Scope and Limitations of the Preparation of Aminophosphines R-NH($CH_2CH_2PPh_2$) and Aminodiphosphines R-N($CH_2CH_2PPh_2$)$_2$ via Michael Addition of Amines to Vinylphosphines

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This paper is dedicated to Professor Bernard L. Shaw (University of Leeds) on the occasion of his Retirement.

Abstract: The addition of a range of amines to vinyldiphenylphosphine oxide was examined under different reaction conditions. The methodology provides mixed phosphorus-nitrogen donor ligands R-NH($CH_2CH_2PPh_2$) **3** and R-N($CH_2CH_2PPh_2$)$_2$ **4**, which could be prepared in high yields and purity in two simple steps. Labelling study revealed a non-concerted mechanism and the X-ray crystal structure of **1e** is reported.

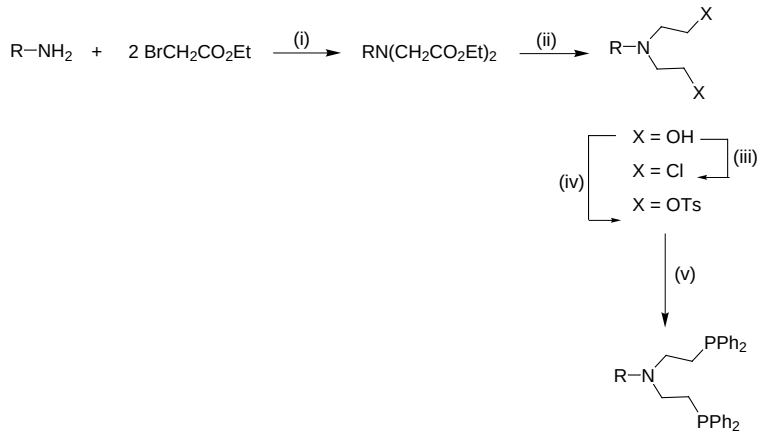
Key words: Michael additions, aminations, ligands, phosphorus, nucleophilic additions

In a previous paper,[1] we reported the coordination behaviour of phosphorus-nitrogen-phosphorus donor ligands R-N($CH_2CH_2PPh_2$)$_2$ to palladium, including the ability of these ligands to adopt various coordination modes depending on the nature of the nitrogen substituents, as well as the oxidation state of the metal centre. Conventional methods of synthesis of these ligands[1,2] involve three or four synthetic steps, giving overall yields of around 27–54% (Scheme 1). As part of the effort to generate analogous ligands for fast screening of catalysts, we sought an efficient synthetic methodology that will allow preparation of this class of ligands in high yields with simple synthetic steps.

The Michael addition of amines to a vinylphosphorus moiety (Scheme 2) is very attractive as it reduces the number of synthetic steps and produces no side products. Yet, there is no systematic study on these reactions. The few literature examples involving secondary amines[3] (R_2NH) reported these reactions to proceed in low to moderate yields and there were hardly any examples of double addition.[4] In this paper, we report the optimised reaction conditions under which alkylaminophosphines **3** and **4** could be generated in high yields (75–90%) in two steps and the scope and limitations of these reactions.

Reaction between vinyldiphenylphosphine and amines. No reaction was observed when vinyldiphenylphosphine was heated in neat 10 molar equivalents of *n*-butylamine; the ^{31}P NMR spectrum of the reaction mixture showed only the presence of the starting phosphine even after heating for 48 hours.

Although certain reactions were reported to be catalysed by strong bases,[3,4] our effects using sodium acetate and butyllithium failed to induce any clean reaction between vinyldiphenylphosphine and *n*-butylamine in the presence or absence of solvents. As the related Michael addition of P-H bonds to double bonds is known to proceed via a radical mechanism,[5] a reaction mixture of the amine and vinylphosphine was irradiated or heated with 2,2′-azobisisobutyronitrile (AIBN) in toluene for 48 hours. Again, no reaction was observed under these conditions.



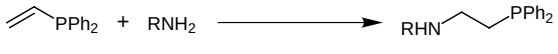
Preparation of aminodiphosphine ligands; Reagents and conditions: (i) Na_2CO_3, EtOH, reflux; (ii) $LiAlH_4$; (iii) $SOCl_2$; (iv) TsCl, pyridine; (v) $KPPh_2$

Scheme 1

Table 1 Reaction Time and Isolated Yield for Aminophosphine Oxides **1**

Entry	Amine	Product	Method A[a] Reaction Time/h (% Yield)	Method B[b] Reaction Time/min (% Yield)
1	*n*-Propylamine	**1a**	2 (82)	40 (92)
2	*i*-Propylamine	**1b**	24 (85)	60 (92)
3	*n*-Butylamine	**1c**	1 (85)	10 (94)
4	*sec*-Butylamine	**1d**	24 (75)	80 (94)
5	*tert*-Butylamine	**1e**	79 (77)	300 (90)
6	Benzylamine	**1f**	24 (76)	60 (90)

[a] In 10 molar excess of neat amine.
[b] In the presence of MeOH.



Scheme 2

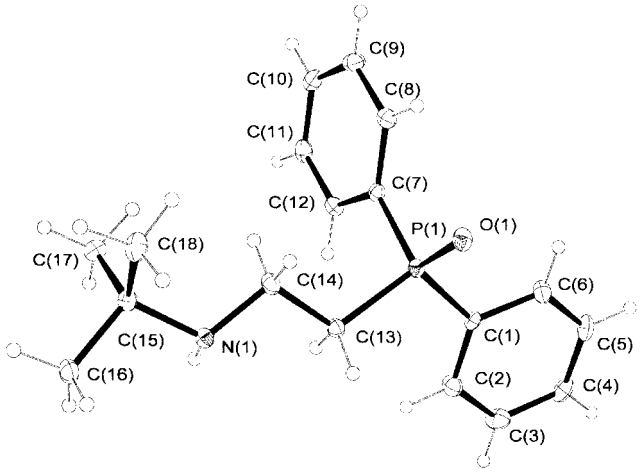
Synthesis of alkylaminophosphine oxides (Scheme 3). There have been numerous reports of the single addition of amines to vinyldiphenyphosphine oxide under various reaction conditions.[6–10] By introducing a pentavalent phosphorus atom, we do indeed find a range of primary alkyl amines to undergo addition with vinyldiphenylphosphine oxide to give the aminophosphine oxides **1**, in good to excellent yields (Table 1).

