The 'one-pot' syntheses of α,α′-diphosphino-substituted imines: a unique reaction of bulky bis(dialkylamino)chlorophosphines

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The reaction between various bis(dialkylamino)chlorophosphines and *N*-isopropyl-substituted lithium amides afforded bis(α,α′-phosphino)imines in a 'one-pot' procedure. These compounds react with sulfur to generate intramolecularly hydrogen-bonded ylide derivatives. The molecular structure of $(Pr^i_2N)_2PCH_2C(=NBu^t)CH_2P(NPr^i)_2$ has been determined by X-ray crystallography.

Introduction

Currently there is a considerable resurgence of interest in the use of heteroatom substituents at phosphorus to 'tune' both the steric requirements and basicity of phosphine-containing ligands. This is due, in part, to the ease and considerable scope associated with the synthesis of phosphorus–heteroatom bonds, exemplified by P–O and P–N bond formation.[1] It is therefore somewhat surprising that despite both the continued use of bidentate *P*,*P*′-ligands in many industrially important catalytic processes,[2] and the on-going development of so-called 'hemi-labile' phosphorus-containing systems (*e.g.* bidentate *P*,*O*-[3] *P*,*N*-[4] and *P*,*S*-ligands[5]),[6] there remain few examples of chelating ligands which possess a diaminophosphine component.[1a,c]

As the application of phosphorus-based donors in catalysis continues apace, simple, high-yielding preparative routes to novel, easily tailored ligand systems are of growing commercial importance. During studies into the use of bis(dialkylamino)phosphino substituents, the simple 'one-pot' synthesis of bis(α,α′-phosphino)-substituted imines has been studied in detail, while the basis of a more general route to compounds containing the $R_2PCH_2C=NR'$ motif has been established.

Results and discussion

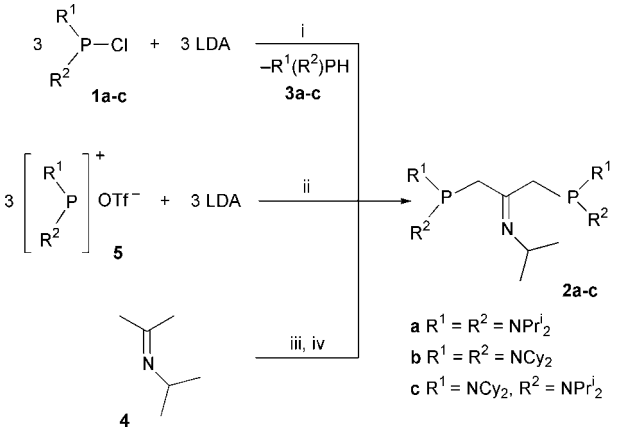
Treating a solution of LDA (lithium diisopropylamide) with a solution of bis(dialkylamino)chlorophosphines **1** (Et_2O, 0 °C) in a 1 : 1 molar ratio cleanly affords bis(α,α′-phosphino)imines **2** and the corresponding secondary phosphines **3**,[7] in equimolar amounts [^{31}P NMR spectroscopy] (Scheme 1, Table 1).[8] The addition of less than stoichiometric amounts of LDA leads to the formation of mixtures of **2**, **3** and unchanged **1**. Similarly, the reaction of the phosphenium salt $[(Pr^i_2N)_2P][CF_3SO_3]$ **5** with LDA (Et_2O) also forms **2a** in good yield (73%) with concomitant formation of secondary phosphine **3a** and elimination of lithium triflate. It is noteworthy that although a number of phosphorus-containing products were generated from the reaction between **5** and $HNPr^i_2$ in the presence of NEt_3 or 1,4-diazabicyclo[2.2.2]octane (dabco), none was readily identifiable. This suggests that the formation of **2** does not necessitate the generation of an intermediate $[(Pr^i_2N)_2P]^+$ moiety, but favours a concerted mechanism as outlined below.

It seems most likely that the imine $Me_2C=NPr^i$ **4** is generated during the reaction between **1** and LDA *via* an *N*-analogue of the Meerwein–Ponndorf–Verley reaction (Scheme 2), similar reactions having been reported previously for

Table 1 Selected ^{31}P NMR and IR spectroscopic data

Product	R^1	R^2	R^3	δ ^{31}P ($^4J_{PP}$/Hz)[a]	Yield[b] (%)	IR[c]
2a	NPr^i_2	NPr^i_2	Pr^i	45.4, 52.9 (11.0)	80	1625
2b	NCy_2	NCy_2	Pr^i	53.9, 59.3 (25.0)	75	1621
2c	NPr^i_2	NCy_2	Pr^i	49.6, 56.6 (13.0)[d] 49.8, 56.1 (20.0)[d]	[e]	1625[f]
2d	NPr^i_2	NPr^i_2	Cy	46.5, 53.5 (12.0)	70	1619
2e	NPr^i_2	NPr^i_2	Bu^t	47.6, 55.8 (37.0)	83	1629

[a] In $CDCl_3$, 300 MHz. [b] Isolated yield after work-up. [c] Solution cell, KBr windows, CH_2Cl_2, cm^{-1}. [d] In Et_2O. [e] Product isolated as a mixture of two inseparable diastereomers, formed quantitatively according to ^{31}P NMR spectroscopy. [f] In Et_2O, severely broadened.

