Synthesis and Structure of Bis(phosphaallyl) Complexes with Two-co-ordinate Phosphorus†

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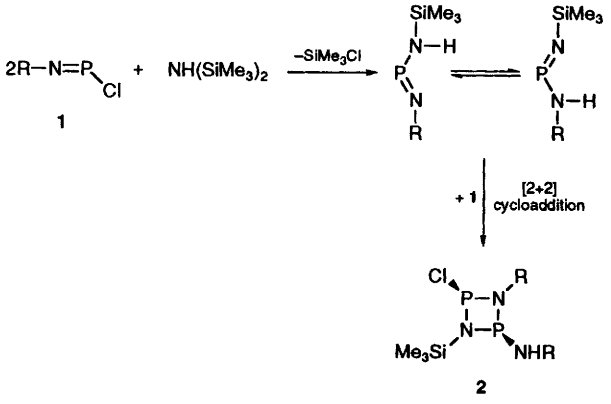
The compound $(2,4,6\text{-Bu}^t{}_3C_6H_2)N(H)PN(SiMe_3)P(Cl)N(C_6H_2Bu^t{}_3\text{-}2,4,6)$ was prepared and its crystal structure determined. It is one of the rare examples of non-symmetrically substituted cyclophosphazanes. A series of bis- and mono-phosphaallyl complexes $[M\{(Me_3Si)NPN(C_6H_2Bu^t{}_3\text{-}2,4,6)\}_2]$ (M = Zn or Cd), $[Zn(Bu^tNPNBu^t)_2]$, $[Zn\{(4\text{-Pr}^iC_6H_4)NPN(C_6H_2Bu^t{}_3\text{-}2,4,6)\}_2]$, $[Zn\{R'NPN(C_6H_2Bu^t{}_3\text{-}2,4,6)\}_2]$ ($R' = Bu^t$ or adamantyl) and $[Zn\{(2,4,6\text{-Bu}^t{}_3C_6H_2)NPN(C_6H_2Bu^t{}_3\text{-}2,4,6)\}Me]$ have been prepared from cyclic aminophosphazanes and aminoiminophosphanes. The structure of the spirocyclic bis(1,3-diaza-2-phosphaallyl)zinc complex $[Zn(RNPNR')_2]$ ($R = R' = C_6H_3Pr^i{}_2\text{-}2,6$) was determined.

Recently the stabilization of low-co-ordination number phosphorus has attracted considerable interest.[1] Numerous systems with carbon–phosphorus multiple bonds[2-4] have been characterized as well as diphosphenes.[5] Some of the latest investigations have considered phosphorus–nitrogen systems with low-co-ordinated phosphorus.[6-8] Most of these compounds are stabilized by sterically demanding ligands or by co-ordination to transition-metal fragments. We have reported a series of crystallographically characterized As–N compounds with arsenic having co-ordination number two.[9] In this case the low-co-ordinated arsenic centre was generated from a cyclic arsazane with three-co-ordinated arsenic by reaction with zinc or cadmium ions leading to spirocyclic complexes. These complexes have metal–nitrogen bonds in contrast to numerous examples with metal–arsenic or –phosphorus co-ordination. Herein, we report the extension of this method to a series of bis(phosphaallyl) complexes.

Results and Discussion

Our investigations were carried out with NH functionalized phosphazanes, chlorophosphazanes and aminoiminophosphanes, and dimethylzinc and bis[bis(trimethylsilyl)amido]-zinc or -cadmium respectively, as starting reagents. Elimination of methane or hexamethyldisilazane leads to the desired phosphaallyl complexes. Variation of the organic substituents on the P–N starting compounds should lead to various types of complexes and to a different reactivity.

A series of aminoiminophosphanes starting with chloroiminophosphane **1**[10] in which phosphorus is two-co-ordinated has been prepared by salt elimination using lithiated primary amines. Until now no trimethylsilyl-substituted system was known. Our intention was to generate a trimethylsilyl-substituted aminoiminophosphane by chlorotrimethylsilane elimination from hexamethyldisilazane and the chloroiminophosphane **1**. In fact this reaction led to a yellow solid **2** precipitating from hexane (Scheme 1). The ^{31}P NMR spectrum exhibited two signals at δ 176.9 and 207.7 with a coupling constant $^3J(PP) = 82$ Hz. A single-crystal structure determination (see below) revealed a chloro-substituted P_2N_2 four-membered ring. We suggest for the formation of this compound a three-step mechanism starting with chlorotrimethylsilane elimination, followed by a prototropic shift isomerization accompanied by a [2 + 2] cycloaddition reaction with another molecule of the starting material **1**.



Scheme 1 $R = C_6H_2Bu^t{}_3\text{-}2,4,6$

Table 1 Selected bond lengths (pm) and angles (°) for compound **2**

P(1)–N(2)	168.7(2)	P(1)–N(3)	171.2(2)
P(2)–N(1)	168.9(2)	P(2)–N(2)	175.7(2)
P(2)–N(3)	174.7(2)	N(2)–Si	176.3(2)
P(1)–Cl	216.3(2)		
N(2)–P(1)–N(3)	84.31(11)	N(3)–P(1)–Cl	109.18(9)
N(2)–P(2)–Cl	98.92(9)	C(21)–N(1)–P(2)	120.3(2)
N(1)–P(2)–N(2)	107.86(11)	N(1)–P(2)–N(3)	102.60(11)
N(2)–P(2)–N(3)	81.24(11)	P(1)–N(2)–P(2)	97.36(11)
P(1)–N(2)–Si	130.53(14)	P(2)–N(2)–Si	127.18(14)
P(1)–N(3)–P(2)	96.75(11)	P(1)–N(3)–C(11)	136.0(2)
P(2)–N(3)–C(11)	120.3(2)		