As might be expected, increasing steric demand of the substituent (entries 1, 2, and 3–5) on the amine leads to slower reactions. In contrast, substituted anilines do not undergo any reaction at all under these conditions.

Effect of using a protic solvent. The rates of reactions are dramatically accelerated by the presence of methanol, in some cases from days to a matter of hours (Table 1). This leads us to postulate that the reaction must involve a charged intermediate, which presumably is stabilised (Scheme 4).

In deuterated methanol[d_4], the addition of *n*-butylamine proceeded with 100% isotope incorporation at the α-position, whereas the corresponding reaction employing *tert*-butylamine leads only to 60% incorporation (Scheme 4). This suggests that the reaction is not concerted under these conditions, the protonation step being accelerated in the presence of a proton source. The difference in the amount of deuterium incorporation is interesting, although it is not entirely clear why it should be so.

Crystals of $^{t}BuNHCH_2CH_2P(O)Ph_2$ **1e** were obtained by slow recrystallisation from dichloromethane/petroleum ether. The ORTEP drawing of the X-ray crystal structure is shown in the Figure. It is interesting to note that the C-N-C-C-P bonds are virtually planar in this molecule. Intermolecular hydrogen N-H---O bonding is also observed in the solid-state structure (unit cell structure, bond distances and angles are given as Supplementary data).

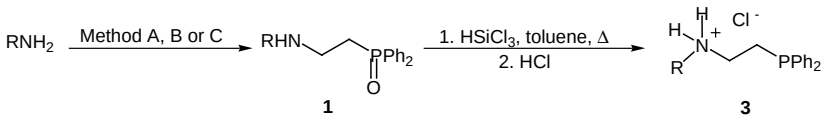


Figure

Synthesis of aminodiphosphine oxides (2a-d). These were prepared with the amine and vinyldiphenylphosphine oxides in a 1:2 ratio. The results are summarised in Table 2. Two methods were evaluated: (i) the reaction in the presence of methanol (Method C), or (ii) in the presence of the corresponding amine hydrochloride salt $RNH_3^+Cl^-$ (Method D).

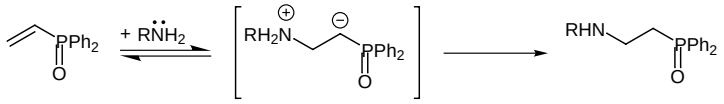
There were limitations to the double addition reactions. The second addition to vinyldiphenylphosphine oxide is slower. Branched amines are reluctant to undergo a second addition, probably due to unfavourable steric hindrance.

An example of the addition of octylamine to vinyldiphenylphosphine oxide in the presence of the alkylamine hydrochloride salt has been reported.[6a] When we repeated the procedure with the linear amines (Method D), we found that high reaction temperatures[11] are necessary. As a result, the yields decrease dramatically with increased volatility of the amine. Reactions are generally faster in the presence of the amine chloride salt. This is presumably due to a concentrated reaction mixture and the presence of



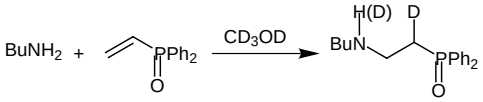
R = ^{n}Pr (**a**); ^{i}Pr (**b**); ^{n}Bu (**c**); ^{s}Bu (**d**); ^{t}Bu (**e**); benzyl (**f**)

Scheme 3



Scheme 4

an acidic proton. On the other hand, the reaction in methanol gives higher yields, because the reactions tend to be much cleaner and isolation of the product is much easier. Interestingly, the addition of benzylamine does not work in the presence of the amine hydrochloride salt.



Scheme 5

Reduction of the aminophosphines. This could be carried out simply by using standard reduction procedure of utilising trichlorosilane and base in refluxing toluene. Aminodiphosphines **4** were isolated as white solids and the aminophosphines **3** as their hydrochloride salts in good to excellent yields (82−96%).

Scope and limitations of different procedures for the hydroamination of vinyldiphenylphosphine oxides were evaluated. Alkylaminophosphines (**2a**−**2f**) and aminodiphosphines (**4a**−**d**) could be easily prepared in two simple synthetic steps in good yields. The catalytic activity of these and other related ligands are currently under investigation and will be reported elsewhere.[12]

All reactions involving air-sensitive phosphorous (III) ligands were carried out under N_2/Ar atm using standard Schlenk line techniques. Mps were determined on Electrothermal Gallenhamp melting point apparatus and are uncorrected. Infra- red spectra were recorded on a Perkin-Elmer Paragon 1000 FTIR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded using Bruker AM360 or AMX400 spectrometer in $CDCl_3$, unless otherwise stated, referenced to TMS (δ = 0 ppm). The chemical shifts (δ) are in parts per million (ppm). The coupling constants (*J*) are in Hertz (Hz). The following abbreviations are used: s (singlet), t (triplet), q (quartet), m (multiplet), d (doublet), br (broad). ^{31} P NMR spectra were referenced to H_3PO_4. Mass spectra (MS) and high resolution mass spectra (HRMS) were recorded using FAB technique by the Mass Spectrometry Service within The University of London's Intercollegiate Research Services (ULIRS). Mass data are reported in mass units (*m/z*), and values in brackets show the relative intensity from the base peak (as 100%). Commercially available reagents were purchased from Avocado, Lancaster or Aldrich chemical companies. Vinyldiphenylphosphine[13] and vinyldiphenylphosphine oxide[14] were prepared according to published procedures.

