Aminoalkylferrocenyldichlorophosphanes: facile synthesis of versatile chiral starting materials†

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A series of racemic and optically pure aminoalkylferrocenyldichlorophosphanes has been prepared by reaction of phosphorus trichloride with the corresponding lithiated aminoalkylferrocene precursors. Crystal structures of racemic 1-dichlorophosphanyl-2-*N*,*N*-dimethylaminomethylferrocene, racemic 1-dichlorophosphanyl-2-*N*,*N*-dimethylaminomethyl-3-triphenylsilylferrocene and (*S*)-*N*,*N*-dimethyl-1-[(*R*)-2-(dichlorophosphanyl)ferrocenyl]ethylamine reveal short intramolecular N···P distances, which are suggestive of weak N → P dative bonds. The aminoalkylferrocenyldichlorophosphanes can be used for the preparation of the corresponding primary phosphanes, one of which was characterised by X-ray crystallography. Optically pure (*R*)-*N*,*N*-dimethyl-1-[(*S*)-2-(phosphanyl)ferrocenyl]ethylamine can easily be lithiated twice to give the first enantiomerically pure lithium–phosphorus *closo* cluster compound, which was also structurally characterised.

Introduction

Phosphane-based ligands with a ferrocene backbone have been of interest in organometallic and coordination chemistry since the first synthesis of 1,1′-bis(diphenylphosphanyl)ferrocene in the mid-1960s.[1] Chiral ferrocenylphosphanes were first prepared by Hayashi *et al.* in the 1970s.[2] Their synthetic strategy was based on the fact that enantiomerically pure *N*,*N*-dimethyl-1-ferrocenylethylamine (**7**), first prepared and optically resolved by Ugi *et al.*,[3] can be functionalised diastereoselectively to obtain planar-chiral ferrocene derivatives.[4] Since this pioneering work, many ferrocene-containing ligands have been developed and coordinated to catalytically active metal centres.[5] The number of applications of these complexes in homogeneous catalysis has been growing ever since. Initially used for asymmetric hydrogenation,[6] Grignard reactions[7] or hydrosilylations,[2] further functionalisation, such as replacement of the dimethylamino group by another phosphanyl group or variation of the substituents at the phosphorus atoms, have created specific ligands for highly active catalyst systems, a well-known example being the JOSIPHOS ligand.[8]

Dichlorophosphanes have proved to be extremely versatile precursors for the synthesis of organophosphorus compounds. However, ferrocenyldichlorophosphanes, which are of interest due to the reactivity of the P–Cl bonds, are not readily accessible. While 1,1′-bis(dichlorophosphanyl)ferrocene, as well as its dihalo homologues, can be obtained in reasonable yield,[9,10] the synthesis of the monosubstituted derivative, ferrocenyldichlorophosphane, is associated with severe problems and gives only low yields.[11]

Primary phosphanes, in which a ferrocene unit is attached to the phosphorus atom, are not very well investigated, though they are promising precursors for phosphanido and phosphinidene complexes, as well as other compounds containing phosphorus in a low coordination number. In addition to the known phosphanylferrocene[12] and 1,1′-bis(phosphanyl)ferrocene,[13] we recently reported on the synthesis of primary aminoalkylferrocenylphosphanes by reduction of the corresponding ferrocenylphosphonates.[14] We showed that racemic 2-(*N*,*N*-dimethylaminomethyl)phosphanylferrocene (**5**) can easily be dilithiated. The resulting dilithium phosphanediide crystallises as a hexamer containing all-*R*- or all-*S*-configured units with a central $Li_{12}P_6$ cluster, which, according to theoretical studies, can be described as a *closo* cluster according to Wade's rules.[15]

We herein report the facile and convenient synthesis of novel racemic and enantiomerically pure aminoalkylferrocenyldichlorophosphanes. These compounds can easily be converted to the corresponding primary phosphanes. Furthermore, we present the structure of the first enantiomerically pure dilithium phosphanediide, which forms an aggregate with a central $Li_{12}P_6$ *closo* cluster.

Results and discussion

Readily available aminoalkylferrocenylphosphanes were used as starting materials for the syntheses of the ferrocenyldichlorophosphanes. As shown in Scheme 1, *N*,*N*-dimethylaminomethylferrocene (**1**)[16] was further functionalised by *ortho*-selective lithiation and subsequent treatment with an electrophile. Compound **1** was also used as a starting material for racemic 2-*N*,*N*-dimethylaminomethyl-1-triphenylsilylferrocene (**2**), one of whose *ortho*-positions is blocked with a sterically demanding triphenylsilyl group, which was chosen to study steric influences on the chemistry of the target compounds and to explore the possibility of introducing potential silyl anchor groups for immobilization on a solid support. Silane **2** is readily available by reaction of *ortho*-lithiated **1** with triphenylsilyl chloride. It is a crystalline compound whose crystal structure is shown in Fig. 1. It has not yet appeared in the literature, although similar compounds, such as its tin analogue, a *para*-fluorophenyl-substituted derivative and the