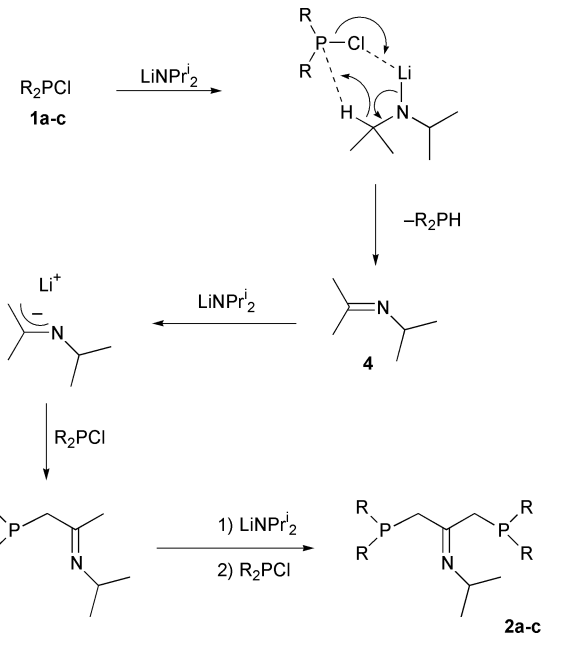


Scheme 1 *Reagents and conditions*: i, 0 °C to r.t., Et_2O, 12 h; ii, $R^1 = R^2 = NPr^i_2$, 0 °C to r.t., Et_2O, 12 h; iii, $R^1 = R^2 = NPr^i_2$, Bu^nLi/tmeda, −78 °C, 40 min, hexane; iv, **1a** −78 °C to r.t., hexane. OTf = O_3SCF_3 (triflate).

certain transformations involving this amide base.[9] It would appear that imine **4** is then rapidly deprotonated by LDA to generate an intermediate aza-allyl anion, which subsequently undergoes substitution by chlorophosphines **1**, a process that is repeated to form **2**.

Low temperature ^{31}P NMR spectroscopic studies (Et_2O) of the reaction between LDA and compound **1a** indicate that the secondary phosphine **3a** and phosphino-imine **2a** are formed simultaneously in a 1 : 1 molar ratio as the only phosphorus-containing products, on the NMR timescale at 243 K (no reaction is observed below this temperature). There was no evidence to support the claim that $(Pr^i_2N)_3P$ **6** is involved in the formation of **2a** from LDA and **1a**, despite a previous report to the contrary.[8]†

Attempts to identify compound **4** directly during reactions of **1a** and LDA by GC-MS were unsuccessful. However, its intermediacy is supported by the observation that **2a** can also be synthesized (30% yield) by treating an authentic sample of **4** with two equivalents of Bu^nLi/tmeda (hexane, −78 °C) followed by the addition of two equivalents of diaminochlorophosphine **1a** (hexane, 0 °C) [Scheme 1]. An extension to this methodology can be used to prepare variously substituted α-phosphino-imines, *e.g.* **7**, from R(Me)C=NR′ and the appropriate chlorophosphine (Scheme 3).[11] A variation on this procedure has recently been utilised for the synthesis of unsymmetrical β-diimines.[12]

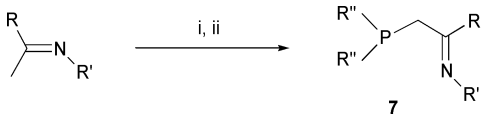


Scheme 2

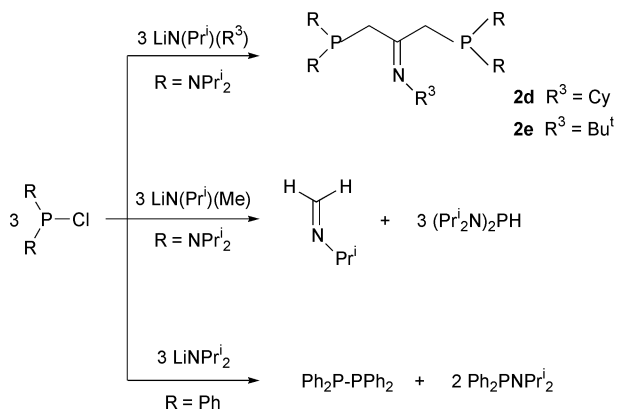
It has proved straightforward to introduce other alkyl substituents at the imine terminus of diphosphines **2** using the 'one-pot' methodology. For example, treatment of diaminochlorophosphine **1a** with unsymmetrical lithium *N*-alkyl-*N*-isopropyl amides [$LiNPr^i(R^3)$] (Et_2O, 0 °C) cleanly affords the corresponding bis(phosphino)imines **2d,2e** (Scheme 4, Table 1). In each case, the 'sacrificial' role of one *N*-isopropyl group is readily apparent, further supporting the intermediacy of an imine such as $Me_2C{=}NR$ (*e.g.* R = Pr^i, **4**). These ideas are endorsed by the observation that the reaction of $LiN(Pr^i)(Me)$ with **1a** affords $H_2C{=}NPr^i$ (GC-MS, IR ν(CN) 1649 cm^{-1})[13] and $(Pr^i_2N)_2PH$ (GC-MS/^{31}P NMR)[7] rather than $\{(Pr^i_2N)_2PCH_2\}_2C{=}NMe$, as a result of hydride abstraction from the more hydridic NCH_3 group.