X-ray Structural Analysis of 1e

Single colourless crystals were obtained by recrystallisation from CH_2Cl_2/petroleum ether (40−60) at r.t. Data were collected in wide-slicing mode using a Nonius Kappa CCD diffractometer, with a detector to crystal distance of 30 mm. Crystal data and details of data collection and refinement are given as supplementary material.

Aminophosphine oxides 1a−1f; General Procedure

Method A: Vinyldiphenylphosphine oxide (0.5 g) was added to a solution of excess *n*-butylamine (10 equiv) and heated at 80 °C in a sealed tube. After the reaction was complete (^{31}P NMR) the excess amine was removed under reduced pressure and the resultant solid was recrystallised from methyl cyclohexane to give the product as a white crystalline solid.

Method B: The appropriate amine (5.5 molar excess) was added to vinyldiphenylphosphine oxide (0.5g, 2.2 mmol) in MeOH (1 mL) and heated at 65 °C in a sealed tube. After the appropriate reaction time (^{31}P NMR) the excess amine was removed under reduced pressure. The resultant solid was filtered off and washed with (3 × 10 mL) petroleum ether (40−60 °C).

[2-(Diphenylphosphine oxide)ethyl]-*n*-propylamine (1a)

Mp: 59−61 °C.

IR (KBr disc): ν = 1179 (P=O), 3291 (N-H) cm^{-1}.

^{1}H NMR (400 MHz; $CDCl_3$): δ = 0.79 (t, 3H, *J* = 7 Hz, *CH*$_3$), 1.36 (m, 3H, CH_3CH_2 and *NH*), 2.44 (m, 4H, CH_2CH_2P and CH_3CH_2N), 2.87 (m, 2H, CH_2P), 7.38−7.70 (m, 10H, *Ph*).

^{31}P NMR (145.7 MHz; $CDCl_3$): δ = +31.9.

^{13}C NMR (90.5 MHz; $CDCl_3$): δ = 11.7 (s, *CH*$_3$), 23.1 (s, CH_3CH_2), 30.4 (d, $^1J_{PC}$ = 71 Hz, CH_2P), 42.9 (s, CH_2CH_2P), 51.6 (s, CH_2N), 128.7 (d, $^3J_{PC}$ = 12 Hz, C_{meta}), 130.7 (d, $^2J_{PC}$ = 9.5 Hz, C_{ortho}), 131.8 (s, C_{para}), 133.0 (d, $^1J_{PC}$ = 98.5 Hz, C_{ipso}).

MS: *m/z* (%) = 288 (100, M$^+$+1), 217 (32, M−PrNHCH$_2$).

HRMS: calcd for $C_{17}H_{22}NOP$ (M$^+$+1) 288.1517. Found: 288.1496.

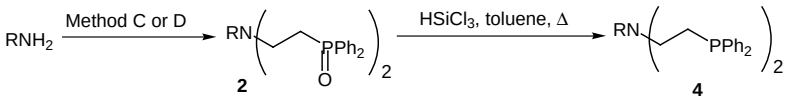
[2-(Diphenylphosphine oxide)ethyl]-*iso*-propylamine (1b)

Mp: 81−83 °C.

IR (KBr disc): ν = 1175 (P=O), 3280 (N-H) cm^{-1}.

^{1}H NMR (400 MHz; $CDCl_3$): δ = 0.91 (d, 6H, *J* = 6 Hz, CH*Me*$_2$), 1.49 (br s, 1H, *NH*), 2.39−2.45 (m, 2H, CH_2P), 2.67 (m, 1H, *CH*Me$_2$), 2.87 (m, 2H, CH_2CH_2P), 7.39−7.69 (m, 10H, *Ph*).

^{31}P NMR (145.7 MHz; $CDCl_3$): δ = +31.9.



R = ^{n}Pr (**a**); ^{n}Bu (**b**); ^{n}Heptyl (**c**); benzyl (**d**)

Scheme 6

Table 2 Preparation of Aminodiphosphine Oxides **2**

Entry	Amine	Product	Method C[a] Reaction Time/h (% Yield)	Method D[b] Reaction Time/h (% Yield)
1	*n*-Propylamine	**2a**	24 (90)	4 (45)
2	*n*-Butylamine	**2b**	10 (91)	4 (65)
3	*n*-heptylamine	**2c**	8 (92)	4 (75)
4	benzylamine	**2d**	144 (90)	–

[a] In the presence of MeOH.
[b] With ammonium salt.

^{13}C NMR (90.5 MHz; $CDCl_3$): δ = 19.5 (s, CH*Me*$_2$), 26.7 (d, $^1J_{PC}$ = 69.5 Hz, *CH*$_2$P), 39.6 (s, *CH*$_2$CH$_2$P), 50.5 (s, *CH*Me$_2$), 129.1 (d, $^3J_{PC}$ = 11 Hz, C_{meta}), 130.8 (d, $^2J_{PC}$ = 10 Hz, C_{ortho}), 133.5 (d, $^1J_{PC}$ = 101.5 Hz, C_{ipso}), 132.6 (s, C_{para}).

Anal. calcd for $C_{17}H_{22}NOP$: C, 71.05; H, 7.7; N, 4.85. Found: C, 70.85; H, 7.8; N, 4.80.

[2-(Diphenylphosphine oxide)ethyl]-*n*-butylamine (1c)
Mp: 56−58 °C (Lit.[15] 64−65 °C).

IR (KBr disc): ν = 1179 (P=O), 3291 (N-H) cm^{-1}.