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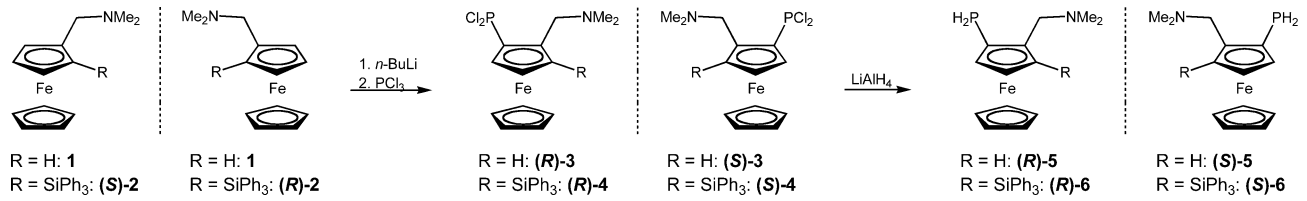


Scheme 1

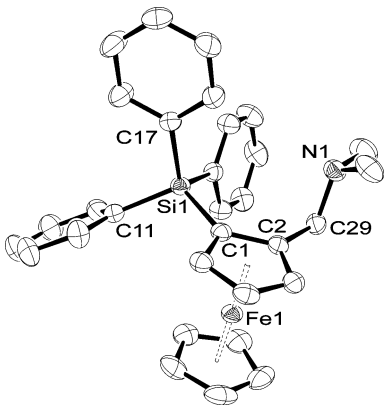


Fig. 1 Molecular structure of **2** (only the *R*-enantiomer is shown) with thermal ellipsoids at 50% probability level. H atoms have been omitted for clarity.

corresponding enantiopure compound derived from (*R*)-**7**, were reported.[17–19]

The precursors **1** and racemic **2** were used as starting materials for the syntheses of the corresponding ferrocenyldichlorophosphanes (Scheme 1). Both were lithiated *ortho*-selectively and treated subsequently with a slight excess of PCl_3 at low temperature. The resulting crystalline dichlorophosphanes (racemic **3** and **4**) are stable in the solid state but decompose slowly in solution, especially in non-polar solvents such as *n*-hexane.

The molecular structure of **3** (Fig. 2) reveals a distorted tetrahedral environment at the P atom. A noteworthy feature is the almost perfect coplanarity of P1, C1, C2, C11 and N1, which is due to a weak N → P dative bond. Thus, the system can be regarded as two annelated coplanar five-membered rings. The N···P distance of 2.443(2) Å is longer than that reported for [(6-methyl-2-pyridyl)bis(trimethylsilyl)methyl]phosphorus dichloride,[20] but rather short in comparison to those reported for tertiary aminomethylarylphosphanes.[21] The P–Cl bonds [P1–Cl1 2.1167(6), P1–Cl2 2.1887(7)] are longer than in structurally characterised aryldichlorophosphanes[22] and 1,1′-bis(dichlorophosphanyl)ferrocene,[10,23] which in general lie between 2.05 and 2.08 Å. The unusually long P1–Cl2 distance (*trans* to the weak N → P bond) is also indicative of a dative interaction between P and N and in accordance with comparable compounds.[20] ^{1}H NMR measurements at room temperature show only one singlet for the two methyl groups attached to nitrogen, that is, the dative bond is not retained in solution.

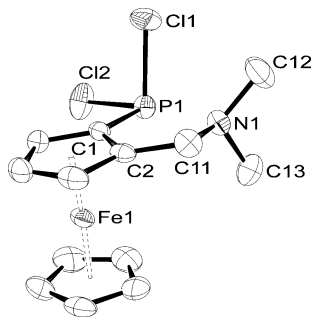


Fig. 2 Molecular structure of **3** (only the *R*-enantiomer is shown) with thermal ellipsoids at 50% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P1–Cl1 2.1167(6), P1–Cl2 2.1887(7), P1–C1 1.800(1), P1···N1 2.443(2), C1–P1–Cl1 99.36(5), C1–P1–Cl2 95.55(5), Cl1–P1–Cl2 94.50(3).

The molecular structure of the dichlorophosphane resulting from **2** as starting material is depicted in Fig. 3. Compared to the structures of **2** and the corresponding primary phosphane **6** (Fig. 4), the dimethylamino group is bent into the plane of the cyclopentadienyl ring towards the phosphorus atom, and this leads to a weak N → P dative bond, similar to that observed for **3**, with an N···P distance of 2.511(1) Å. In this case P1, C1, C2, C11, and N1 are not coplanar, but again the distance between the phosphorus atom and the chlorine atom *trans* to the weak N → P bond [P1–Cl1 2.1635(6) Å] is significantly longer than the distance to the second chlorine atom [P1–Cl2 2.0818(6) Å].

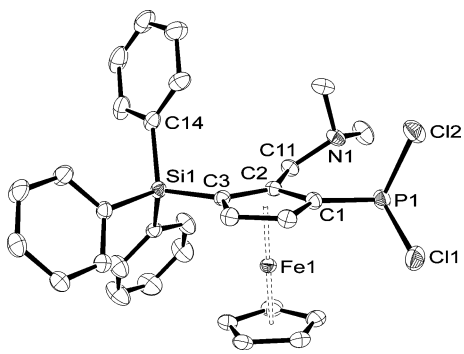


Fig. 3 Molecular structure of **4** (only the *S*-enantiomer is shown) with thermal ellipsoids at 50% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P1–Cl1 2.1635(6), P1–Cl2 2.0818(6), P1–C1 1.795(2), P1···N1 2.511(1), Si1–C3 1.864(2), C1–P1–Cl1 96.39(5), C1–P1–Cl2 102.21(6), Cl1–P1–Cl2 94.43(3).