The molecular structure shows an almost planar four-membered ring with the chlorine and the amino substituent in *cis* position (Fig. 1, Table 1). The same core framework with similar geometry was found by Niecke and co-workers[11] in

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

$\overline{\mathrm{Pr^i{}_2NPN(C_6H_2Bu^t{}_3\text{-}2,4,6)P(Cl)N}}\mathrm{Bu^t}$. The phosphorus–nitrogen bond lengths in the ring vary over a small range [P(1)–N(2) 168.7(2), P(1)–N(3) 171.2(2), P(2)–N(3) 174.7(2), P(2)–N(2) 175.7(2) pm]. The phosphorus–phosphorus distance is 258.63(13) pm, and P(1)–Cl is 216.3(2) pm. Atoms P(1), P(2), N(2), N(3) deviate from planarity by no more than 3.3 pm. The angle of the P–Cl bond with the P(1) • • • P(2) line is 112.00(4)°.

The reaction of compound **2** with bis[bis(trimethylsilyl)amido]-zinc or -cadmium respectively leads to a heteroallyl complex of zinc **3a** or cadmium **3b** containing two-co-ordinated phosphorus (Scheme 2). As a side reaction a second equivalent of $\mathrm{M[N(SiMe_3)_2]_2}$ reacts with the chloride site of compound **2** to give an aminoiminophosphane **4** together with the metal dichloride. On the other hand the reaction of chloroiminophosphane with $\mathrm{M[N(SiMe_3)_2]_2}$ exclusively forms the aminosilylated phosphane.[12]

Niecke and co-workers[13] reported the synthesis of a series of aminoiminophosphanes by facile elimination of LiCl from lithiated primary amines treated with the chloroiminophosphane **1**. In each case the two-co-ordinated phosphorus centre was preserved. The presence of trimethylsilyl groups in **2** increases the activity of the amino proton leading to a prototropic shift and therefore to a deshielding of the low-co-ordinated centre. The subsequent cycloaddition is reversible and was achieved by co-ordination to a metal centre.

Thus it seemed to be desirable to carry out some reactions with cyclic aminophosphazanes and organozinc derivatives. These reactions led to the formation of bis(phosphaallyl) complexes of zinc in the case where the substituents on nitrogen were $\mathrm{C_6H_3Pr^i{}_2\text{-}2,6}$ **5a** or Bu^t **5b** (Scheme 3).[14] We were able to get single crystals from the $\mathrm{C_6H_3Pr^i{}_2\text{-}2,6}$ substituted phosphazane **6a** suitable for crystal structure analysis (Fig. 2, Table 2).

The Zn–N bond lengths are 203.5(2) and 204.1(2) pm. The P–N bond lengths [all 160.3(2) pm] are in the range of those reported for similar metal complexes.[6,15] The N–P–N angles in the phosphaallyl fragments [97.9(2) and 97.6(2)°] cause the low-co-ordinated phosphorus centre to be exposed, and is thus unprotected by steric hindrance. The two four-membered rings connected by the Zn atom are identical in terms of bond lengths and angles. The co-ordination sphere of the metal atom is a distorted tetrahedron giving rise to an angle between the two rings of 62.3°.

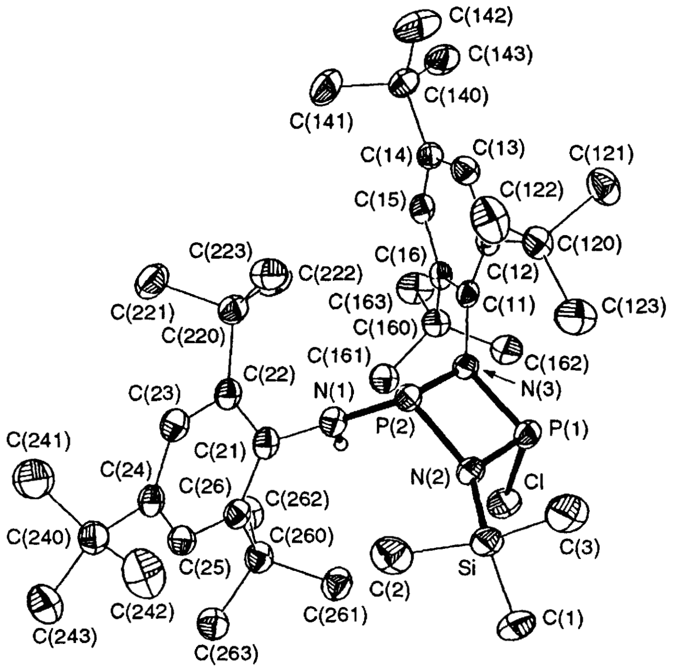


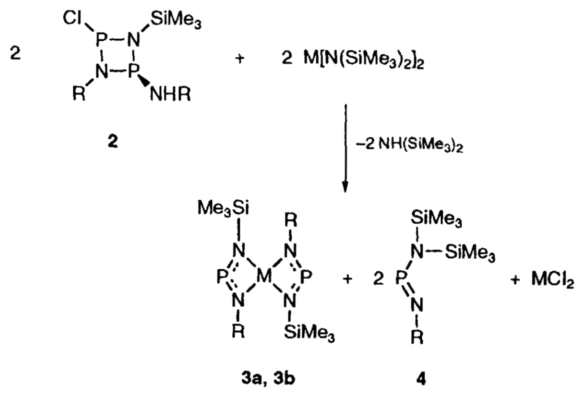
Fig. 1 Crystal structure of compound **2**

The Bu^t-substituted complex **6b** was characterized by ^{31}P NMR spectroscopy.