^{1}H NMR (400 MHz; $CDCl_3$): δ = 0.80 (t, 3H, *J* = 7 Hz, *CH*$_3$), 1.22 (m, 2H, CH$_3$*CH*$_2$), 1.35 (m, 2H, CH$_3$CH$_2$*CH*$_2$), 1.55 (br. s, 1H, *NH*), 2.44 (m, 4H, *CH*$_2$P and *CH*$_2$N), 2.89 (m, 2H, *CH*$_2$CH$_2$P), 7.37−7.7 (m, 10H, *Ph*).

^{31}P NMR (145.7 MHz; $CDCl_3$): δ = +31.9.

^{13}C NMR (90.5 MHz; $CDCl_3$): δ = 13.9 (s, *CH*$_3$), 20.4 (s, CH$_3$*CH*$_2$), 30.4 (d, $^1J_{PC}$ = 71 Hz, *CH*$_2$P), 32.1 (s, CH$_3$CH$_2$*CH*$_2$), 42.9 (s, *CH*$_2$CH$_2$PPh$_2$), 49.4 (s, *CH*$_2$N), 128.7 (d, $^3J_{PC}$ = 11.5 Hz, C_{meta}), 130.7 (d, $^2J_{PC}$ = 9.5 Hz, C_{ortho}), 131.9 (s, C_{para}), 133.0 (d, $^1J_{PC}$ = 98.5 Hz, C_{ipso}).

MS: *m/z* (%) = 302 (100, M$^+$+1), 217 (35, M$^+$+1−BuNCH$_2$).

HRMS: calcd for $C_{18}H_{24}NOP$ (M$^+$+1) 302.1674. Found: 302.168.

[2-(Diphenylphosphine oxide)ethyl]-*sec*-butylamine (1d)
Mp: 62−64 °C.

IR (KBr disc): ν = 1180 (P=O), 3288 (N-H) cm^{-1}.

^{1}H NMR (400 MHz; $CDCl_3$): δ = 0.75 (t, 3H, *J* = 7 Hz, *CH*$_3$CH$_2$), 0.87 (d, 3H, *J* = 7 Hz, *CH*$_3$CH), 1.29 (dm, 2H, CH$_3$*CH*$_2$), 1.38 (br s, 1H, *NH*), 2.39 (m, 3H, *CH*$_2$P and *CH*N), 2.85 (m, 2H, *CH*$_2$CH$_2$P), 7.37−7.69 (m, 10H, *Ph*).

^{31}P NMR (145.7 MHz; $CDCl_3$): δ = +31.9.

^{13}C NMR (90.5 M Hz; $CDCl_3$): δ = 10.1 (s, *CH*$_3$CH$_2$), 19.6 (s, *CH*$_3$CH), 29.4 (s, CH$_3$*CH*$_2$), 29.8 (d, $^1J_{PC}$ = 71 Hz, *CH*$_2$P), 40.2 (d, $^2J_{PC}$ = 2 Hz, *CH*$_2$CH$_2$P), 54.3 (s, *CH*N), 128.0 (d, $^3J_{PC}$ = 11.5 Hz, C_{meta}), 130.0 (d, $^2J_{PC}$ = 11.0 Hz, C_{ortho}), 131.0 (s, C_{para}), 133.1 (d, $^1J_{PC}$ = 90 Hz, C_{ipso}).

Anal. calcd for $C_{18}H_{24}NOP$: C, 71.75; H, 8.0; N, 4.65. Found: C, 71.25; H, 7.9; N, 4.50.

[2-(Diphenylphosphino oxide)ethyl]-*tert*-butylamine (1e)
Mp: 115−119 °C.

IR (KBr disc): ν = 1187(P=O), 3277 (N-H) cm^{-1}.

^{1}H NMR (400 MHz; $CDCl_3$): δ = 0.95 (s, 9H, C*Me*$_3$), 2.41 (m, 2H, *CH*$_2$P), 2.82 (m, 2H, *CH*$_2$CH$_2$P), 7.37−7.69 (m, 10H, *Ph*).

^{31}P NMR (145.7 MHz; $CDCl_3$): δ = +31.9.

^{13}C NMR (90.5 MHz; $CDCl_3$): δ = 28.9 (s, C*Me*$_3$), 31.2 (d, $^1J_{PC}$ = 71 Hz, *CH*$_2$P), 35.9 (s, *CH*$_2$CH$_2$P), 50.6 (s, *C*Me$_3$), 128.0 (d, $^3J_{PC}$ = 11.5 Hz, C_{meta}), 130.7 (d, $^2J_{PC}$ = 9 Hz, C_{ortho}), 131.8 (s, C_{para}), 133.1 (d, $^1J_{PC}$ = 98.5 Hz, C_{ipso}).

MS: *m/z* (%) = 302 (100, M$^+$+1), 246 (35, M−^{t}Bu).

HRMS: calcd for $C_{18}H_{24}NOP$ (M$^+$+1) 302.1674. Found: 302.1685.

[2-(Diphenylphosphine oxide)ethyl]-benzylamine (1f)
Mp: 108−109 °C (Lit.[16] 115−117 °C).

IR (KBr disc): ν = 1183 (P=O), 3278 (N-H) cm^{-1}.

^{1}H NMR (400 MHz; $CDCl_3$): δ = 1.61 (br s, 1H, *NH*), 2.46 (m, 2H, *CH*$_2$P), 2.91 (m, 2H, *CH*$_2$CH$_2$P), 3.67 (s, 2H, Ph*CH*$_2$), 7.16−7.68 (m, 15H, *Ph*).

^{31}P NMR (145.7 MHz; $CDCl_3$): δ = +32.2.

^{13}C NMR (90.5 MHz; $CDCl_3$): δ = 30.4 (d, $^1J_{CP}$ = 71 Hz, *CH*$_2$P), 42.4 (s, *CH*$_2$CH$_2$P), 53.7 (s, Ph*CH*$_2$), 127.0−139.9 (C_{arom}).