Overall, it would appear that the initial hydride transfer between compound **1a** and LDA outlined in Scheme 2 occurs because simple substitution, which would lead to formation of $(Pr^i_2N)_3P$ **6**, is blocked due to unfavourable steric interactions between the bulky amide substituents. Despite an unverified report of the ^{31}P NMR spectrum of **6** (*vide supra*) and two brief accounts of its generation, little convincing data have been reported which support the existence of what would be an extremely sterically encumbered tris(amino)phosphine.[8,14]

Notably, phosphino-imine formation only occurs when bulky dialkylamino substituents (*e.g.* NPr^i_2 or NCy_2) are present on the chlorophosphines **1**. The less bulky derivatives, $(R'_2N)_2PCl$ (R′ = Me or Et), react with LDA to afford intractable mixtures of phosphorus-containing products, which include trace amounts of the corresponding tris(amino)phosphines, $(R'_2N)_2PNPr^i_2$, according to ^{31}P NMR spectroscopy, but show no evidence of imine formation.[15] Similarly, the direct reaction between Ph_2PCl and LDA, irrespective of the nature of the solvent, affords a mixture of the product from reductive coupling, Ph_2PPPh_2 (δ −14.2),[16] and



Scheme 3 *Reagents and conditions:* i, Bu^nLi/tmeda, −78 °C to r.t., hexane, 12 h (R = H, Me or Ph; R′ = Ph, $C_6H_3Pr^i_2$-2,6); ii, R''_2PCl (R″ = NPr^i_2 or Ph), 0 °C, reflux, 3 h.



Scheme 4

† It is important to note the coincidence between the reported ^{31}P NMR chemical shift for $(Pr^i_2N)_3P$ **6**, δ +133.6 (solvent not specified),[8,10] and that for its most convenient precursor, namely **1a** {^{31}P NMR (Et_2O, 273 K): δ +133.6}, suggesting a previously incorrect assignment of the former.

the aminophosphine $Ph_2P(NPr^i_2)$ (δ +37.1),[17] resulting from substitution, in an approximately 1 : 2 ratio (Scheme 4).‡

It is noteworthy that when the reaction between compound **1a** and LDA is undertaken in THF instead of Et_2O the major product becomes $(Pr^i_2N)_2P–P(NPr^i_2)_2$,[18] with only trace amounts of **2** being detectable (<5% by ^{31}P NMR spectroscopy). This solvent dependency is presumed to reflect small changes in the degree of chloride dissociation from **1a** that occurs in each of the solvents.[19,20]§ The formation of products resulting from reductive coupling is perhaps not surprising since LDA is known to act as a one-electron donor to species with favourable reduction potentials.[21] However, as expected neither nucleophilic substitution nor imine formation was observed to occur when the corresponding $\sigma^4\lambda^5$-thioxophosphine $(Pr^i_2N)_2P(S)Cl$ was treated with LDA in Et_2O, presumably due to a combination of steric hindrance and the lack of a vacant orbital at phosphorus to accommodate initial hydride transfer (as required by the mechanism outlined in Scheme 2).

All the phosphino-imine derivatives **2** (with the exception of **2c**) are readily isolated after appropriate work-up as colourless solids. Crystals of **2e** suitable for an X-ray crystallographic study were grown from a concentrated hexane solution at −30 °C.¶ The structural parameters associated with the planar imine moiety (sum of angles about C(2) = 360.0°) are typical for this type of functional group (Fig. 1).[22] The phosphorus atom P(1) is orientated such that its lone pair is directed away from both the lone pair on the imine nitrogen N(1) and the second phosphorus P(2). This induces a staggered conformation along the PCCCP backbone such that P(2) and P(1) lie, respectively, 1.5447 Å above and −0.8824 Å below the plane defined by [N(1)–C(3)–C(2)–C(1)]. Changes in the extent of this 'twist' are believed to be the cause of the considerable variation in the $^4J_{PP}$ coupling constants observed (**2a**–**2e**, Table 1), although no significant difference in this parameter was observed for **2a** at either reduced or elevated temperatures. The bond distances P(2)–C(3) and P(1)–C(1) are unremarkable and consistent with P–C single bonds.[1f] As is observed for many aminophosphines, the four P–N bond distances are significantly shorter than that associated with a true P–N single bond, while the sums of angles about nitrogen atoms N(2) to N(5) [358.4, 359.9, 360.0, 360.0°, respectively] indicate significant sp^2 character.[23]

Diphosphino-imine **2a** readily reacts with sulfur, initially forming the corresponding bis($\sigma^4\lambda^5$-thiophosphoryl)imine **8** [AB system: δ +70.9 and +72.6 ($^4J_{PP}$ 10.0 Hz)] (Scheme 5) which rearranges on standing (~12 hours, 25 °C) to afford the new hydrogen-bonded ylide tautomer **9**. This can be isolated after recrystallisation from dichloromethane (−30 °C) as an almost colourless solid in 61% yield. Its identity is clearly apparent from NMR spectroscopy with characteristic signals observed for the *C*=N, P=*C*H (confirmed from *J*-modulated ^{13}C NMR spectra) and N–*H* fragments. Unlike previous examples of this type of tautomerisation,[24] structure **9** is believed to be favoured over the C–H acid form as a result of the formation of an intramolecular S–H–N hydrogen bond, affording a six-membered ring system. The stability of this arrangement is demonstrated by the lack of reactivity of **9** towards strong bases {$NaN(SiMe_3)_2$ in C_6D_6 or LDA · tmeda in Et_2O} and to transition metals {$Mo(CO)_4(pip)_2$ (pip = piperidine) or $RhCl(PPh_3)_3$}.