Starting from enantiomerically pure (*S*)–*N*,*N*-dimethyl-1-ferrocenylethylamine ((*S*)-**7**)[3] and following the same synthetic pathway (Scheme 2), (*S*,*R*)-**8**‡ was prepared with a diastereomeric excess of 92%. The minor diastereomer could easily be removed

‡ In all compounds with C-centre and planar chirality, the first letter describes the configuration at the carbon centre and the second the configuration of the substituted cyclopentadienyl ring.[1]

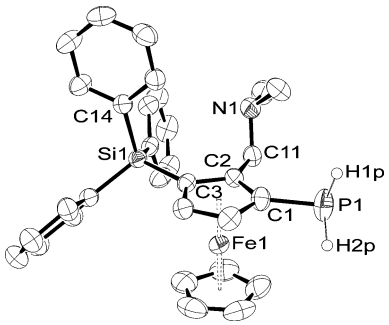
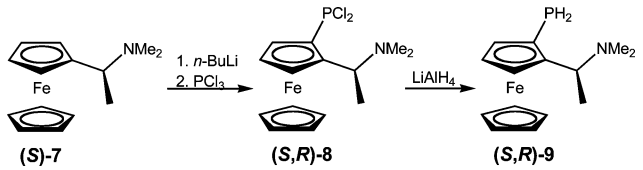


Fig. 4 Molecular structure of **6** (only the *S*-enantiomer is shown) with thermal ellipsoids at 50% probability level. H atoms (except at P1) have been omitted for clarity. Selected bond lengths (Å) and angles (°): P1–H1p 1.40(5), P1–H2p 1.33(5), P1–C1 1.809(3), H1p–P1–H2p 98(3).



Scheme 2 ‡.

by recrystallisation. The corresponding enantiomer (*R*,*S*)-**8** could be obtained analogously starting from (*R*)-**7**.

Enantiomerically pure **8** crystallises in the chiral space group $P2_12_12_1$ [Flack parameter $x = -0.01(1)$]. The structure (Fig. 5) resembles that of **3**, but due to steric repulsion between the methyl group (C12) at the chiral carbon atom and the ferrocenyl moiety, P1, C1, C2, C11 and N1 are not coplanar. Therefore, the interaction between P and N is weaker [P1 ··· N1 2.574(2) Å], but may still be regarded as a dative bond. This is also reflected in the different P–Cl bond lengths: again the P–Cl bond *trans* to P ··· N is significantly longer [P1–Cl1 2.1553(8) Å]. Compound **8** is more stable in solution than **3**, probably due to the weaker P ··· N interaction and therefore slightly lower reactivity of the P–Cl bonds.

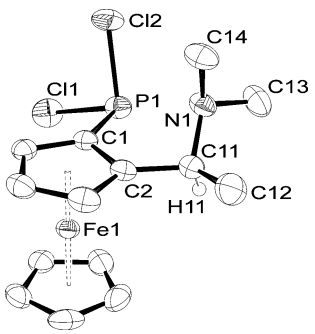
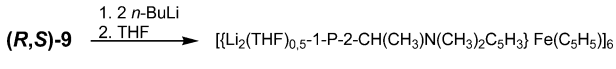


Fig. 5 Molecular structure of (*S*,*R*)-**8** with thermal ellipsoids at 50% probability level. H atoms (except H11) have been omitted for clarity. Selected bond lengths (Å) and angles (°): P1–Cl1 2.1553(8), P1–Cl2 2.0841(7), P1–C1 1.787(2), P1 ··· N1 2.574(2), C1–P1–Cl1 96.38(6), C1–P1–Cl2 101.45(6), Cl1–P1–Cl2 94.64(3).

The dichlorophosphanes are suitable starting materials for the syntheses of the corresponding primary phosphanes. Thus, compounds **5** and **6** were obtained by reaction of crude **3** or **4** with $LiAlH_4$ (Scheme 1) in shorter time and much better yield than reported by us previously.[14] Phosphane **6** is a crystalline solid whose structure is depicted in Fig. 4. It represents, to the best of our knowledge, the first structurally characterised free primary phosphanylferrocene without any spacer between the phosphanyl group and the ferrocene moiety. It is air-stable in the solid state and it is also one of the very rare examples of primary phosphanes that are stable in solution towards oxygen over a prolonged period of time (at least more than two weeks).[24] All protons, including those at the phosphorus atom, could be located. The P–C bond is within the same range as in other reported aromatic primary phosphanes.[25,26] Also, within the standard deviation, the P–H distances are in a similar range as those observed in other structurally characterised primary phosphanes for which the protons were also located, while the H–P–H angle is slightly bigger.[25,27]

The diastereomerically pure primary phosphane (*S*,*R*)-**9** is obtained analogously from (*S*,*R*)-**8** and $LiAlH_4$ (Scheme 2), as is its enantiomer (*R*,*S*)-**9** from (*R*,*S*)-**8**. We have already shown that **5** can be lithiated twice and that the resulting dilithium phosphanediide forms a hexameric aggregate with a central $Li_{12}P_6$ unit which can be described as a *closo* cluster.[14] To extend this chemistry, a similar reaction was performed with (*R*,*S*)-**9** as starting material.