MS: *m/z* (%) = 336 (100, M$^+$+1), 135 (35, M−POPh$_2$).

HRMS: calcd for $C_{21}H_{22}NOP$ (M$^+$+1) 336.1517. Found: 336.1524.

Deuterium Labelling Experiment
The amine (0.43 mmol), vinyldiphenylphosphine (0.43 mmol) and CD_3OD (0.2 mL) were placed in a 5 mm NMR tube and heated in a thermostated oil bath at 80 ºC. The reaction was monitored by ^{31}P NMR (*n*-butylamine: 6 h; *tert*-butylamine: 18 h). MeOH was removed under reduced pressure and the residues were redissolved in $CDCl_3$. Percentages of incorporation of deuterium were calculated from the integrals corresponding to the methylene proton resonances (Supplementary material).

Aminophosphine Oxides 2a-2d; General Procedure
Method C: To a solution of vinyldiphenylphosphine oxide (0.5 g, 2.4 mmol) in MeOH (1 mL) was added the appropriate amine (1.2 mmol). The reaction mixture was heated in a sealed tube at 80 °C. After the appropriate reaction time, MeOH was removed under reduced pressure. The solid was filtered off and washed with petroleum ether (40−60 °C).

Method D: The amine (1.2 mmol.) was added to a mixture of vinyldiphenylphosphine (2.2 mmol.) and the appropriate amine hydrochloride (0.1 mmol) and the reaction mixture was heated at 140 ºC in a sealed tube for 4 h. The resultant yellow solid was recrystallised from methylcyclohexane.

Bis-[2-(diphenylphosphineoxide)ethyl]-*n*-propylamine (2a)
Mp: 59−61 °C.

IR (KBr disc): ν = 1179 (P=O) cm^{-1}.

^{1}H NMR (400 MHz; $CDCl_3$): δ = 0.68 (t, 3H, *J* = 7 Hz, *CH*$_3$), 1.19 (m, 2H, CH$_3$*CH*$_2$), 2.20−2.29 (m, 6H, *CH*$_2$N and *CH*$_2$P), 2.72 (m, 4H, *CH*$_2$CH$_2$P), 7.35−7.60 (m, 20H).

^{31}P NMR (145.7 MHz; $CDCl_3$): δ = +31.9.

^{13}C NMR (90.5 MHz; $CDCl_3$): δ = 11.8 (s, *CH*$_3$), 20.2 (s, CH$_3$*CH*$_2$), 26.6 (d, $^1J_{PC}$ = 69.5 Hz, *CH*$_2$P), 45.4 (s, *CH*$_2$CH$_2$P), 55.2 (s, *CH*$_2$N), 128.7 (d, $^3J_{PC}$ = 12 Hz, C_{meta}), 130.7 (d, $^2J_{PC}$ = 9.5 Hz, C_{ortho}), 131.4 (s, C_{para}), 133.0 (d, $^1J_{PC}$ = 99 Hz, C_{ipso}).

HRMS: calcd for $C_{31}H_{35}NO_2P_2$ (M$^+$+1) 516.2221. Found: 516.2203.

Bis-[2-(diphenylphosphineoxide)ethyl] *n*-butylamine (2b)
Mp: 234−235 °C.

IR (KBr disc): ν = 1178 (P=O) cm^{-1}.

^{1}H NMR (400 MHz; $CDCl_3$): δ = 0.80 (t, 3H, *J* = 7 Hz, CH_3), 1.22 (m, 2H, CH_3CH_2), 1.52 (m, 2H, $CH_3CH_2CH_2$), 2.83 (m, 6H, CH_2P and CH_2N), 3.17 (m, 4H, CH_2CH_2P), 7.40−7.75 (m, 20H, *Ph*).

^{31}P NMR (145.7 MHz; $CDCl_3$): δ = +30.5.

^{13}C NMR (90.5 MHz; $CDCl_3$): δ = 13.4 (s, CH_3), 19.9 (s, CH_3CH_2), 24.8 (d, $^1J_{PC}$ = 70 Hz, CH_2P), 24.6 (s, $CH_3CH_2CH_2$), 47.2 (s, CH_2CH_2P), 52.5 (s, CH_2N), 129.2 (d, $^3J_{PC}$ = 12 Hz, C_{meta}), 130.8 (d, $^2J_{PC}$ = 10 Hz, C_{ortho}), 131.4 (s, C_{para}), 132.0 (d, $^1J_{PC}$ = 112 Hz, C_{ipso}).

HRMS: calcd for $C_{32}H_{37}NO_2P_2$ (M^++1) 530.2378. Found: 530.2363.

Bis-[2-(diphenylphosphineoxide)ethyl]-*n*-heptylamine (2c)
Mp: 149−150 °C.

IR (KBr disc): ν = 1178 (P=O) cm^{-1}.

^{1}H NMR (400 MHz; $CDCl_3$): δ = 0.79 (t, 3H, *J* = 7 Hz, CH_3), 1.06−1.80 (m, 10H, $CH_3CH_2CH_2CH_2CH_2CH_2$), 2.22−2.28 (m, 6H, CH_2N and CH_2P), 2.71 (m, 4H, CH_2CH_2P), 7.35−7.64 (m, 20H, *Ph*).

^{31}P NMR (145.7 MHz; $CDCl_3$): δ = +31.9.

^{13}C NMR (90.5 MHz; $CDCl_3$): δ = 14.1 (s, CH_3), 22.6, 26.3, 26.9, 27.0, 27.3, 29.2, 29.7, 31.8 (s, aliphatic CH_2's), 45.4 (s, CH_2CH_2P), 53.3 (s, CH_2N), 128.7 (d, $^3J_{PC}$ = 11.5 Hz, C_{meta}), 130.7 (d, $^2J_{PC}$ = 9.5 Hz, C_{ortho}), 131.8 (s, C_{para}), 133.8 (d, $^1J_{PC}$ = 99 Hz, C_{ipso}).