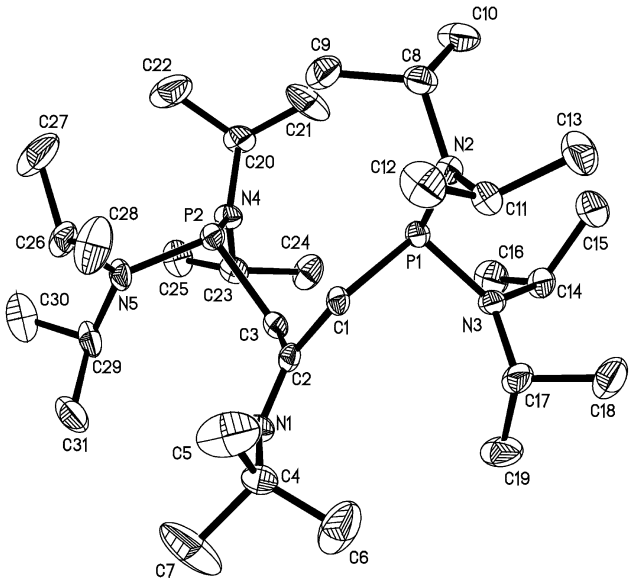
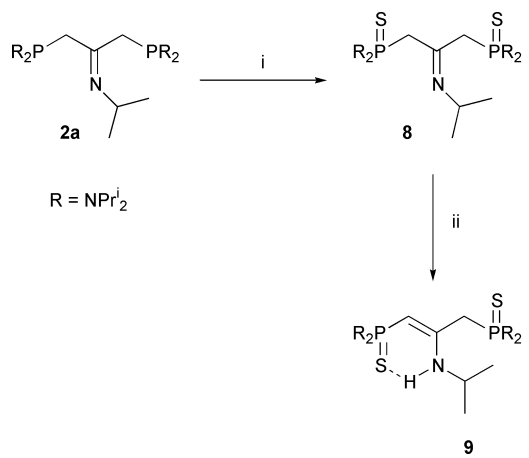


Fig. 1 Molecular structure of compound **2e**. Displacement ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (°): P(1)–N(2) 1.698(4), P(1)–N(3) 1.689(4), P(2)–N(4) 1.699(4), P(2)–N(5) 1.704(4), N(1)–C(2) 1.274(5), C(1)–P(1) 1.871(4), C(1)–C(2) 1.530(6), C(2)–C(3) 1.498(6), and C(3)–P(2) 1.861(5); C(2)–N(1)–C(4) 127.9(4), N(1)–C(2)–C(3) 116.5(4), N(1)–C(2)–C(1) 127.2(4), C(1)–P(1)–N(2) 100.03(19), C(1)–P(1)–N(3) 102.04(19), N(2)–P(1)–N(3) 109.1(2), C(3)–P(2)–N(4) 100.05(19), C(3)–P(2)–N(5) 102.4(2), N(4)–P(2)–N(5) 110.2(2).

Conclusion

It has been shown that sterically encumbered bis(dialkylamino)chlorophosphines exhibit unusual, yet understandable reactivity towards isopropyl-substituted lithium amides undergoing hydride transfer rather than nucleophilic substitution. This observation has led to the synthesis of a family of bulky phosphino-imines **2** in good yields. Compounds **2** make interesting bulky ligands for transition metals. They present both hard imino- and soft phosphino-donor sites making these species potentially 'hemi-labile'. Furthermore, the pres-



Scheme 5 *Reagents and conditions:* i, S_8, CH_2Cl_2, r.t., 1 h; ii, CH_2Cl_2, r.t., 12 h.

‡ These two phosphines were isolated as their sulfides following treatment of the reaction mixture with an excess of sulfur and subsequent separation and purification by flash column chromatography on silica gel using toluene as eluent.

§ The ^{31}P NMR chemical shift for chlorophosphine **1a** exhibits a significant solvent dependency (162.0 MHz, 300 K): δ +133.6 (Et_2O), +135.8 (THF) and +140.0 ($CDCl_3$).

¶ Crystal data for compound **2e**: $C_{31}H_{69}N_5P_2$, M = 573.85, orthorhombic, space group *Pbca*, a = 17.676(6), b = 18.784(8), c = 22.185(11) Å, V = 7366(5) Å^3, Z = 8, μ(Mo-Kα) = 0.143 mm^{-1}, T = 200(2) K; clear colourless plate, Siemens P4 diffractometer, ω scans, 6459 measured, 6032 independent reflections (R_{int} = 0.0304). The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically using full matrix least squares based on F^2 to give $R1$ = 0.0776, $wR2$ = 0.2000 (all data) for 3052 independent observed reflections [$I > 2\sigma(I)$] and 343 parameters. CCDC reference number 156002. See http://www.rsc.org/suppdata/nj/b0/b009867l/ for crystallographic data in CIF or other electronic format.

ence of σ-electron withdrawing and π-electron donating substituents at phosphorus could have significant implications in catalysis.[1g] A study of the coordination chemistry of ligands **2** has been initiated and preliminary results will be reported elsewhere;[25] their coordination geometry should contrast with the many examples of related *ortho*-phenylene-bridged P–N ligands that have been reported.[4]

Experimental

All manipulations were performed under an atmosphere of dry argon or nitrogen. Solvents were distilled from the appropriate drying agent and stored under argon or nitrogen prior to use. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker AC200, WM250, ARX 300 or JEOL 270 spectrometers at ambient probe temperatures. C_6D_6 and $CDCl_3$ were distilled from P_2O_5 and degassed prior to use. ^{1}H and ^{13}C chemical shifts in ppm were referenced using the partially deuteriated solvent as internal reference. ^{31}P downfield shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4; where appropriate a sealed capillary tube containing C_6D_6–PPh_3 or $C_6D_5CD_3$–PPh_3 was placed inside a normal 5 mm NMR tube to provide a deuterium lock and an internal reference. Coupling constants and linewidths are reported in Hertz. Infrared spectra were obtained in a solution cell with KBr windows on either a Perkin-Elmer FT-IR1725X or Mattson Research Series 1 spectrometer, mass spectra on a Ribermag R10 10E, Kratos Concept, or AutospecQ instrument. GC-MS were performed using a Perkin-Elmer Turbomass spectrometer/Perkin-Elmer Autosystem XL gas chromatograph. Satisfactory elemental analyses have been obtained for all isolated products. Melting points are uncorrected.