Another interesting feature was found while trying to synthesize some new aminoiminophosphanes of the type reported by Niecke and co-workers.[13] Thus reaction of the chloroiminophosphane **1** with lithiated 4-isopropylaniline lead to a cyclic amino phosphazane **7**, as demonstrated by ^{31}P NMR spectroscopy (δ 120.5), and not to the expected monomer (Scheme 4). This supports the conclusion that low-co-ordinated phosphorus is stabilized in this case by the electronic and steric effects of the substituents. The low-co-ordination site at phosphorus was subsequently achieved by complexation with zinc (compound **8**) similar to the above described examples (Scheme 5).

Table 2 Selected bond lengths (pm) and angles (°) for complex **6a**

Zn–N(2)	204.1(2)	N(1)–P(1)	160.3(2)
Zn–N(1)	203.5(2)	N(2)–P(2)	160.3(2)
N(1)–Zn–N(1A)	72.69(11)	N(2)–Zn–N(1)	119.04(8)
N(2)–Zn–N(1A)	144.36(8)	N(2A)–Zn–N(2)	72.63(11)
N(1)–Zn–N(2)	119.04(8)	P(1)–N(1)–Zn	94.84(9)
N(1A)–P(1)–N(1)	97.6(2)	N(2)–P(2)–N(2A)	97.9(2)



Scheme 2 R = $\mathrm{C_6H_2Bu^t{}_3\text{-}2,4,6}$; M = Zn **3a** or Cd **3b**

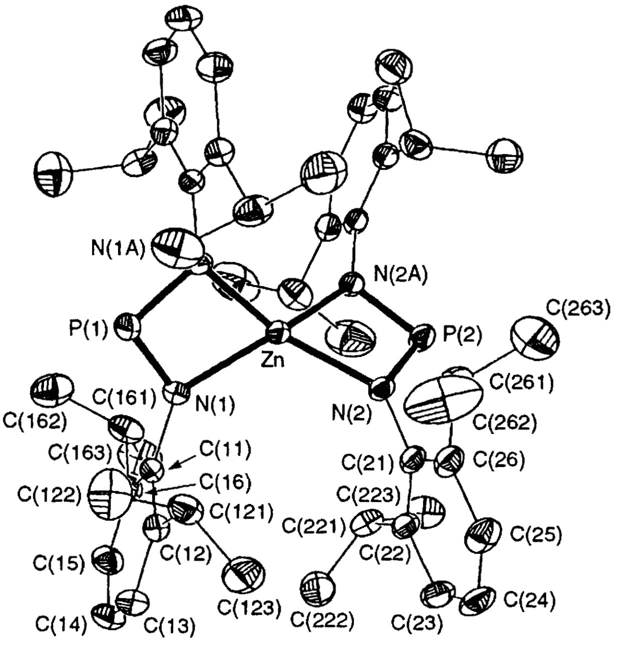
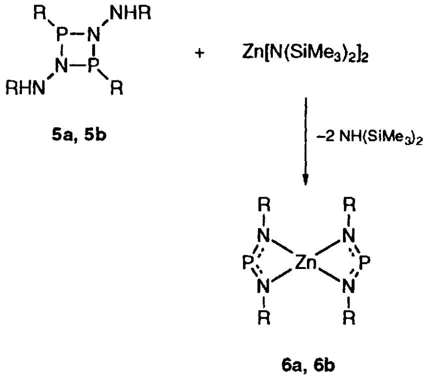
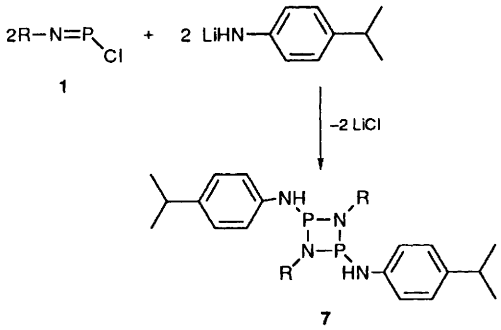


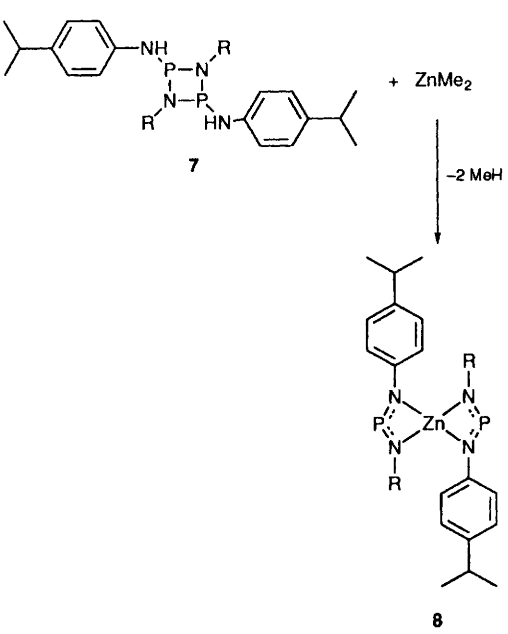
Fig. 2 Crystal structure of complex **6a**



Scheme 3 R = $C_6H_3Pr^i{}_2$-2,6 **a** or Bu^t **b**



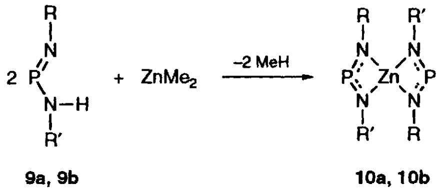
Scheme 4 R = $C_6H_2Bu^t{}_3$-2,4,6



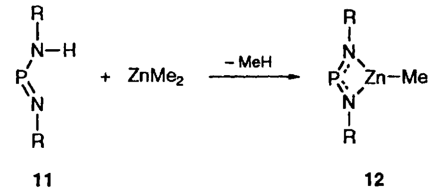
Scheme 5 R = $C_6H_2Bu^t{}_3$-2,4,6

Obviously, it should be possible to form phosphaallyl complexes with NH-functionalized aminoiminophosphanes and organozinc compounds. For this purpose we employed some of the compounds reported by Niecke and co-workers.[13] The substituents were $C_6H_2Bu^t{}_3$-2,4,6 and adamantyl **9a** or Bu^t **9b**, respectively. In both cases we were able to characterize the resulting phosphaallyl complexes **10a** and **10b** by spectroscopic methods (Scheme 6).