(1)

With two equivalents of *n*-butyllithium, deprotonation occurred at 0 °C in *n*-hexane to give a deep red solution and some red precipitate, which dissolved upon adding a few drops of THF. Dark violet octahedral crystals of (*R*,*S*)-**10** slowly formed. The compound crystallises in the chiral space group $P2_12_12_1$ [Flack parameter $x = -0.02(1)$] and reveals the expected hexameric structure of like-configurated ferrocenylphosphanediide units associated through phosphorus–lithium contacts to a central $Li_{12}P_6$ cluster with almost the same geometrical properties as reported for dilithiated **5** (Fig. 6). To the best of our knowledge, (*R*,*S*)-**10** is the first enantiomerically pure LiP cluster, and it can be described as a *closo* cluster according to Wade's rules.[15]

Conclusions

We have reported a facile method of preparing three novel racemic (**3** and **4**) and optically pure (**8**) aminoalkylferrocenyldichlorophosphanes, which were characterised by X-ray crystallography and whose potential as starting materials for the syntheses of a wide variety of ferrocene-containing phosphorus compounds is presently being investigated further. We demonstrated that these aminoalkylferrocenyldichlorophosphanes can easily be converted to the corresponding primary phosphanes (**5**, **6** and **9**), which are thus now conveniently accessible in good yields. The structure of a rare example of an air-stable primary phosphane (**6**) could be determined. Finally, the synthesis and structure of the first chiral LiP *closo* cluster compound was presented.

Experimental

General considerations

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry high-purity nitrogen.

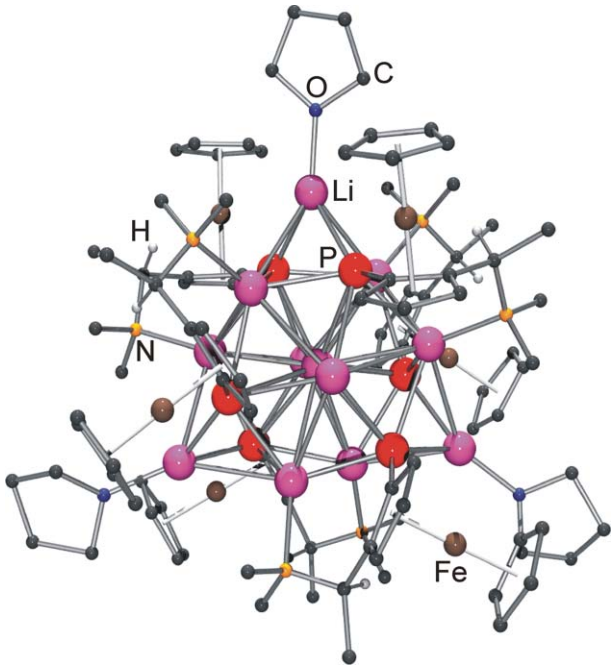


Fig. 6 Molecular structure of (*R*,*S*)-**10**. H atoms (except at chiral centres) have been omitted for clarity.

THF was distilled from sodium/benzophenone. Diethyl ether, toluene, *n*-hexane and dichloromethane were taken from an MBRAUN Solvent Purification System MB SPS-800 and stored over potassium mirror. Ethanol was degassed in a nitrogen stream in an ultrasonic bath. ^{1}H, ^{7}Li, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer and referenced to tetramethylsilane (TMS).[28] Mass spectra were recorded on a VG Analytics ZAB-HSQ spectrometer. FT-IR spectra were recorded on a Perkin-Elmer Spectrum 2000 spectrometer. Melting points were determined in sealed glass capillaries under nitrogen and are uncorrected. *N*,*N*-dimethylaminomethylferrocene (**1**)[16] and both enantiomers of *N*,*N*-dimethyl-1-ferrocenylethylamine (**7**)[3] were synthesised according to literature procedures. Other chemicals were obtained from commercial sources and used as supplied, except PCl_3, which was distilled and saturated with nitrogen prior to use.

Synthetic procedures

Racemic 2-*N*,*N*-dimethylaminomethyl-1-triphenylsilylferrocene (2). A solution of *n*-BuLi (9.47 ml; 22.63 mmol; 2.39 M in *n*-hexane) was slowly added to a solution of **1** (5.00 g, 20.58 mmol) in diethyl ether (50 ml). The mixture was stirred for 8 h and cooled to 0 °C. A solution of triphenylsilyl chloride (6.80 g, 23.06 mmol) in diethyl ether (50 ml) was then added over a period of 2 h. After stirring overnight at room temperature, the mixture was filtered and the filtrate evaporated to dryness. The orange solid was recrystallised from diethyl ether. Yield 8.74 g (84.7%). Mp. 116–117 °C. ^{1}H NMR (+20 °C, 400.13 MHz, $CDCl_3$/TMS): δ = 1.76 (s, 6H, $N(CH_3)_2$), 2.80 (d, $^{2}J_{HH}$ = 12.8 Hz, 1H, CH_2N), 2.96 (d, $^{2}J_{HH}$ = 12.8 Hz, 1H, CH_2N), 4.02 (s, 5H, C_5H_5), 4.11 (s, 1H, C_5H_3), 4.36 (s, 1H, C_5H_3), 4.66 (s, 1H, C_5H_3), 7.38 (m, 9H, *m*- and *p*-H of C_6H_5), 7.67 (d, $^{3}J_{HH}$ = 7.2 Hz, 6H, *o*-H of C_6H_5) ppm. ^{13}C NMR (25 °C, 100.6 MHz, $CDCl_3$/TMS): δ = 44.8 ($N(CH_3)_2$), 58.8 (CH_2N), 66.5 ($C_{Fc}Si$), 69.3 (C_5H_5), 70.4 (C_5H_3), 73.9 (C_5H_3), 76.5 (C_5H_3), 91.1 ($C_{Fc}CH_2N$), 127.5 (*m*-C_{Ph}), 129.1 (*p*-C_{Ph}), 135.8 (*i*-C_{Ph}), 136.4 (*o*-C_{Ph}) ppm. FT-IR $\tilde{\nu}$/cm^{-1} (KBr): 3093 (w), 3069 (m), 3047 (w), 3013 (w), 2993 (w), 2973 (w), 2944 (w), 2854 (w), 2811 (m), 2757 (s), 1485 (w), 1455 (m), 1429 (s), 1400 (w), 1380 (w), 1360 (w), 1321 (w), 1258 (m), 1226 (w), 1188 (w), 1171 (m), 1154 (w), 1136 (m), 1107 (s), 1081 (w), 1042 (m), 1023 (m), 999 (m), 954 (w), 846 (w), 833 (w), 816 (s), 759 (w), 744 (s), 705 (s), 681 (m), 638 (w), 552 (m), 527 (m), 511 (s), 493 (s), 450 (w), 443 (w). MS (EI pos., 14 eV) *m*/*z*: 501 [M$^+$] (100%), 457 [(M–NMe_2)$^+$] (38.7%), 259 [($SiPh_3$)$^+$] (25.5%). Elemental analysis for $C_{31}H_{31}FeNSi$ (%): Calc.: C 74.24, H 6.23, N 2.79; found: C 74.21, H 6.26, N 2.71.