1a,[26] **1c**,[27] **4**,[28] and **5**[29] were prepared according to literature procedures, or minor modifications thereof. Bu^nLi (1.6 M, hexanes) was obtained from Aldrich. Amines (Aldrich and Lancaster) used in the preparation of the lithium amides were pre-dried over KOH pellets and subsequently stored under nitrogen over activated 4 Å molecular sieves.

Preparations

Lithium amides. These reagents were prepared by treating a solution of the appropriate amine in diethyl ether with a stoichiometric amount of Bu^nLi at −78 °C and used without further purification.

$(Pr^i_2N)_2P(S)Cl$. A Schlenk was charged with compound **1a** (1.0 g, 3.7 mmol) and CH_2Cl_2 (10 cm^3). An excess of sulfur (0.15 g, 4.6 mmol) was added slowly as a solid under a flow of nitrogen. The solution was stirred at r.t. for 48 h. Volatile components were removed under reduced pressure and the product extracted from any unchanged sulfur using pentane (3 × 10 cm^3). Removal of pentane *in vacuo* afforded $(Pr^i_2N)_2P(S)Cl$ as a white solid which was sufficiently pure for further use (0.99 g, 98%). ^{31}P NMR (109.4 MHz, CH_2Cl_2): δ +68.7 (pent., $^{3}J_{PH}$ 22.0 Hz).

$(Pr^i_2N)_2PCH_2C(=NPr^i)CH_2P(NPr^i_2)_2$ 2a. A suspension of compound **1a** (10 g, 37.0 mmol) in ether (20 cm^3) was added to a cold (0 °C) solution of LDA (prepared as above). The mixture was allowed to warm to room temperature, where it became progressively pale yellow and the formation of a white precipitate occurred. Subsequently, the reaction was stirred for 12 h at room temperature. Removal of volatiles *in vacuo* afforded an orange solid. Extraction with pentane (3 × 20 cm^3) afforded a clear pale yellow solution. Concentration and recrystallisation from the pentane solution at −30 °C afforded colourless crystals of **2a** (5.52 g, 80%), mp 130–132 °C (Found: C, 62.1; H, 12.5; N, 12.1. $C_{30}H_{67}N_5P_2$ requires C, 64.3; H, 12.1; N, 12.5%); ^{1}H NMR (270.0 MHz; C_6D_6) δ 3.98 (1 H, sept., $^{3}J_{HH}$ 6.0, $CNC\mathit{H}(CH_3)_2$), 3.35 (8 H, sept. d, $^{3}J_{HH}$ 7.0, $^{3}J_{PH}$ 12.0, PNCH), 3.10 (2 H, s, CH_2), 3.08 (2 H, s, CH_2), 1.37 (6 H, d, $^{3}J_{HH}$ 6.0, $C{=}NCH(C\mathit{H}_3)_2$), 1.26 (24 H, dd, $^{3}J_{HH}$ 7.0, $^{4}J_{PH}$ 12.0, $PNCH(C\mathit{H}_3)_2$) and 1.19 (24 H, d, $^{3}J_{HH}$ 7.0 Hz, $PNCH(C\mathit{H}_3)_2$); ^{13}C NMR (62.9 MHz; $CDCl_3$) δ 166.0 (dd, $^{2}J_{PC}$ 15.0 and 9.5, C=N), 50.2 (s, C=N*C*H), 46.6 (d, $^{2}J_{PC}$ 11.0, PNCH), 46.5 (d, $^{2}J_{PC}$ 11.0, PNCH), 44.4 (dd, $^{1}J_{PC}$ 12.0, $^{3}J_{PC}$ 6.0, CH_2), 33.7 (dd, $^{1}J_{PC}$ 19.0, $^{3}J_{PC}$ 8.0, CH_2), 24.3 (br d, $^{3}J_{PC}$ 6.0, $PNCH(\mathit{C}H_3)_2$), 24.0 (br d, $^{3}J_{PC}$ 6.0, $PNCH(\mathit{C}H_3)_2$), 23.7 (d, $^{3}J_{PC}$ 7.0 Hz, $PNCH(\mathit{C}H_3)_2$) and 23.6 (s, $C{=}N\mathit{C}HMe_2$); *m*/z (EI) 245 (9.3%, $[Pr^i_2N]_2PCH_2$).

From imine ***4***. Bu^nLi (23.0 cm^3, 1.6 M, 36.6 mmol) was added dropwise to a cooled (−78 °C) solution of imine **4** (2.05 g 18.3 mmol) and tmeda (5.6 cm^3, 37.0 mmol) in hexane (20 cm^3) and subsequently stirred at this temperature for 40 min. A suspension of compound **1a** (9.76 g, 36.6 mmol) in hexane (50 cm^3) was then added dropwise at −78 °C over a period of 5 min. The mixture was stirred at room temperature overnight, the volatiles were removed under reduced pressure and the product was extracted with hexane (3 × 10 cm^3). Prolonged cooling of a concentrated pentane solution (−30 °C) afforded **2a** as a colourless solid (3.0 g, 30%).