Finally, the aminoiminophosphane **11** reported by Lappert and co-workers[6] reacted with dimethylzinc to give the mono(phosphaallyl) complex **12** (Scheme 7). One of the Zn–C bonds is retained.



Scheme 6 R = $C_6H_2Bu^t{}_3$-2,4,6; R′ = adamantyl **a** or Bu^t **b**



Scheme 7 R = $C_6H_2Bu^t{}_3$-2,4,6

Table 3 Phosphorus-31 NMR data of the (1,3-diaza-2-phosphaallyl)-metal complexes

Compound	δ_P
3a	326.9
3b	344.2
6a	349.9
6b	351.6
8	349.6
10a	369.6
10b	368.0
12	365.0

Table 3 summarizes the ^{31}P NMR chemical shifts of the (1,3-diaza-2-phosphaallyl)metal complexes. The values vary only over a small range of the low-field part of the ^{31}P NMR scale, confirming the similarity of the geometry and binding of the metal to the phosphaallyl fragment. They are also consistent with values reported for similar lithium complexes[15] and for an aluminium complex.[7]

We conclude that steric hindrance in aminoiminophosphanes and aminophosphazanes gives rise to different reaction pathways and products. With decreasing steric demand of the organic substituent on the nitrogen sites the formation of bis(phosphaallyl) complexes occurs, electronic stabilization by the metal centre gives rise to P–N bond cleavage and the formation of two two-co-ordinated phosphorus centres.

Experimental

Reactions were performed and worked up using standard Schlenk techniques, and products were handled under dry, oxygen-free nitrogen. Solvents were dried, distilled and stored using standard procedures. Infrared spectra were obtained using a Bio-Rad FTS7 spectrometer, NMR spectra on a Bruker 250M spectrometer and mass spectra on a Finnigan MAT System 8230 spectrometer. Microanalyses were performed by the analytical laboratories of the University of Göttingen.

Preparations.—$(2,4,6\text{-}Bu^t{}_3C_6H_2)N(H)PN(SiMe_3)P(Cl)N(C_6H_2Bu^t{}_3\text{-}2,4,6)$ **2**. To a solution of compound **1**[10] (3.25 g, 10.0 mmol) in hexane (80 cm^3) was added hexamethyldisilazane (0.81 g, 5.0 mmol) at room temperature. The mixture was stirred for 18 h at room temperature. The yellow precipitate was filtered off. A solution of **2** in hexane at –20 °C gave after 2 d colourless plates suitable for single-crystal X-ray diffraction. Yield: 83% (2.92 g). M.p. 143 °C. Mass spectrum (field desorption, FD): *m/z* 703 (M^+, 40) and 101 (C_8H_5, 100%). δ_H(250 MHz, C_6D_6, $SiMe_4$) 0.07 (s, 9 H, $SiMe_3$), 1.31 (s, 18 H, CMe$_3$), 1.32 (s, 18 H, CMe$_3$), 1.66 (s, 9 H, CMe$_3$), 1.80 (s, 9 H, CMe$_3$), 6.81 (br, 1 H, NH) and 7.15 (br, 4 H, H$_{aryl}$). δ_C(63 MHz, C$_6$D$_6$, SiMe$_4$) 2.9 (s), 31.4 (s), 31.5 (s), 31.6 (s), 32.0 (s), 34.4 (s), 34.5 (s), 34.6 (s), 34.7 (s), 121.9 (s), 122.1 (s), 135.1 (s), 135.3 (s), 141.3 (s), 143.2 (s), 147.4 (s) and 150.4 (s). δ_P(101 MHz, C$_6$D$_6$, 85% H$_3$PO$_4$) 176.9 [d, ^3J(PP) = 82] and 207.7 [d, ^3J(PP) = 82 Hz]. δ_{Si}(50 MHz, C$_6$D$_6$, SiMe$_4$) 5.57 [d, ^3J(SiP) = 14] and 5.93 [d, ^3J(SiP) = 14 Hz]. IR (Nujol): $\tilde{\nu}$/cm^{-1} 3410w, 1260s, 1013s and 854s (Found: C, 64.8; H, 9.7; N, 6.2; P, 7.3. Calc. for $C_{39}H_{68}ClN_3P_2Si$: C, 66.5; H, 9.75; N, 5.95; P, 8.8%).

[M{Me$_3$SiNPN(C$_6$H$_2$Bu$^t_3$-2,4,6)}$_2$] (M = Zn **3a** *or* Cd **3b**). The chlorophosphazane **2** (1.40 g, 2.0 mmol) was stirred together with 2.0 mmol M[N(SiMe$_3$)$_2$]$_2$ (M = Zn, 0.71 g; Cd, 0.87 g) in toluene (40 cm^3) at ambient temperature for 18 h. The precipitated solid was filtered off and identified as ZnCl$_2$ and CdCl$_2$, respectively. The solvent was removed *in vacuo* and the residue was treated with hexane giving a yellow solid identified as the complex **3a** or **3b**, 0.30 (35) and 0.34 g (41%).