Racemic 1-dichlorophosphanyl-2-*N*,*N*-dimethylaminomethylferrocene (3). A solution of *n*-BuLi (9.47 ml, 22.63 mmol, 2.39 M in *n*-hexane) was slowly added to a solution of **1** (5.0 g, 20.58 mmol) in diethyl ether (50 ml). The mixture was stirred for 8 h and slowly (over a period of 2 h) added to a solution of PCl_3 (3.39 g, 24.69 mmol) in diethyl ether (20 ml) at −80 °C. The mixture was warmed to room temperature overnight and filtered. The solvent was evaporated and the residue dried *in vacuo*. Recrystallisation from a mixture of toluene and *n*-hexane (1 : 10) gave pure **3** as red crystals. Yield 5.88 g (83.1%). Mp. 117 °C (decomp.). ^{1}H NMR (+20 °C, 400.13 MHz, C_6D_6/TMS): δ = 2.00 (s, 6H, $N(CH_3)_2$), 2.65 (d, $^{2}J_{HH}$ = 14.0 Hz, 1H, CH_2), 3.37 (d, $^{2}J_{HH}$ = 14.0 Hz, 1H, CH_2), 3.90 (br. s, 1H, C_5H_3), 3.96 (s, 5H, C_5H_5), 4.12 (br. s, 1H, C_5H_3), 4.76 (br. s, 1H, C_5H_3) ppm. ^{13}C{^{1}H} NMR (+20 °C, 100.16 MHz, C_6D_6/TMS): δ = 45.4 ($N(CH_3)_2$), 57.8 (d, $^{3}J_{PC}$ = 2.4 Hz, CH_2), 70.0 (br. s, C_5H_3), 70.7 (br. s, C_5H_3), 70.8 (C_5H_5), 71.0 (br. s, C_5H_3), 81.5 (d, $^{1}J_{PC}$ = 63.3 Hz, $C_{Fc}P$), 92.6 (d, $^{2}J_{PC}$ = 13.5 Hz, $C_{Fc}CH_2$) ppm. ^{31}P{^{1}H} NMR (+20 °C, 161.98 MHz, C_6D_6/TMS): δ = 145.6 ppm. FT-IR $\tilde{\nu}$/cm^{-1} (KBr): 3095 (w), 2956 (w), 2865 (m), 2833 (m), 2786 (w), 1460 (m), 1409 (w), 1347 (w), 1261 (w), 1225 (m), 1165 (m), 1106 (w), 1077 (w), 1030 (s), 1002 (m), 954 (w), 825 (s), 503 (m), 488 (w), 458 (m), 438 (s). MS (EI pos. 70 eV) *m*/*z*: 343 [M$^+$] (61.8%), 308 [(M–Cl)$^+$] (9.1%), 265 [(M–Cl–$HNMe_2$)$^+$] (14.1%), 187 [($Fe(C_5H_4)PCl$ + H)$^+$] (100%), 152 [($Fe(C_5H_4)P$ + H)$^+$] (57.4%), 109 [($CH_2(C_5H_3)P$ + H)$^+$] (39.4%). Elemental analysis for $C_{13}H_{16}Cl_2FeNP$ (%): Calc.: C 45.39, H 4.69, N 4.07; Found: C 45.31, H 4.74, N 3.96.