From compound ***5***. An ether solution (10 cm^3) of compound **5** (0.25 g, 0.66 mmol) was treated with a solution of LDA (0.66 mmol) in ether (10 cm^3) at 0 °C, allowed to warm to room temperature and stirred overnight. Subsequent removal of solvent *in vacuo* and extraction of the product with hexane (3 × 2 cm^3) followed by removal of solvent afforded **2a** as a white solid (0.09 g, 73% yield).

$(Cy_2N)_2PCH_2C(=NPr^i)CH_2P(NCy_2)_2$ (2b). An analogous procedure to that used for the preparation of compound **2a** was employed using **1b** (0.5 g, 1.17 mmol) suspended in ether (30 cm^3) and LDA (1.17 mmol) in ether (10 cm^3). After extraction and removal of volatile components *in vacuo*, diphosphine-imine **2b** was isolated as an off-white solid after washing with CH_3CN (3 × 10 cm^3) (0.26 g, 75%), mp 185–188 °C (Found: C, 73.1; H, 11.0; N, 7.9. $C_{54}H_{99}N_5P_2$ requires C, 74.0; H, 11.4; N, 8.0%); *m*/z (FAB+) 877 ($[M - H]^+$).

Reaction of $(Pr^i_2N)(Cy_2N)PCl$ 1c with LDA. A similar experimental procedure to that used for the preparation of compound **2a** was employed, using $(Pr^i_2N)(Cy_2N)PCl$ **1c** (5.91 g, 17.04 mmol) in ether (20 cm^3) and LDA (17.04 mmol) in ether (50 cm^3) at 0 °C. After stirring overnight at r.t. the solvent was removed *in vacuo* and the product extracted off the inorganic salts using pentane (3 × 20 cm^3). On removal of the solvent under reduced pressure an intractable mixture of diastereomeric products (**2c**) was isolated as a waxy orange solid. Direct attempts at purification *via* column chromatography (silica) or thiolation with S_8 followed by chromatography (silica) led to decomposition, while recrystallisation from a variety of solvents was unsuccessful.

$(Pr^i_2N)_2PCH_2C(=NCy)CH_2P(NPr^i)_2$ 2d. An identical experimental procedure to that used for the preparation of compound **2a** was employed. A suspension of **1a** (2.0 g, 7.5 mmol) in ether (30 cm^3) was added to a cold (0 °C) solution of $LiN(Pr^i)(Cy)$ [prepared as above using Bu^nLi (1.6 M, 7.5 mmol, 4.7 cm^3) and $HN(Pr^i)(Cy)$ (7.5 mmol, 1.2 cm^3)]. After stirring at r.t. for 12 h, removal of all volatile components under vacuum followed by extraction with hexane (20 cm^3) and its subsequent removal *in vacuo* gave a viscous yellow oil. Washing the oil with CH_3CN (3 × 10 cm^3) followed by drying *in vacuo* afforded **2d** as a white solid (3.2 g, 70%), mp 114–118 °C (Found: C, 65.0; H, 12.1; N, 11.2. $C_{33}H_{71}N_5P_2$ requires C, 66.1; H, 11.9; N, 11.7%); ^{1}H NMR (250.1 MHz; $CDCl_3$) δ 3.41 (9 H, m, C=NCH and PNCH), 2.92 (2 H, s,

PCH_2), 1.74 (2 H, br s, PCH_2), 1.45–1.08 (58 H, m, CH_2 and CH_3); ^{13}C NMR (62.9 MHz; $CDCl_3$) δ 166.4 (dd, $^2J_{PC}$ 15.0 and 9.0, C=N), 59.8 (d, $^4J_{PC}$ 4.0, C=NCH), 47.0 (d, $^2J_{PC}$ 11.0, PN*C*H), 46. 8 (d, $^2J_{PC}$ 11.0, PNCH), 45.0 (dd, $^1J_{PC}$ 12.0, $^3J_{PC}$ 5.0, CH_2), 34.5 (s, CH_2), 34.3 (dd, $^1J_{PC}$ 20.0, $^3J_{PC}$ 8.0, CH_2), 26.1 (s, CH_2), 25.5 (s, CH_2), 24.7 (pseudo t, $^3J_{PC}$ 7.0, PNCH(CH_3)$_2$), 24.4 (d, $^3J_{PC}$ 7.0, PNCH(CH_3)$_2$) and 24.1 (d, $^3J_{PC}$ 7.0 Hz, PNCH(CH_3)$_2$).