Complex **3a**: m.p. 203 °C; mass spectrum (electron impact, EI) m/z 818 (M^+, 100) and 761 (M^+ − C$_4$H$_9$, 28%); δ_H(250 MHz, CDCl$_3$, SiMe$_4$) −1.59 (s, 18 H, Me$_3$Si), 1.22 (s, 36 H, CMe$_3$), 1.30 (s, 72 H, CMe$_3$) and 7.12 (s, 4 H, H$_{aryl}$); δ_P(101 MHz, CDCl$_3$, 85% H$_3$PO$_4$) 326 (s); IR (Nujol) $\tilde{\nu}$/cm^{-1} 1086s and 841s (Found: C, 59.7; H, 9.4; N, 6.5. Calc. for $C_{42}H_{76}N_4P_2Si_2Zn$: C, 61.5, H, 9.35; N, 6.85%).

Complex **3b**: m.p. 174 °C; mass spectrum (EI) m/z 869 (M^+, 64) and 378 ($C_{21}H_{38}N_2PSi$, 100%); δ_H(250 MHz, C$_6$D$_6$–CDCl$_3$, SiMe$_4$) −0.04 (s, 18 H, Me$_3$Si), 1.19 (s, 72 H, CMe$_3$) and 7.23 (s, 4 H, H$_{aryl}$); δ_C(63 MHz, C$_6$D$_6$, SiMe$_4$) 3.9 (s), 31.9 (s), 33.4 (s), 34.8 (s), 36.7 (s), 122.5 (s), 141.3 (s), 141.7 (s) and 144.5 (s); δ_P(101 MHz, C$_6$D$_6$–CDCl$_3$, 85% H$_3$PO$_4$) 344.0 (s); δ_{Si}(50 MHz, C$_6$D$_6$–CDCl$_3$, SiMe$_4$) 1.63 [d, ^3J(SiP) = 23 Hz]; IR (Nujol) $\tilde{\nu}$/cm^{-1} 1098s and 849s (Found: C, 58.9; H, 8.9; N, 6.0. Calc. for $C_{42}H_{76}CdN_4P_2Si_2$: C, 58.15; H, 8.85; N, 6.45%).

[(2,6-Pr$^i_2$C$_6$H$_3$)N(H)PN(C$_6$H$_3$Pr$^i_2$-2,6)]$_2$ **5a**. A 3.03 mol dm^{-3} solution of LiBu^n (28.1 cm^3, 85.0 mmol) in hexane was added dropwise at −60 °C to a solution of 2,6-diisopropylaniline (15.1 g, 85.0 mmol) in diethyl ether (100 cm^3). To complete the lithiation the solution was warmed to room temperature and then refluxed for 1.5 h. Finally, PCl$_3$ (5.9 g, 43.0 mmol) in diethyl ether (30 cm^3) was added dropwise at −60 °C. Again the mixture was warmed to ambient temperature and filtered through Celite. All volatiles were removed *in vacuo* to afford a colourless oil which was purified by crystallization from hexane (10 cm^3) at −40 °C giving 4.2 g (26%) of compound **5a** as a white solid product. M.p. 183 °C. Mass spectrum (EI): m/z 764 (M^+, 2) and 589 (M^+ − C$_{12}$H$_{17}$N, 100%). δ_H(100 MHz, C$_6$D$_6$, SiMe$_4$) 1.09 [d, 24 H, CH*Me*$_2$, ^3J(HH) = 7], 1.29 [d, 24 H, CH*Me*$_2$, ^3J(HH) = 7], 3.23 [spt, 4 H, C*H*Me$_2$, ^3J(HH) = 7], 4.04 [spt, 4 H, C*H*Me$_2$, ^3J(HH) = 7 Hz], 5.58 (s, 2 H, NH) and 7.00 (m, 12 H, H$_{aryl}$). δ_P(101 MHz, C$_6$D$_6$, 85% H$_3$PO$_4$) 118.7 (s). IR (Nujol): $\tilde{\nu}$/cm^{-1} 3373w (NH) (Found: C, 73.9; H, 8.7; N, 6.9. Calc. for $C_{48}H_{70}N_4P_2$: C, 75.4; H, 9.2; N, 7.3%).

[Zn{(2,6-Pr$^i_2$C$_6$H$_3$)NPN(C$_6$H$_3$Pr$^i_2$-2,6)}$_2$] **6a**. To a solution of compound **5a** (0.90 g, 1.2 mmol) in toluene (60 cm^3) was added dropwise a solution of Zn[N(SiMe$_3$)$_2$]$_2$ (0.45 g, 1.2 mmol) in the same solvent (10 cm^3). The mixture was refluxed for 18 h. Cooling to room temperature led to precipitation of a white solid. The solution was concentrated *in vacuo* to *ca.* 20 cm^3, the white solid filtered off and dried *in vacuo* to give complex **6a** (0.46 g, 47%). Slow cooling of a hot solution of **6a** (0.15 g) in toluene gave colourless blocks suitable for X-ray analysis. M.p. 352 °C (decomp.). Mass spectrum (EI): m/z 826 (M^+, 18) and 651 (M^+ − C$_{12}$H$_{17}$N, 100%). δ_H(250 MHz, C$_6$D$_6$, SiMe$_4$) 1.13 [d, 48 H, CH*Me*$_2$, ^3J(HH) = 7], 2.63 [spt, 8 H, C*H*Me$_2$, ^3J(HH) = 7 Hz] and 7.00 (m, 12 H, H$_{aryl}$). δ_P(161 MHz, C$_6$D$_6$, 85% H$_3$PO$_4$) 349.9 (s). IR (Nujol): $\tilde{\nu}$/cm^{-1} 1261s, 1091s and 800s (Found: C, 68.5; H, 8.6; N, 6.4. Calc. for $C_{48}H_{68}N_4P_2Zn$: C, 69.65; H, 8.35; N, 6.4%).