HRMS: calcd for $C_{35}H_{43}NO_2P_2$ (M^++1) 572.2847. Found: 572.2863.

Bis-[2-(diphenylphosphineoxide)ethyl]benzylamine (2d)
Mp: 169−170 °C.

IR (KBr disc): ν = 1178 (P=O) cm^{-1}.

^{1}H NMR (360 MHz; $CDCl_3$): δ = 2.31 (m, 4H, CH_2P), 2.78 (m, 4H, CH_2CH_2P), 3.49 (s, 2H, PhCH_2), 7.04−7.64 (m, 25H, *Ph*).

^{31}P NMR (145.7 MHz; $CDCl_3$): δ = +31.7.

^{13}C NMR (90.5 MHz; $CDCl_3$): δ = 26.9 (d, $^1J_{PC}$ = 69.4 Hz, CH_2P), 45.6 (d, $^2J_{PC}$ = 22.4 Hz, CH_2CH_2P), 58.0 (s, PhCH_2), 127.1−138.3 (C_{arom}).

HRMS: calcd for $C_{35}H_{35}NO_2P_2$ (M^++1) 564.2221. Found: 564.2219.

Reduction of Aminophosphines Oxides 1 to 3; General Procedure
The appropriate aminophosphine oxide (0.5g) was suspended in toluene (25 mL). Et_3N (6 mL) was added and the mixture was stirred whilst cooled to 0 °C. Trichlorosilane (5 equiv) was then added dropwise and the mixture was then refluxed for 3.5 h. After cooling to r.t., the reaction mixture was diluted with Et_2O (100 mL), and a few drops of sat. Na_2CO_3 were added to destroy excess reducing agent. The mixture was filtered under Ar and concentrated to leave a yellow oil. The residue was dissolved in Et_2O (25 mL) and continuously purged with Ar whilst concd HCl was added dropwise until the formation of a white precipitate. In some cases, a small amount of H_2O (approx 2 mL) was added to encourage precipitation. The HCl salt was subsequently filtered off and dried under vacuum.

[2-(Diphenylphosphino)ethyl]-*n*-propylamine•HCl Salt (3a)
Yield: 89%; mp: 137−139 °C.

IR (KBr disc): ν = 3411 (N-H) cm^{-1}.

^{1}H NMR (360 MHz; $CDCl_3$): δ = 0.80 (t, 3H, *J* = 7.4 Hz, CH_3), 1.74 (m, 2H, CH_3CH_2), 2.65-2.79 (m, 4H, CH_2N and CH_2P), 2.93 (br. m, 2H, CH_2CH_2P), 7.28−7.42 (m, 10H, *Ph*), 9.70 (br. s, 2H, NH_2).

^{31}P NMR (145.7 MHz; $CDCl_3$): δ = −20.1.

^{13}C NMR (90.5 MHz; $CDCl_3$): δ = 11.2 (s, CH_3), 19.5 (s, CH_3CH_2), 24.1 (d, $^1J_{PC}$ = 15 Hz, CH_2P), 45.2 (d, $^2J_{PC}$ = 27 Hz, CH_2CH_2P), 49.2 (s, CH_2N), 128.7 (d, $^3J_{PC}$ = 7 Hz, C_{meta}), 129.3 (s, C_{para}), 132.7 (d, $^2J_{PC}$ = 19 Hz, C_{ortho}), 136.0 (d, $^1J_{PC}$ = 11 Hz, C_{ipso}).

HRMS: calcd for $C_{17}H_{22}NP$ (M^++1) 272.1568. Found: 272.1585.

[2-(Diphenylphosphino)ethyl]-*iso*-propylamine•HCl Salt (3b)
Yield: 84%; mp: 170 °C.

^{1}H NMR (360 MHz; $CDCl_3$): δ = 1.25 (d, 6H, *J* = 6.5 Hz, CHMe_2), 2.72 (m, 2H, CH_2P), 2.92 (br m, 2H, CH_2CH_2P), 3.13 (septet, 1H, *J* = 6.5 Hz, $CHMe_2$), 7.23−7.44 (m, 10H, *Ph*), 9.61 (br s, 2H, NH_2).

^{31}P NMR (145.7 MHz; $CDCl_3$): δ = −18.8.

^{13}C NMR (90.5 MHz; $CDCl_3$): δ = 19.1 (s, CH_3), 24.3 (d, $^1J_{PC}$ = 15 Hz, CH_2P), 42.3 (d, $^2J_{PC}$ = 27 Hz, CH_2CH_2P), 50.1 ($CHMe_2$), 128.8 (d, $^3J_{PC}$ = 7 Hz, C_{meta}), 129.2 (s, C_{para}), 132.8 (d, $^2J_{PC}$ = 19 Hz, C_{ortho}), 136.2 (d, $^1J_{PC}$ = 12 Hz, C_{ipso}).

IR (KBr disc): ν = 3436 (N-H) cm^{-1}.

Anal. calcd for $C_{17}H_{23}ClNP$: C, 66.35; H, 7.5; N, 4.55: Found: C, 66.25; H, 7.55; N, 4.50.

[2-(Diphenylphosphino)ethyl]-*n*-butylamine•HCl Salt (3c)
Yield: 88%; mp: 124−125 °C.

IR (KBr disc) ν = 3415 (N-H) cm^{-1}.

^{1}H NMR (360 MHz; $CDCl_3$): δ = 0.79 (t, 3H, *J* = 7 Hz, CH_3), 1.25 (sextet, 2H, *J* = 7 Hz, CH_3CH_2), 1.71 (m, 2H, $CH_3CH_2CH_2$), 2.64 (m, 2H, CH_2P), 2.80 (t, 2H, J = 8 Hz, CH_2N), 2.94 (m, 2H, CH_2CH_2P), 7.28−7.40 (m, 10H, *Ph*), 9.50 (br d, 2H, NH_2).