$(Pr^i_2N)_2PCH_2C(=NBu^t)CH_2P(NPr^i)_2$ 2e. An identical experimental procedure to that used for the preparation of compound **2a** was employed. A suspension of **1a** (2 g, 7.5 mmol) in ether (10 cm^3) was added to a cold (0 °C) solution of $LiN(Pr^i)(Bu^t)$ [prepared as above using Bu^nLi (1.6 M, 7.5 mmol, 4.7 cm^3) and $HN(Pr^i)(Bu^t)$ (7.5 mmol, 1.2 cm^3)]. Recrystallisation from pentane at −30 °C afforded a first batch of colourless crystals of **2e** (1.0 g); subsequent concentration and cooling to −30 °C gave a further 0.2 g (total yield 1.2 g, 83%), mp 142–144 °C (Found: C, 64.8; H, 12.0; N, 12.1. $C_{31}H_{69}N_5P_2$ requires C, 65.0; H, 12.2; N, 12.2%); ^1H NMR (270.0 MHz; C_6D_6) δ 3.36 (8 H, m, PNCH), 3.14 (2 H, s, CH_2), 3.07 (2 H, s, CH_2), 1.54 (9 H, s, CNC(CH_3)$_3$), 1.27 (24 H, dd, $^3J_{HH}$ 7.0, $^3J_{PH}$ 17.0, PCH(CH_3)$_2$) and 1.21 (24 H, dd, $^3J_{HH}$ 7.0, $^4J_{PH}$ 3.2 Hz, PNCH(CH_3)$_2$); ^{13}C NMR (100.6 MHz; C_6D_6) δ 163.1 (dd, $^2J_{PC}$ 17.0 and 10.0, C=N), 55.6 (s, C=NC), 47.1 (m, PNCH), 45.9 (dd, $^1J_{PC}$ 14.0, $^3J_{PC}$ 6.0, CH_2), 37.5 (dd, $^1J_{PC}$ 21.0, $^3J_{PC}$ 4.5, CH_2), 31.7 (s, C(CH_3)$_3$), 24.8 (d, $^3J_{PC}$ 8.0, PNCH(CH_3)$_2$), 24.8 (d, $^3J_{PC}$ 8.0, PNCH(CH_3)$_2$), 24.6 (d, $^3J_{PC}$ 6.0, PNCH(CH_3)$_2$) and 24.0 (d, $^3J_{PC}$ 6.0 Hz, PNCH(CH_3)$_2$); *m*/z (EI) 573 (M^+).

Reaction of Ph_2PCl with LDA. To a cold (0 °C) ether solution (20 cm^3) of LDA (5.6 mmol) was added a cold ether solution (10 cm^3) of Ph_2PCl (1.0 cm^3, 5.6 mmol). The mixture was allowed to warm to room temperature and stirred overnight. Volatiles were removed *in vacuo* and the mixture extracted with pentane (3 × 10 cm^3) that was subsequently removed under reduced pressure. Ether (10 cm^3) and an excess of sulfur (0.25 g) were added before stirring overnight. Volatiles were removed *in vacuo* and the mixture was separated by column chromatography on silica gel using toluene as eluent to afford $Ph_2P(S)NPr^i_2$ (R_f 0.5; 0.88 g, 52%) and $Ph_2P(S)=P(S)Ph_2$ (R_f 0.3; 0.61 g, 25%).

Reaction of $(Pr^i_2N)_2PCl$ with $LiN(Me)(Pr^i)$. A suspension of compound **1a** (2.0 g, 7.5 mmol) in ether (10 cm^3) was added to an ether solution (10 cm^3) of $LiN(Me)(Pr^i)$ (7.5 mmol) at 0 °C. After stirring at room temperature overnight a ^{31}P NMR spectrum of the mixture showed a single resonance corresponding to $(Pr^i_2N)_2PH$ (^{31}P: δ +42.1{$^1J_{PH}$ 254.0 Hz}). All volatile components were isolated by vacuum distillation and subjected to analysis by GC-MS. *m*/z (EI) 71 (M^+) and 132 ($M^+ - NPr^i_2$).

$(Pr^i_2N)_2PCH_2C(=NC_6H_3Pr^i_2\text{-}2,6)CH_3$ 7. A solution of Bu^nLi (2.4 mmol) was added dropwise from a syringe to a cold (−78 °C) solution of $Me_2C=N(C_6H_3Pr^i_2\text{-}2,6)$ (2.4 mmol, 0.52 g) and tmeda (2.5 mmol, 0.4 cm^3) in hexane (10 cm^3) to afford a clear solution and a bright yellow precipitate which was stirred at r.t. for 16 h. A solution of compound **1a** (2.4 mmol, 0.64 g) in hexane was then added slowly at 0 °C. On warming to r.t. the mixture was heated to reflux for 3 h. The resulting clear yellow solution was isolated by filtration. The white solid was washed with hexane (3 × 5 cm^3) and the washings were combined. A dark yellow viscous oil was obtained on removing all volatiles *in vacuo*. Recrystallisation from the minimum of hot acetonitrile afforded colourless crystals of **7** (0.49 g); subsequent concentration and cooling to −30 °C afforded a further 0.4 g, a total yield of 0.89 g, 83% (Found: C, 72.0; H, 11.0; N, 9.8. $C_{27}H_{50}N_3P$ requires C, 72.4; H, 11.3; N, 9.4%); ν_{max} (KBr, CH_2Cl_2)/cm^{-1} 1635 (C=N); ^1H NMR (301.5 MHz, $CDCl_3$) δ 7.00 (3H, m, C_6H_3), 3.46 (4 H, d. sept., $^3J_{HH}$ 7.0, $^3J_{PH}$ 11.0, PNCH), 2.99 (2 H, s, PCH_2), 2.79 (2 H, sept., $^3J_{HH}$ 7.0, CCHMe_2), 1.75 (3 H, s, CH_3), 1.14 (24 H, dd, $^3J_{PH}$ 7.0, $^4J_{PH}$ 17.0, PNCH(CH_3)$_2$) and 1.04 (12 H, d, $^3J_{HH}$ 7.0 Hz, CCHMe_2); ^{13}C NMR (75.8 MHz, $CDCl_3$) δ 171.0 (s, C=N), 146.9 (s, C_{ipso} of C_6H_3), 137.2 (s, *o*-C of C_6H_3), 123.3 (s, *p*-C of C_6H_3), 123.3 (s, *m*-C of C_6H_3), 47.6 (d, $^2J_{PC}$ 11.0, PNCH), 45.6 (d, $^1J_{PC}$ 15.5, CH_2), 28.0 (s, C*C*HMe$_2$), 24.5 (d, $^3J_{PC}$ 7.0, PNCMe_2), 24.2 (s, CCHMe_2), 23.8 (s, CCHMe_2) and 21.9 (d, $^3J_{PC}$ 10.0 Hz, CH_3); ^{31}P NMR (122.1 MHz): δ +47.5 (s).

