1.6 M in hexane, 0.32 mL, 0.51 mmol) was added dropwise, and the mixture allowed to warm to room temperature before recooling to −78 °C. A solution of **10** (205 mg, 0.51 mmol) in degassed THF (10 mL) was cooled to −78 °C and added through a cannula to the phosphoramidate anion solution. The mixture was stirred at −78 °C for 7 h, and solvent removed in vacuo. The dark brown residue was dissolved in acetone and preadsorbed onto silica gel before purification by column chromatography (SiO_2; acetone/petroleum ether 1:2). The product was subsequently triturated (diethyl ether/petroleum ether 1:1) to afford **14** as a yellow powder (138 mg, 63 %). M.p. 126 – 128 °C; IR: $\tilde{\nu}$ = 2212, 2179 (C≡N), 2021 cm^{-1} (C≡O); ^1H NMR (270 MHz): δ = 5.33 (s, 5H; Cp), 3.92 (q, J = 7.2 Hz, 2H; CH_2), 1.54 (s, 9H; CMe_3), 1.41 (t, J = 7.2 Hz, 3H; Me); ^{13}C NMR (100.6 MHz): δ = 213.5 (CO), 86.2 (Cp), 60.9 (CMe_3), 41.9 (NCH_2), 29.5 (CMe_3), 15.4 (Me); FAB-MS: *m*/*z* (%): 287 (100) $[M]^+$, 259 (30) $[M-CO]^+$, 231 (5) $[CpFe(CNtBu)CNH]^+$, 176 (10) $[CpFeCNEt]^+$, 148 (10) $[CpFeCN]^+$; HRMS calcd for $C_{14}H_{19}N_2F_6FeOP$: 287.0847; found: 287.0853.

Carbonylcyclopentadienyldi[(*R*)-1,2,3,4-tetrahydro-1-naphthylisocyanide)-iron(II) hexafluorophosphate (15): A solution of **8d** (283 mg, 1 mmol) in THF was cooled to −78 °C and MeLi (0.62 mL, 1 mmol of 1.6 M solution in diethyl ether) was added to it. The reaction mixture was allowed to warm to room temperature before recooling to −78 °C. The solution was then transferred through a cannula into a suspension of **9** (187 mg, 0.5 mmol) in degassed THF. The mixture was then stirred at −78 °C for 6 h, after which the reaction was quenched with MeOH and the solvent removed in vacuo. The resultant dark brown residue was purified by chromatography (SiO_2; acetone/hexane 1:2) to yield a yellow solid. Crystallisation from diethyl ether afforded **15** as yellow crystals (250 mg, 78 %). M.p. >285 °C; IR: $\tilde{\nu}$ = 2180, 2146 (C≡N), 2021 cm^{-1} (C≡O); ^1H NMR (400 MHz): δ = 7.32 – 7.03 (m, 8H; Ar), 5.21 (q, 2H; J = 5.5 Hz, CH), 5.02 (s, 5H; Cp), 2.79 – 2.62 (m, 4H), 2.13 – 2.01 (m, 4H), 1.84 – 1.73 (m, 4H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 211.6 (CO), 136.9, 131.7, 131.75, 130.1, 129.2, 128.9, 128.8, 127.2 (Ar), 85.3 (Cp), 57.1 (CH), 30.5 (CH_2), 28.8 (CH_2), 19.5 (CH_2); MS: *m*/*z* (% = 548 (89) $[M]^+$, 520 (100) $[M-CO]^+$.

Carbonylcyclopentadienyldi[(*S*)-1,2,2-trimethylpropylisocyanide]iron(II) hexafluorophosphate (16): A solution of **8e** (237 mg, 1 mmol) in THF was cooled to −78 °C and MeLi (0.62 mL, 1 mmol of 1.6 M solution in diethyl ether) was added to it. The reaction mixture was allowed to warm to room temperature before recooling to −78 °C. The solution was then transferred through a cannula into a suspension of **9** (187 mg, 0.5 mmol) in degassed THF. The mixture was then stirred at −78 °C for 7 h, after which the reaction was quenched with MeOH and the solvent removed in vacuo. The resultant dark brown residue was purified by chromatography (SiO_2; acetone/hexane 1:2) to yield an orange oil. Crystallisation from diethyl ether afforded **16** as yellow crystals (173 mg, 67 %). $[\alpha]_d^{20}$ = +12.6 (c = 1.55 in CH_2Cl_2); m.p. 274 – 275 °C; IR ($CHCl_3$): $\tilde{\nu}$ = 2202, 2178 (C≡N), 2021 cm^{-1} (C≡O); ^1H NMR (400 MHz): δ = 5.08 (s, 5H; Cp), 3.79 (q, 2H; J = 6.7 Hz, C*H*Me), 1.30 (t, 6H; J = 6.7 Hz, $CHCH_3$), 0.92 (s, 18H; *t*Bu); ^{13}C NMR (100.6 MHz): δ = 211.0 (CO), 84.4 (Cp), 64.2 (CH), 34.3 ($C(CH_3)_3$), 25.2 ($C(CH_3)_3$), 15.8 ($CHCH_3$); MS: *m*/*z* (%): 516 (59) $[M]^+$, 488 (100) $[M-CO]^+$; elemental analysis calcd (%) for $C_{20}H_{31}N_2F_6FeOP$ (516.29): C 46.50, H 6.05, N 5.45; found: C 46.3, H 5.9, N 5.7.