Racemic 1-dichlorophosphanyl-2-*N*,*N*-dimethylamino-methyl-3-triphenylsilylferrocene (4). The procedure for the preparation of **3** was followed using **2** (2.00 g, 3.99 mmol), *n*-BuLi (1.70 ml, 4.06 mmol, 2.39 M in *n*-hexane) and PCl_3 (0.57 g, 4.15 mmol). Recrystallisation from a mixture of toluene and *n*-hexane (1 : 5) gave pure product. Crystals for X-ray analysis were obtained at −20 °C from a dichloromethane solution which was layered with *n*-hexane. Yield 2.04 g (84.9%). Mp. 129–130 °C. ^{1}H NMR (+20 °C, 400.13 MHz, C_6D_6/TMS): δ = 1.83 (s, 6H, $N(CH_3)_2$), 2.79 (dd, $^{2}J_{HH}$ = 14.0 Hz, $^{4}J_{PH}$ = 1.6 Hz, 1H, CH_2N), 3.58 (d, $^{2}J_{HH}$ = 14.0 Hz, 1H, CH_2N), 4.04 (s, 5H, C_5H_5), 4.24 (d, $^{3}J_{HH}$ = 2.4 Hz, 1H, C_5H_2 *o* to Si), 5.07 (d, $^{3}J_{HH}$ = 2.4 Hz, 1H, C_5H_2 *o* to P), 7.19 (m, 9H, *m*- and *p*-H of C_6H_5), 7.64 (d, $^{3}J_{HH}$ = 6.4 Hz, 6H, *o*-H of C_6H_5) ppm. ^{13}C{^{1}H} NMR (+20 °C, 100.16 MHz, C_6D_6/TMS): δ = 45.1 ($N(CH_3)_2$), 58.7 (d, $^{3}J_{PC}$ = 3.9 Hz, CH_2N), 68.7 ($C_{Fc}Si$), 71.8 (C_5H_5), 74.3 (C_5H_2 o to Si), 79.1 (C_5H_2 o to P), 87.0 (d, $^{1}J_{PC}$ = 65.6 Hz, $C_{Fc}P$), 97.7 (d, $^{2}J_{PC}$ = 8.6 Hz, $C_{Fc}CH_2N$), 130.1 (*p*-C_{Ph}), 135.1 (*i*-C_{Ph}), 136.5 (*o*-C_{Ph}) ppm. The signal for *m*-C_{Ph} is overlapped by the solvent signal. ^{31}P{^{1}H} NMR (+20 °C,

161.98 MHz, C_6D_6/TMS): $\delta = 134.0$ ppm. FT-IR $\tilde{\nu}$/cm^{-1} (KBr): 3068 (m), 3048 (m), 2959 (m), 2866 (m), 2833 (m), 2787 (w), 1469 (m), 1428 (s), 1409 (m), 1338 (w), 1311 (w), 1261 (m), 1217 (m), 1188 (w), 1127 (m), 1108 (s), 1021 (m), 1004 (m), 934 (w), 826 (m), 740 (m), 704 (s), 591 (w), 533 (w), 506 (s), 467 (s). MS (EI pos. 14 eV) *m*/*z*: 529 [(M–2HCl)$^+$] (15.7%), 407 [(M–2HCl–HNMe$_2$–Ph)$^+$] (9.1%), 294 [(SiPh$_3$Cl)$^+$] (100%), 217 [(SiPh$_2$Cl)$^+$] (8.6%), 154 [(Ph$_2$)$^+$] (19.3%), 66 [(CpH)$^+$] (15.5%). MS (EI pos. 70 eV, scan from $m/z = 540$ to $m/z = 660$ only, due to short lifetime of M$^+$) *m*/*z*: 601 [M$^+$] (100%), 566 [(M–Cl)$^+$] (15.9%), 551 [(M–Cl–Me)$^+$] (29.1%) Elemental analysis for $C_{31}H_{30}Cl_2FeNPSi$ (%): Calc.: C 61.81, H 5.02, N 2.33; Found: C 61.90, H 4.99, N 2.27.

(*S*)-*N*,*N*-Dimethyl-1-[(*R*)-2-(dichlorophosphanyl)-ferrocenyl]-ethylamine ((*S*,*R*)-8). The same procedure as for **3** was followed using (*S*)-**7** (3.00 g, 11.67 mmol), *n*-BuLi (5.37 ml, 12.83 mmol, 2.39 M in *n*-hexane) and PCl_3 (1.93 g, 14.05 mmol) giving orange-red plates from toluene and *n*-hexane (1 : 10). Yield 3.30 g (79.0%). Mp. 121–122 °C. ^{1}H NMR (+20 °C, 400.13 MHz, C_6D_6/TMS): $\delta = 0.72$ (d, $^3J_{HH} = 6.8$ Hz, 3H, CH_3), 1.86 (s, 6H, N(CH$_3$)$_2$), 3.89 (m, 3H, 2H of C_5H_3 and C*H*–CH$_3$), 3.99 (s, 5H, C_5H_5), 4.79 (br. s, 1H, C_5H_3) ppm. ^{13}C{^{1}H} NMR (+20 °C, 100.16 MHz, C_6D_6/TMS): $\delta = 8.5$ (CH–*C*H$_3$), 38.9 (N(CH$_3$)$_2$), 58.7 (*C*H–CH$_3$), 68.9 (d, $^3J_{PC} = 1.1$ Hz, C_5H_3 *m* to P and to CHN), 70.2 (br. s, C_5H_3 *o* to CHN), 70.9 (C_5H_5), 71.7 (d, $^2J_{PC} = 2.0$ Hz, C_5H_3 *o* to P), 82.7 (d, $^1J_{PC} = 62.6$ Hz, C_{Fc}P), 97.5 (d, $^2J_{PC} = 14.5$ Hz, *C*$_{Fc}$CHN) ppm. ^{31}P{^{1}H} NMR (+20 °C, 161.98 MHz, C_6D_6/TMS): $\delta = 141.9$ ppm. FT-IR $\tilde{\nu}$/cm^{-1} (KBr): 3110 (w), 2978 (m), 2946 (m), 2876 (m), 2837 (w), 2790 (w), 1469 (m), 1451 (s), 1410 (w), 1373 (m), 1335 (w), 1294 (w), 1244 (s), 1186 (m), 1170 (m), 1105 (m), 1074 (m), 1044 (w), 1002 (m), 933 (m), 839 (m), 816 (s), 776 (w), 556 (w), 513 (w), 494 (w), 465 (s), 449 (s). MS (EI pos. 70 eV) *m*/*z*: 357 [M$^+$] (20.8%), 201 [(M–Fe–Cp–Cl)$^+$] (22.1%), 166 [(M–Fe–Cp–2Cl)$^+$] (100%), 134 [(M–Fe–Cp–PCl$_2$)$^+$] (15.2%), 72 [(CH$_3$CH=NMe$_2$)$^+$] (37.1%). Elemental analysis for $C_{14}H_{18}Cl_2FeNP$ (%): Calc.: C 46.97, H 5.07, N 3.91; Found: C 47.04, H 4.99, N 3.79.