1,3-Bis[bis(diisopropylamino)thiophosphoryl]-2-isopropyliminopropane 8. To a solution of compound **2a** (0.10 g, 0.18 mmol) in $CDCl_3$ (0.5 cm^3) was added an excess of sulfur (13.0 mg, 0.40 mmol). The solution was monitored by ^{31}P NMR spectroscopy until complete conversion into **8** had occurred. ν_{max} (KBr, $CDCl_3$)/cm^{-1} 1620; ^1H NMR (301.5 MHz, $CDCl_3$) δ 3.90 (13H, m, PNCH and CNCH(CH_3)$_2$), 3.73 (2H, s, CH_2), 3.68 (2H, s, CH_2), 1.41 (12H, d, $^3J_{HH}$ 7.0, PNCH(CH_3)$_2$), 1.40 (12H, d, $^3J_{HH}$ 7.0, PNCH(CH_3)$_2$) and 1.14 (6H, d, $^3J_{HH}$ 6.0 Hz, CNCH(CH_3)$_2$); ^{13}C NMR (50.3 MHz; $CDCl_3$) δ 156.5 (pseudo triplet, $^2J_{PC}$ 7.0), 51.2 (br t, $^4J_{PC}$ 2.0, C=NCH), 46.8 (d, $^2J_{PC}$ 5.0, PNCH), 46.2 (d, $^2J_{PC}$ 5.0, PNCH), 45.2 (d, $^1J_{PC}$ 79.0, CH_2), 41.3 (d, $^1J_{PC}$ 79.0, CH_2), 24.0 (d, $^3J_{PC}$ 2.5, PNCH(CH_3)$_2$), 23.6 (d, $^3J_{PC}$ 5.0, PNCH(CH_3)$_2$) and 23.3 (d, $^3J_{PC}$ 3.0 Hz, PNCH(CH_3)$_2$); ^{31}P NMR (81.0 MHz; $CDCl_3$) δ +70.9 ($^4J_{PP}$ 10.0, $^3J_{PH}$ 16.0) and +72.6 ($^4J_{PP}$ 10.0, $^3J_{PH}$ 16.0 Hz).

Hydrogen-bonded thio tautomer 9. An excess of elemental sulfur (0.03 g, 0.94 mmol) was added directly to a stirred dichloromethane solution (10 cm^3) of compound **2a** (0.20 g, 0.36 mmol) at room temperature. The solution became yellow almost immediately and gradually turned red upon stirring for approximately 12 h. After 24 h at room temperature the mixture was filtered to remove unchanged sulfur, concentrated and placed at −30 °C. Pale yellow cubic crystals of **9** (0.14 g, 61%) were isolated after prolonged cooling, mp 132–134 °C (Found: C, 56.9; H, 8.9; N, 11.0. $C_{30}H_{67}N_5P_2S_2$ requires C, 57.8; H, 10.9; N, 11.2%); ν_{max} (KBr, $CDCl_3$ solution)/cm^{-1} 3264mbr, 2475w, 1610wsh, 1584m and 1538m; ^1H NMR (270 MHz; C_6D_6) δ 8.21 (1 H, br t, $^4J_{PH}$ 6.0, NH), 4.35 (2 H, br d, $^2J_{PH}$ 17.0, PCH_2), 4.18 (1 H, dd, $^2J_{PH}$ 7.0, $^4J_{PH}$ 2.5, PCH), 3.93 (8 H, m, PNCH), 3.39 (1 H, sept., $^3J_{HH}$ 6.0, CNC*H*(CH_3)$_2$), 1.45 (24 H, d, $^3J_{HH}$ 7.0, PNCH(CH_3)$_2$), 1.39 (24 H, d, $^3J_{HH}$ 7.0, PNCH(CH_3)$_2$) and 1.13 (6 H, d, $^3J_{HH}$ 6.0 Hz, CNCH(CH_3)$_2$); ^{13}C NMR (67.9 MHz; C_6D_6) δ 152.2 (dd, $^2J_{PC}$ 18.0, 7.0, CN), 83.1 (dd, $^1J_{PC}$ 152.0, $^3J_{PC}$ 8.0, PCH), 47.9 (d, $^2J_{PC}$ 5.0, P(S)NCH), 46.3 (d, $^2J_{PC}$ 6.0, P(S)NCH), 43.8 (s, C=N*C*H), 37.2 (dd, $^1J_{PC}$ 85.0, $^3J_{PC}$ 4.0, PCH_2), 24.1 (d, $^3J_{PC}$ 5.0, PNCH(CH_3)$_2$), 24.0 (d, $^3J_{PC}$ 6.0, PNCH(CH_3)$_2$), 23.9 (d, $^3J_{PC}$ 2.0, PNCH(CH_3)$_2$), 23.5 (d, $^3J_{PC}$ 3.0 Hz, PNCH(CH_3)$_2$) and 22.0 (s, CN*C*H$_3$); ^{31}P NMR (81.0 MHz; $CDCl_3$) δ +66.7 (s) and +66.6 (s); *m*/z (EI) 623 (M^+), 523 ($M - N\{Pr^i_2\}_2$) and 262 ([{Pr^i_2N}$_2$P=S]$^+$).

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