^{31}P NMR (145.7 MHz; $CDCl_3$): δ = −20.2.

^{13}C NMR (90.5 M Hz; $CDCl_3$): δ = 13.4 (s, CH_3), 19.9 (s, CH_3CH_2), 24.1 (d, $^1J_{PC}$ = 14 Hz, CH_2P), 27.7 (s, $CH_3CH_2CH_2$), 44.9 (d, $^2J_{PC}$ = 26.5 Hz, CH_2CH_2P), 47.2 (s, CH_2N), 128.7 (d, $^3J_{PC}$ = 7 Hz, C_{meta}), 129.3 (s, C_{para}), 132.7 (d, $^2J_{PC}$ = 19 Hz, C_{ortho}), 136.0 (d, $^1J_{PC}$ = 11 Hz, C_{ipso}).

IR (KBr disc): ν = 3415 (N-H) cm^{-1}.

HRMS: calcd for $C_{18}H_{24}NP$ (M^++1) 286.1725. Found: 286.1728.

[2-(Diphenylphosphino)ethyl]-*sec*-butylamine•HCl Salt (3d)
Yield: 92%; mp: 138−139 °C.

IR (KBr disc): ν = 3412 (N-H) cm^{-1}.

^{1}H NMR (360 MHz; $CDCl_3$): δ = 0.79 (t, 3H, *J* = 7 Hz, CH_3CH_2), 1.21 (d, 3H, *J* = 6.5 Hz, CH_3CH), 1.52 (m, 1H, CH_3CH_2), 1.84 (m, 1H, CH_3CH_2), 2.77 (m, 2H, CH_2P), 2.80−2.90 (m, 3H, *CH*N and CH_2CH_2P), 7.23−7.51 (m, 10H, *Ph*), 9.58 (br. d, 2H, NH_2).

^{31}P NMR (145.7 MHz; $CDCl_3$): δ = −19.3.

^{13}C NMR (90.5 MHz; $CDCl_3$): δ = 9.9 (s, CH_3), 15.4 (s, CH_3), 23.9 (d, $^1J_{PC}$ = 12 Hz, CH_2P), 25.8 (s, CH_3CH_2), 41.9 (d, $^2J_{PC}$ = 26 Hz, CH_2CH_2P), 55.4 (s, *CH*N), 128.9 (d, $^3J_{PC}$ = 7 Hz, C_{meta}), 129.4 (s, C_{para}), 132.0 (d, $^2J_{PC}$ = 19 Hz, C_{ortho}), 135.3 (d, $^1J_{PC}$ = 11 Hz, C_{ipso}).

HRMS: calcd for $C_{18}H_{24}NP$ (M^++1) 286.1725. Found: 286.1728.

[2-(Diphenylphosphino)ethyl]-*tert*-butylamine•HCl Salt (3e)[3]
Yield: 82%; mp: 208−209 °C.

IR (KBr disc): ν = 3412 (N-H) cm^{-1}.

^{1}H NMR (360 MHz; $CDCl_3$): δ = 1.28 (s, 9H, CMe_3), 3.04 (m, 2H, CH_2CH_2P), 3.15 (m, 2H, CH_2P), 7.35−7.63 (m, 10H, *Ph*).

^{31}P NMR (145.7 MHz; $CDCl_3$): δ = −19.9.

^{13}C NMR (90.5 MHz; $CDCl_3$): δ = 25.0 (d, $^1J_{PC}$ = 14 Hz, CH_2P), 26.0 (s, CMe_3), 39.4 (d, $^2J_{PC}$ = 28 Hz, CH_2CH_2P), 56.9 (s, *C*Me$_3$),

128.8 (d, $^3J_{PC}$ = 7 Hz, C_{meta}), 129.1 (s, C_{para}), 132.7 (d, $^2J_{PC}$ = 19 Hz, C_{ortho}), 136.1 (d, $^1J_{PC}$ = 12 Hz, C_{ipso}).

HRMS: calcd for $C_{18}H_{24}NP$ (M^++1) 286.1725. Found: 286.1728.

[2-(Diphenylphosphino)ethyl]benzylamine•HCl Salt (3f)[3]
Yield: 94%; mp: 164−165 °C.

^{1}H NMR (360 MHz; $CDCl_3$): δ = 2.59 (m, 2H, CH_2P), 2.82 (m, 2H, CH_2CH_2P), 3.89 (t, 2H, J = 5 Hz, PhCH_2), 7.20−7.50 (m, 15H, *Ph*), 10.09 (br s, 2H, NH_2).

^{31}P NMR (145.7 MHz; $CDCl_3$): δ = −20.4.

^{13}C NMR (90.5 MHz; $CDCl_3$): δ = 23.1 (d, $^1J_{PC}$ = 15.5 Hz, CH_2P), 43.1 (d, $^2J_{PC}$ = 27 Hz, CH_2CH_2P), 50.0 (s, PhCH_2), 128.8−136.1 (C_{arom}).

IR (KBr disc): ν = 3412 (N-H) cm^{-1}.

HRMS: calcd for $C_{21}H_{22}NP$ (M^++1) 320.1568. Found: 320.1559.

Reduction of Aminodiphosphine Oxides 2 to 4; General Procedure
The appropriate diphosphine oxide (0.5g) was suspended in toluene (30 mL). Et_3N (6 mL) was added and the mixture was stirred at 0 °C for 10 minutes. Trichlorosilane (10 equiv) was then added dropwise to the reaction mixture before refluxing for 3.5 h. After cooling to ambient temperature, the solution was diluted with Et_2O (100 mL) and a few drops of Na_2CO_3 were added to destroy excess reducing agent. The reaction mixture was filtered and dried ($MgSO_4$), before evaporating to dryness under reduced pressure, leaving a creamy white solid, which was recrystallised from MeOH.