Racemic 1-phosphanyl-2-*N*,*N*-dimethylaminomethylferrocene (5). Crude **3** can be used directly without further purification. Crude **3**, obtained from **1** (1.0 g, 4.12 mmol), was dissolved in diethyl ether (40 ml, solution became slowly turbid due to decomposition of **3**) and was added to a slurry of $LiAlH_4$ (0.15 g, 3.95 mmol) in diethyl ether (10 ml) at 0 °C. The mixture was stirred at room temperature overnight and carefully hydrolysed with slightly basic (one prill of KOH) water (25 ml) at 0 °C. After stirring for 2 h at room temperature the organic layer was separated and dried over $MgSO_4$. After filtration the solvent was removed and the oily residue dried *in vacuo.* **5** can be further purified by bulb-to-bulb distillation at 80 °C bath temperature in vacuum (*ca.* 10^{-3} torr). Yield 0.92 g (81.2% based on **1**). The spectroscopic data of **5** are in agreement with those reported previously.[14]

Racemic 1-phosphanyl-2-*N*,*N*-dimethylaminomethyl-3-triphenylsilylferrocene (6). The procedure for the synthesis of **5** was followed starting from crude **4** obtained from **2** (2.00 g, 3.99 mmol). The yellow-orange solid was recrystallised from ethanol. Crystals were grown from a diethyl ether solution at −20 °C. Yield 1.77 g (83.1% based on **2**). Mp. 143–144 °C. ^{1}H NMR (+20 °C, 400.13 MHz, C_6D_6/TMS): $\delta = 1.75$ (s, 6H, N(CH$_3$)$_2$), 3.14 (d, $^2J_{HH} = 12.5$ Hz, 1H, CH$_2$N), 3.21 (d, $^2J_{HH} = 12.5$ Hz, 1H, CH$_2$N), 3.72 (dd, $^1J_{PH} = 199.9$ Hz, $^2J_{HH} = 12.2$ Hz, 1H, PH), 3.89 (dd, $^1J_{PH} = 198.0$ Hz, $^2J_{HH} = 12.2$ Hz, 1H, PH), 3.93 (s, 5H, C_5H_5), 4.25 (d, $^3J_{HH} = 2.2$ Hz, 1H, C_5H_2 *o* to Si), 4.32 (d, $^3J_{HH} = 2.2$ Hz, 1H, C_5H_2 *o* to P), 7.21 (m, 9H, *m*- and *p*-H of C_6H_5), 7.84 (m, 6H, *o*-H of C_6H_5) ppm. ^{13}C{^{1}H} NMR (+20 °C, 100.16 MHz, C_6D_6/TMS): $\delta = 44.6$ (N(CH$_3$)$_2$), 57.1 (d, $^3J_{PC} = 3.2$ Hz, CH$_2$N), 70.3 (d, $^3J_{PC} = 1.0$ Hz, C_{Fc}Si), 70.8 (d, $^1J_{PC} = 8.6$ Hz, C_{Fc}P), 70.9 (C_5H_5), 78.0 (d, $^3J_{PC} = 2.8$ Hz, C_5H_2 *o* to Si), 78.9 (d, $^2J_{PC} = 6.9$ Hz, C_5H_2 *o* to P), 95.9 (d, $^2J_{PC} = 11.9$ Hz, *C*$_{Fc}$CH$_2$N), 127.9 (*m*-C$_{Ph}$), 129.5 (*p*-C$_{Ph}$), 136.3 (*i*-C$_{Ph}$), 136.9 (*o*-C$_{Ph}$) ppm. ^{31}P NMR (+20 °C, 161.98 MHz, C_6D_6/TMS): $\delta = -149.2$ (t, $^1J_{PH} = 198.4$ Hz) ppm. FT-IR $\tilde{\nu}$/cm^{-1} (KBr): 3068 (m), 3047 (m), 2969 (m), 2939 (m), 2857 (m), 2811 (s), 2762 (s), 2297 (m, PH), 2255 (m, PH), 1483 (w), 1456 (m), 1427 (s), 1398 (w), 1342 (w), 1317 (w), 1257 (m), 1218 (w), 1178 (w), 1127 (s), 1106 (s), 1076 (m), 1044 (w), 1026 (m), 1003 (m), 843 (m), 818 (s), 741 (m), 703 (s), 681 (m), 638 (w), 583 (m), 499 (s), 456 (m). MS (EI pos. 14 eV) *m*/*z*: 533 [M$^+$] (10.6%), 488 [(M–HNMe$_2$)$^+$] (100%). Elemental analysis for $C_{31}H_{32}FeNPSi$ (%): Calc.: C 69.79, H 6.05, N 2.63; Found: C 69.77, H 5.99, N 2.57.