[Zn(Bu^{t}NPNBu^t)$_2$] **6b**. The reaction was carried out under the same conditions as that leading to compound **6a**. The phosphazane **5b**[14] (0.35 g, 1.0 mmol) and Zn[N(SiMe$_3$)$_2$]$_2$ (0.39 g, 1.0 mmol) led to 0.25 g (63%) of compound **6b**. M.p. 87 °C. Mass spectrum (EI): m/z 410 (M^+, 21) and 143 ($C_6H_{12}N_2P$, 100%). δ_H(250 MHz, C$_6$D$_6$, SiMe$_4$) 1.33 (s, 18 H, CMe$_3$) and 1.34 (s, 18 H, CMe$_3$]. δ_C(63 MHz, C$_6$D$_6$, SiMe$_4$) 33.1 (s), 33.3 (s), 35.1 (s) and 35.2 (s). δ_P(101 MHz, C$_6$D$_6$, 85% H$_3$PO$_4$) 351.6 (s) Found: C, 45.9; H, 8.8; N, 12.4. Calc. for $C_{16}H_{36}N_4P_2Zn$: C, 46.6; H, 8.8; N, 12.45%).

[(2,4,6-Bu$^t_3$C$_6$H$_2$)NPNH(C$_6$H$_4$Pr^i-4)]$_2$ **7**. 4-Isopropylaniline (1.35 g, 10.0 mmol) in hexane (50 cm^3) was lithiated with LiBu^n (0.64 g, 10.0 mmol) in hexane (4.23 cm^3). The mixture was stirred for 2 h at room temperature. After complete lithiation a solution of compound **1** (3.25 g, 10.0 mmol) in hexane (30 cm^3) was added at room temperature. The reaction mixture was stirred for 18 h at room temperature. The precipitated lithium chloride was filtered off. The volume of the remaining solution was reduced and cooled to −18 °C leading to a yellow precipitate of compound **7** in 64% yield (5.42 g). M.p. 107 °C. Mass spectrum (EI): m/z 848 (M^+, 10) and 290 ($C_{18}H_{29}NP$, 100%). δ_H(250 MHz, C$_6$D$_6$, SiMe$_4$) 1.09 [d, 12 H, CH*Me*$_2$, ^3J(HH) = 7], 1.39 (s, 18 H, CMe$_3$), 1.58 (s, 36 H, CMe$_3$), 2.62 [spt, 2 H, C*H*Me$_2$, ^3J(HH) = 7 Hz], 6.01 (br, 2 H, NH), 7.15 (m, 8 H, H$_{aryl}$) and 7.57 (s, 4 H, H$_{aryl}$). δ_C(101 MHz, C$_6$D$_6$, SiMe$_4$) 14.3 (s), 23.0 (s), 24.1 (s), 31.9 (s), 33.5 (s), 36.7 (s), 123.1 (s), 123.7 (s), 126.8 (s), 135.5 (s), 142.1 (s), 143.4 (s), 144.6 (s) and 144.9 (s). δ_P(101 MHz, C$_6$D$_6$, 85% H$_3$PO$_4$) 120.5 (s). IR (Nujol): $\tilde{\nu}$/cm^{-1} 3404w (NH) and 1253s (Found: C, 74.3; H, 9.8; N, 6.3. Calc. for $C_{54}H_{82}N_4P_2$: C, 76.4; H, 9.75; N, 6.6%).

[Zn{(4-Pr^{i}C$_6$H$_4$)NPN(C$_6$H$_2$Bu$^t_3$-2,4,6)}$_2$] **8**. To a solution of [(2,4,6-Bu$^t_3$C$_6$H$_2$)NPNH(C$_6$H$_4$Pr^i-4)]$_2$ (0.85 g, 1.0 mmol) in hexane (30 cm^3) was added ZnMe$_2$ (0.05 g, 0.5 mmol) dissolved in toluene (0.3 cm^3) and refluxed for 18 h. A pale yellow solid was formed after cooling the reaction mixture to −18 °C. The precipitate was filtered off and characterized. Complex **8** was formed in 32% yield (0.29 g). M.p. 177 °C. Mass spectrum (EI): m/z 912 (M^+,10) and 290 ($C_{18}H_{29}NP$, 100%). δ_H(250 MHz, C$_6$D$_6$, SiMe$_4$) 1.14 [d, 12 H, ^3J(HH) = 7, CH*Me*$_2$], 1.31 (s, 36 H, CMe$_3$), 1.34 (s, 18 H, CMe$_3$), 2.69 [spt, 2 H, ^3J(HH) = 7 Hz, C*H*Me$_2$], 6.97 (m, 4 H, H$_{aryl}$), 7.39 (m, 4 H, H$_{aryl}$) and 7.51 (s, 4 H, H$_{aryl}$). δ_P(101 MHz, C$_6$D$_6$, 85% H$_3$PO$_4$) 368.0 (s). IR (Nujol): $\tilde{\nu}$/cm^{-1} 1241s, 997s and 836s (Found: C, 69.8; H, 8.7; N, 5.9. Calc. for $C_{54}H_{80}N_4P_2Zn$: C, 71.05; H, 8.85; N, 6.15%).