Bis-[2-(Diphenylphosphino)ethyl]-*n*-propylamine (4a)
Yield: 96%; mp: 83−84 °C (Lit.[17] 75.5−76.5 °C).

^{1}H NMR (360 MHz; $CDCl_3$): δ = 0.78 (t, 3H, J = 7 Hz, CH_3), 1.28 (sextet, 2H, J = 7 Hz, CH_3CH_2), 2.06 (m, 4H, CH_2P), 2.33 (t, 2H, J = 7 Hz, CH_2N), 2.54 (m, 4H, CH_2CH_2P), 7.23−7.38 (m, 20H, *Ph*).

^{31}P NMR (145.7 MHz; $CDCl_3$): δ = −19.0.

^{13}C NMR (90.5 MHz; $CDCl_3$): δ = 11.9 (s, CH_3), 20.3 (s, CH_3CH_2), 25.2 (d, $^1J_{PC}$ = 12 Hz, CH_2P), 49.5 (d, $^2J_{PC}$ = 23 Hz, CH_2CH_2P), 55.6 (s, CH_2N), 128.4 (d, $^3J_{PC}$ = 6.5 Hz, C_{meta}), 128.6 (s, C_{para}), 132.7 (d, $^2J_{PC}$ = 18.5 Hz, C_{ortho}), 136.0 (d, $^1J_{PC}$ = 13 Hz, C_{ipso}).

MS: *m/z* (%) = 484 (20, M^++1), 284 (100, M−CH_2PPh_2).

HRMS: calcd for $C_{31}H_{35}NP_2$ (M^++1) 484.2337: Found: 484.2323.

Bis-[2-(Diphenylphosphino)ethyl]-*n*-butylamine (4b)
Yield: 89%; mp: 134−136 °C.

^{1}H NMR (360 MHz; $CDCl_3$): δ = 0.80 (t, 3H, J = 7 Hz, CH_3), 1.20 (m, 4H, $CH_3CH_2CH_2$), 2.06 (m, 4H, CH_2P), 2.35 (t, 2H, J = 7 Hz, CH_2N), 2.52 (m, 4H, CH_2CH_2P), 7.25–7.35 (m, 20H, Ph).

^{31}P NMR (145.7 MHz; $CDCl_3$): δ = −19.0.

^{13}C NMR (90.5 MHz; $CDCl_3$): δ = 14.1 (s, CH_3), 20.7 (s, CH_3CH_2), 25.2 (d, $^1J_{PC}$ = 12 Hz, CH_2P), 29.2 (s, $CH_3CH_2CH_2$), 49.5 (d, $^2J_{PC}$ = 23 Hz, CH_2CH_2P), 53.3 (s, CH_2N), 128.4 (d, $^3J_{PC}$ = 6.5 Hz, C_{meta}), 128.6 (s, C_{para}), 132.7 (d, $^2J_{PC}$ = 18 Hz, C_{ortho}), 138.6 (d, $^1J_{PC}$ = 13 Hz, C_{ipso}).

MS: *m/z* (%) = 498 (35, M^++1), 298 (100, M−CH_2PPh_2).

HRMS: calcd for $C_{32}H_{37}NP_2$ (M^++1) 498.2497. Found: 498.2480.

Bis-[2-(Diphenylphosphino)ethyl]-*n*-heptylamine (4c)
Yield: 93%; mp: 67 °C.

^{1}H NMR (360 MHz; $CDCl_3$): δ = 0.84 (t, 3H, J = 7 Hz, CH_3), 1.16−1.22 (m, 10H, aliphatic CH_2's), 2.05 (m, 4H, CH_2P), 2.33 (t, 2H, J = 7.0 Hz, CH_2N), 2.52 (m, 4H, CH_2CH_2P), 7.23−7.37 (m, 20H, *Ph*).

^{31}P NMR (145.7 MHz; $CDCl_3$): δ = −19.1.

^{13}C NMR (90.5 MHz; $CDCl_3$): δ = 14.1 (s, CH_3), 27.1 (s, CH_3CH_2), 27.4 (s, $CH_3CH_2CH_2$), 29.2 (s, $CH_3CH_2CH_2CH_2$), 31.8 (s, $CH_3CH_2CH_2CH_2CH_2$), 49.5 (d, $^2J_{PC}$ = 23 Hz, CH_2CH_2P), 53.6 (CH_2N), 128.4 (d, $^3J_{PC}$ = 6.5 Hz, C_{meta}), 128.6 (s, C_{para}), 132.7 (d, $^2J_{PC}$ = 18.5 Hz, C_{ortho}), 138.6 (d, $^1J_{PC}$ = 13 Hz).

HRMS: calcd for $C_{35}H_{43}NP_2$ (M^++1) 540.2949. Found: 540.2938.

Bis-[2-(Diphenylphosphino)ethyl]-benzylamine (4d)[18]
Yield: 95%; mp: 164−165 °C.

^{1}H NMR (360 MHz; $CDCl_3$): δ = 2.20 (m, 4H, CH_2P), 2.62 (m, 4H, CH_2CH_2P), 3.58 (s, 2H, PhCH_2), 7.25−7.36 (m, 25H, *Ph*).

^{31}P NMR (145.7 MHz; $CDCl_3$): δ = −19.8.

^{13}C NMR (90.5 MHz; $CDCl_3$): δ = 25.4 (d, $^1J_{PC}$ = 12.5 Hz, CH_2P), 49.4 (d, $^2J_{PC}$ = 22 Hz, CH_2CH_2P), 58.0 (s, PhCH_2), 126.9−139.2 (C_{arom}).

HRMS: calcd for $C_{35}H_{35}NP_2$ (M^++1) 532.2323. Found: 532.2300.

Supplementary material
Crystal data for **1e**, and details of data collection and refinement are given.

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