(*S*)-*N*,*N*-Dimethyl-1-[(*R*)-2-(phosphanyl)ferrocenyl]ethylamine ((*S*,*R*)-9). The procedure for the synthesis of **5** was applied starting from crude (*S*,*R*)-**8** resulting from (*S*)-**7** (1.00 g, 3.89 mmol). Yield 0.95 g (84.5% based on (*S*)-**7**).

(*R*,*S*)-10. (*R*,*S*)-**9** (0.2 g, 0.69 mmol) was dissolved in *n*-hexane (10 ml). At 0 °C *n*-BuLi (0.59 ml, 1.4 mmol, 2.39 M in *n*-hexane) was slowly added. Immediately, a fluffy red precipitate formed which redissolved almost completely upon further addition of *n*-BuLi. The mixture was allowed to warm to room temperature and stirred for 30 min. THF was slowly added until the solid was completely dissolved (*ca.* 1 ml). Deep violet octahedral crystals of (*R*,*S*)-**10** grew at room temperature over a few days. Yield 0.22 g (*ca.* 95%, crystals contain solvent). ^{31}P{^{1}H} NMR (+20 °C, 161.98 MHz, THF/C_6D_6/TMS), $\delta = -176.6$ ppm. ^{31}P{^{1}H} NMR (+20 °C, 161.98 MHz, *n*-hexane/C_6D_6/TMS), $\delta = -219.0$ (m, v. br.) ppm. ^{7}Li NMR (+20 °C, 155.50 MHz, THF/C_6D_6/TMS), $\delta = 0.8$ ppm. ^{7}Li NMR (+20 °C, 155.50 MHz, *n*-hexane/C_6D_6/TMS), $\delta = 11.5$ (m, v. br.) ppm. The spectroscopic data of (*R*,*S*)-**10** are in agreement with those reported previously.[14]

X-ray crystallography

Suitable crystals were mounted in perfluoropolyalkyl ether. Crystallographic measurements were made using a Stoe-IPDS imaging plate diffractometer for compounds **2**, **3** and (*R*,*S*)-**10**, a Siemens SMART CCD diffractometer for compounds **6** and (*S*,*R*)-**8** and an Oxford Diffraction Xcalibur S diffractometer for compound **4**. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques (SHELX97).[29] All non-hydrogen atoms, except for some solvent molecules, were refined anisotropically, hydrogen atoms were either located and refined isotropically or included in a riding mode. A highly disordered solvent molecule (*n*-hexane) in the structure of compound **4** and two highly disordered solvent molecules (*n*-hexane) in the structure of compound (*R*,*S*)-**10** were removed using the program SQUEEZE.[30] Crystal data and details of data collection and refinement are given in Table 1.

Table 1 Crystal data for compounds **2**, **3**, **4**, **6**, (*S*,*R*)-**8**, (*R*,*S*)-**10**

Compound	**2**	**3**	**4**	**6**	(*S*,*R*)-**8**	(*R*,*S*)-**10**
Empirical formula	$C_{31}H_{31}FeNSi$	$C_{31}H_{16}Cl_2FeNP$	$C_{31}H_{30}Cl_2FeNPSi{\cdot}C_6H_{14}$	$C_{31}H_{32}FeNPSi$	$C_{14}H_{16}Cl_2FeNP$	$C_{96}H_{132}Fe_6Li_{12}N_6O_3P_6{\cdot}3C_6H_{14}$
Formula weight	501.51	343.99	688.54	533.49	358.01	2280.76
T/K	213(2)	208(2)	130(2)	213(2)	213(2)	213(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_12_12_1$	$P2_12_12_1$
a/Å	10.4014(9)	10.2696(10)	10.2987(1)	10.0968(15)	8.2995(12)	16.0644(16)
b/Å	10.6429(11)	10.7620(9)	21.9790(2)	12.1986(18)	11.9091(16)	26.933(3)
c/Å	13.2272(12)	13.4203(13)	14.6812(1)	12.968(2)	15.662(2)	28.661(3)
α/°	74.919(11)	90	90	65.532(3)	90	90
β/°	75.272(10)	100.198(12)	95.219(1)	71.067(3)	90	90
γ/°	69.639(11)	90	90	85.882(3)	90	90
V/Å^3	1303.6(2)	1459.8(2)	3309.39(5)	1371.5(4)	1548.0(4)	12400(10)
Z	2	4	4	2	4	4
ρ_{calcd}/Mg m^{-3}	1.278	1.565	1.382	1.292	1.536	1.222
μ(Mo-K$_\alpha$)/mm^{-1}	0.644	1.489	0.730	0.672	1.408	0.808
F(000)	528	704	1448	560	736	4824
No. of reflns collected	17 134	22 888	49 152	8247	11 360	88 150
No. of independent reflns	7088	4071	9966	6459	3683	19 542
$R1$ (observed data)	0.0560	0.0437	0.0487	0.0757	0.0258	0.0542
$wR2$ (observed data)	0.0680	0.0599	0.1042	0.1372	0.0583	0.0921
Flack parameter x	—	—	—	—	−0.010(11)	−0.023(11)

CCDC reference numbers are 628375 (**2**), 617194 (**3**), 628376 (**4**), 628374 (**6**), 617193 ((*S*,*R*)-**8**) and 617195 ((*R*,*S*)-**10**).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b617257a

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