X-ray crystallography of 16: A crystal of **16** was mounted on a thin glass fibre using silicon grease and cooled on the diffractometer to 100 K using an Oxford Cryostream low temperature attachment. Approximate unit cell dimensions were determined by the Nonius Collect program[27] from five index frames of width 2° in ϕ using a Nonius Kappa CCD diffractometer, with a detector to crystal distance of 30 mm. The Collect program was then used to calculate a data collection strategy to 99.5 % completeness for θ = 27.5° by using a combination of 2° ϕ and ω scans of 10 60 s deg^{-1} exposure time. The crystal was indexed using the DENZO-SMN package,[28] and positional data were refined along with diffractometer constants to give the final unit cell parameters. Integration and scaling (DENZO-SMN, Scalepack[28]) resulted in unique data sets corrected for Lorentz and polarisation effects and for the effects of crystal decay and absorption by a combination of averaging of equivalent reflections and an overall volume and scaling correction. The structure was solved using SHELXS-97[29] and refined by alternating least-squares cycles and difference Fourier synthesis (SHELXL-97[29]) with the aid of the program XSeed.[30] In general all non-hydrogen atoms were modelled anisotropically, while hydrogen atoms were assigned an isotropic thermal parameter 1.2 times that of the parent atom (1.5 for terminal atoms) and allowed to ride, except for acidic protons which were located on the final difference Fourier map and refined freely. All calculations were carried out with either a Silicon Graphics Indy workstation or an IBM compatible PC. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-168587. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for ***16***: $C_{20}H_{31}F_6FeN_2OP$, M_r = 516.29 g mol^{-1}, orthorhombic, $P2_12_12_1$, a = 11.3149(8), b = 12.1826(11), c = 17.9756(10) Å, V = 2477.8(3) $Å^3$, Z = 4, $Mo_{K\alpha}$, λ = 0.71073, ρ_{calcd} 1.384 Mg m^{-3}, μ = 0.731 mm^{-1}, max/min transmission 0.8105/0.7585, T = 120(2) K, crystal size 0.40 × 0.30 × 0.30 mm^3, theta range 2.71 – 27.49°. Reflections collected: 12 680, independent reflections: 5634, parameters 289, $R1$ [$I > 2\sigma(I)$] = 0.0577, $wR2$ (F^2, all data) = 0.1495, largest diff. peak/hole: 0.674/ − 0.660 e $Å^{-3}$.

Synthesis of triisocyanide cyclopentadienyliron complex

Cyclopentadienyltri[(*S*)-1,2,2-trimethylpropylisocyanide]iron(II) hexafluorophosphate (17):

A solution of **16** (51.6 mg, 0.1 mmol) in THF was cooled to −30 °C and added dropwise to a suspension of trimethylamine-*N*-oxide (30.0 mg, 0.4 mmol) in THF. The reaction mixture was stirred at −30 °C for 2 h and then allowed to rise to room temperature. The solvent was removed in vacuo, and the residue was extracted with chloroform and washed with water. The organic layer was dried over Na_2SO_4. Removal of the solvent in vacuo gave **17** as a yellow solid [37 mg, 62 % based on **16** (67 % theoretical maximum)]; $[\alpha]_D^{20}$ = +19.3 (c = 0.15 in CH_2Cl_2); m.p. 111 – 113 °C; IR ($CHCl_3$): $\tilde{\nu}$ = 2187, 2145 cm^{-1} (C≡N); ^1H NMR (400 MHz): δ = 4.77 (s, 5H; Cp), 3.76 (q, J = 6.8 Hz, 3H; CH), 1.33 (d, J = 6.8 Hz, 9H; CH_3), 0.99 (s, 27H; $C(CH_3)_3$); ^{13}C NMR (100.6 MHz): δ = 81.9 (Cp), 63.8 (CH), 34.8 ($C(CH_3)_3$), 25.6 ($C(CH_3)_3$), 16.6 (CH_3); MS: *m*/*z* (%): 454 (100) $[M-PF_6]^+$, 343 (57) $[M-PF_6-CNCH(CH_3)C(CH_3)_3]^+$, 232 (27) $[M-PF_6-CNCH(CH_3)C(CH_3)_3]^+$; elemental analysis calcd (%) for $C_{38}H_{38}N_3F_6FeP$ (737.55): C 52.09, H 7.40, N 7.01; found: C 52.0, H 7.5, N 6.9.

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