[Zn{(C$_{10}$H$_{15}$)NPN(C$_6$H$_2$Bu$^t_3$-2,4,6)}$_2$] **10a** (C$_{10}$H$_{15}$ = adamantyl). Compound **9a**[13] (0.88 g, 2.0 mmol) was dissolved in hexane (40 cm^3). To this solution ZnMe$_2$ (0.05 g, 0.5 mmol) in toluene (0.3 cm^3) was added. After heating the mixture for 2 h a white precipitate was formed. Complex **10a** was isolated by filtration in 0.37 g (39%) yield. M.p. 314 °C. Mass spectrum (EI): m/z 945 (M^+, 70), 888 (M^+ − C$_4$H$_9$, 6) and 135 (C$_{10}$H$_{15}$, 100%). δ_H(250 MHz, C$_6$D$_6$, SiMe$_4$) 1.39 (s, CMe$_3$), 1.40 (s, CMe$_3$), 1.56 (m, 30 H, H$_{adamantyl}$] and 7.40 (s, H$_{aryl}$). δ_P(101 MHz, C$_6$D$_6$, 85% H$_3$PO$_4$) 369.6 (s). IR (Nujol): $\tilde{\nu}$/cm^{-1} 1275s and 1122s (Found: C, 70.1; H, 9.3; N, 5.6. Calc. for $C_{56}H_{88}N_4P_2Zn$: C, 71.2; H, 9.4; N, 5.95%).

[Zn{Bu^{t}NPN(C$_6$H$_2$Bu$^t_3$-2,4,6)}$_2$] **10b**. To a solution of compound **9b**[13] (0.72 g, 1.0 mmol) in hexane (40 cm^3) was added ZnMe$_2$ (0.05 g, 0.5 mmol) in toluene (0.3 cm^3). The reaction was completed by refluxing the mixture for 2 h. The precipitated white solid was separated and characterized; yield of complex **10b** 0.53 g (67%). M.p. 264 °C (decomp.). Mass spectrum (EI): m/z 786 (M^+, 100) and 729 (M^+ − C$_4$H$_9$, 16%). δ_H(250 MHz, CDCl$_3$, SiMe$_4$) 1.07 (s, 18 H, CMe$_3$), 1.27 (s, 36 H, CMe$_3$), 1.49 (s, 18 H, CMe$_3$) and 7.28 (br, 4 H, H$_{aryl}$). δ_C(63 MHz, CDCl$_3$, SiMe$_4$) 31.7 (s), 33.8 (s), 34.1 (s), 34.4 (s), 34.6 (s), 36.8 (s), 121.9 (s), 123.2 (s), 143.1 (s) and 143.7 (s). δ_P(101 MHz, CDCl$_3$, 85% H$_3$PO$_4$) 368.0 (s). IR (Nujol): $\tilde{\nu}$/cm^{-1} 1104s, 1027s

Table 4 Crystallographic data for compounds **2** and **6a**

	2	**6a**
Empirical formula	$C_{39}H_{68}ClN_3P_2Si$	$C_{48}H_{68}N_4P_2Zn$
M	704.4	828.4
Data collection at T/°C	−123(2)	−120(2)
Crystal dimensions/mm	0.1 × 0.4 × 0.5	0.3 × 0.4 × 0.6
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a/pm	1168.6(3)	2336.7(5)
b/pm	1300.5(4)	937.0(2)
c/pm	1552.7(4)	2390.4(5)
α/°	110.74(2)	90
β/°	90.05(2)	116.61(2)
γ/°	103.64(2)	90
U/nm^3	2.135(2)	4.679(2)
Z	2	4
D_c/Mg m^{-3}	1.096	1.176
μ/mm^{-1}	0.221	0.629
F(000)	768	1776
Measured 2θ range/°	7–45	7–45
Data measured, unique, observed	6755, 5566, 5549	3060, 3047, 3040
R^a, $wR2^b$ [$I > 2\sigma(I)$]	0.0435, 0.1009	0.0307, 0.0652
(all data)	0.0570, 0.1184	0.0384, 0.0724
Goodness of fit S^c	1.047	1.112
Weighting factors a, b^d	0.046, 1.582	0.020, 7.500
Refined parameters	439	250
Largest difference peak, hole/e Å^{-3}	3.82, −3.06	2.15, −2.36

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]^{\frac{1}{2}}$. [c] $S = [\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma(n - p)]^{\frac{1}{2}}$ where n is the number of observed reflections and p the number of parameters refined. [d] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 5 Atomic coordinates (× 10^4) for compound **2**

Atom	x	y	z	Atom	x	y	z
P(1)	8 838(1)	9 080(1)	3 848(1)	C(16)	8 722(2)	8 130(2)	1 165(2)
P(2)	6 687(1)	8 223(1)	3 089(1)	C(160)	9 469(2)	7 330(2)	1 245(2)
N(1)	6 333(2)	6 790(2)	2 603(2)	C(161)	8 762(3)	6 373(2)	1 549(2)
N(2)	7 489(2)	8 622(2)	4 164(2)	C(162)	10 566(3)	8 044(3)	1 926(2)
N(3)	8 111(2)	8 601(2)	2 767(1)	C(163)	9 934(3)	6 734(3)	316(2)
Si	6 942(1)	8 978(1)	5 261(1)	C(21)	5 155(2)	6 142(2)	2 611(2)
Cl	9 647(1)	7 796(1)	3 966(1)	C(22)	4 187(2)	6 319(2)	2 192(2)
C(1)	7 853(3)	8 622(3)	6 039(2)	C(220)	4 210(2)	6 764(2)	1 384(2)
C(2)	5 375(3)	8 140(3)	5 057(2)	C(221)	3 248(3)	5 887(3)	615(2)
C(3)	7 025(3)	10 522(3)	5 760(2)	C(222)	5 367(3)	6 851(3)	910(2)
C(11)	8 286(2)	8 878(2)	1 938(2)	C(223)	3 897(3)	7 914(3)	1 689(2)
C(12)	7 868(2)	9 766(2)	1 835(2)	C(23)	3 077(2)	5 971(2)	2 479(2)
C(120)	7 603(3)	10 838(2)	2 588(2)	C(24)	2 862(2)	5 361(2)	3 057(2)
C(121)	8 348(3)	11 894(2)	2 432(2)	C(240)	1 652(2)	5 094(2)	3 427(2)
C(122)	6 291(3)	10 808(3)	2 482(2)	C(241)	642(3)	5 002(3)	2 760(3)
C(123)	7 925(4)	11 033(3)	3 597(2)	C(242)	1 658(3)	6 075(3)	4 351(2)
C(13)	7 686(2)	9 743(2)	932(2)	C(243)	1 411(3)	3 989(3)	3 617(2)
C(14)	7 953(2)	8 944(2)	158(2)	C(25)	3 815(2)	5 007(2)	3 294(2)
C(140)	7 702(3)	8 899(3)	−830(2)	C(26)	4 962(2)	5 364(2)	3 083(2)
C(141)	6 917(3)	7 722(3)	−1 406(2)	C(260)	5 946(3)	4 851(2)	3 304(2)
C(142)	7 090(3)	9 806(3)	−852(2)	C(261)	6 907(3)	5 729(3)	4 055(2)
C(143)	8 875(3)	9 087(3)	−1 267(2)	C(262)	6 498(3)	4 303(3)	2 400(2)
C(15)	8 516(2)	8 181(2)	302(2)	C(263)	5 460(3)	3 894(3)	3 671(2)

and 801s (Found: C, 66.1; H, 9.5; N, 6.9. Calc. for $C_{44}H_{76}N_4P_2Zn$: C, 67.05; H, 9.7; N, 7.1%).

[Zn{(2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPN(C$_6$H$_2$Bu$^t{}_3$-2,4,6)}Me] **12**. To a solution of compound **11**[6] (0.55 g, 1.0 mmol) in hexane (50 cm^3) was added ZnMe$_2$ (0.10 g, 1.0 mmol) in toluene (0.6 cm^3). The reaction mixture was heated at reflux for 2 h leading to a pale yellow precipitate upon cooling the solution to 0 °C. Yield of complex **12** 0.47 g (74%). M.p. 244 °C. Mass spectrum (EI): m/z 628 (M^+, 10), 571 (M^+ − C_4H_9, 59) and 290 ($C_{18}H_{29}NP$, 100%). δ_H(250 MHz, C_6D_6, SiMe$_4$) −0.10 (s, 3 H, ZnMe), 1.38 (s, 36 H, CMe$_3$), 1.67 (s, 18 H, CMe$_3$) and 7.61 (s, 4 H, H$_{aryl}$). δ_C(63 MHz, C_6D_6, SiMe$_4$) −12.1 (s), 31.9 (s), 33.2 (s), 34.8 (s), 36.9 (s), 123.0 (s), 136.9 (s), 141.1 (s) and 143.6 (s). δ_P(101 MHz, C_6D_6, 85% H_3PO_4) 365.0 (s). IR (Nujol): $\tilde{\nu}$/cm^{-1} 1263s, 1095s and 798s (Found: C, 69.1; H, 9.7; N, 3.9; P, 4.9. Calc. for $C_{37}H_{61}N_2PZn$: C, 70.15; H, 9.75; N, 4.45; P, 4.9%).

Crystal-structure Determinations of Compounds **2** *and* **6a**.—Data were collected on a Siemens-Stoe AED 2 four-circle diffractometer using graphite-monochromated Mo-Kα radiation (λ = 71.073 pm) and ω–2θ scans following the learnt-profile method.[16] The intensity controls were stable to within 3% during the data collection. An absorption correction based on ψ-scans was applied for complex **6a**: merging R decreased from 0.019 to 0.010, maximum and minimum transmission factors 0.55 and 0.50. Both structures were solved by direct methods[17,18] and refined against F^2 by full-matrix least squares[19] on all data.

Table 6 Atomic coordinates ($\times 10^4$) for complex **6a**

Atom	*x*	*y*	*z*
Zn	5000	1415(1)	2500
N(1)	5206(1)	3165(2)	3062(1)
P(1)	5000	4292(1)	2500
N(2)	5574(1)	−340(2)	2812(1)
P(2)	5000	−1463(1)	2500
C(11)	5545(1)	3464(3)	3719(1)
C(12)	6212(1)	3679(3)	3996(1)
C(13)	6520(1)	3946(3)	4640(1)
C(14)	6191(1)	3967(3)	4994(1)
C(15)	5539(1)	3717(3)	4715(1)
C(16)	5204(1)	3460(3)	4075(1)
C(121)	6585(1)	3657(3)	3614(1)
C(122)	6673(2)	5170(3)	3428(2)
C(123)	7230(1)	2891(3)	3947(1)
C(161)	4485(1)	3216(3)	3759(1)
C(162)	4132(1)	4626(3)	3501(1)
C(163)	4237(2)	2499(4)	4179(1)
C(21)	6219(1)	−676(3)	3257(1)
C(22)	6359(1)	−920(3)	3886(1)
C(23)	6993(1)	−1260(3)	4300(1)
C(24)	7462(1)	−1345(3)	4102(1)
C(25)	7316(1)	−1055(3)	3488(1)
C(26)	6695(1)	−700(3)	3053(1)
C(221)	5853(1)	−835(3)	4116(1)
C(222)	6088(1)	−96(3)	4752(1)
C(223)	5581(1)	−2315(3)	4129(1)
C(261)	6541(1)	−368(3)	2380(1)
C(262)	7065(2)	454(5)	2312(2)
C(263)	6362(2)	−1716(4)	1984(2)

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined riding on the respective carbon atom, except for H(7) in compound **2** which was located in the Fourier-difference map and refined with a N–H distance of 88(1) pm. Largest difference peaks: **2** 3.82 e Å^{-3} near to P(1); **6a** 2.15 e Å^{-3} near C(21) and C(26). Crystallographic data are summarized in Table 4, fractional atomic coordinates for **2** and **6a** are given in Tables 5 and 6 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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