Metallation of the Acyclic Phosphazene Ligand $HN[P(NMe_2)_2NSiMe_3]_2$. Synthesis and Crystal Structure of $\{NaN[P(NMe_2)_2NSiMe_3]_2\}_2$, $\{KN[P(NMe_2)_2NSiMe_3]_2\}_\infty$ and $Ca\{N[P(NMe_2)_2NSiMe_3]_2\}_2$†

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The reaction of $HN[P(NMe_2)_2NSiMe_3]_2$ with NaH and KH in 1:1 molar ratio yielded a dimer $\{NaN[P(NMe_2)_2NSiMe_3]_2\}_2$ **1** and a polymer $KN[P(NMe_2)_2NSiMe_3]_2$ **2** with a zigzag chain structure, respectively. The reaction of $Ca[N(SiMe_3)_2]_2\cdot 2thf$ (thf = tetrahydrofuran) with the phosphazene in 1:2 molar ratio in hexane resulted in the formation of a monomeric spirocyclic phosphazene complex $Ca\{N[P(NMe_2)_2NSiMe_3]_2\}_2$ **3** where the mode of chelation is tridentate. The crystal structures of **1**–**3** have been determined.

In the last few years a large amount of work has been carried out on phosphazene derivatives.[1] The chemistry of phosphazene–metal complexes exhibits some interesting facets concerning their structures and their physical properties.[2] We have investigated these species extensively in recent years.[3,4] A survey of the literature reveals that many reports have been published on their complexes with transition metals as well as main group elements. Although alkali-metal and mixed-metal amides (Li, Na, K), which are useful synthetic reagents, have been investigated, [5,6] there are no reports of alkaline-earth metals.[1,7] In view of this we have started to explore this chemistry and recently reported on the synthesis of the first solvent-free chelate and cubic complexes of barium.[8] In this paper, we report on the synthesis and crystal structures of phosphazene derivatives of Na, K and Ca.

Results and Discussion

When $HN[P(NMe_2)_2NSiMe_3]_2$ in toluene is heated to reflux with NaH or KH respectively the alkali-metal (Na, K) phosphazene compounds **1** and **2** are obtained [equations (1) and (2)]. They are quite soluble in hydrocarbons. The reaction of calcium bis(trimethylsilyl)amide with the phosphazene in the molar ratio of 1:2 yields quantitatively a spirocyclic phosphazene derivative **3** after stirring for 16 h at room temperature [equation (3)]. It is supposed that complexation proceeds *via* the elimination of two molecules of $HN(SiMe_3)_2$.

$$2\,HN[P(NMe_2)_2NSiMe_3]_2 + 2\,NaH \longrightarrow \underset{\mathbf{1}}{\{NaN[P(NMe_2)_2NSiMe_3]_2\}_2} + 2\,H_2 \quad (1)$$

$$HN[P(NMe_2)_2NSiMe_3]_2 + KH \longrightarrow \underset{\mathbf{2}}{KN[P(NMe_2)_2NSiMe_3]_2} + H_2 \quad (2)$$

$$2\,HN[P(NMe_2)_2NSiMe_3]_2 + Ca[N(SiMe_3)_2]_2 \longrightarrow \underset{\mathbf{3}}{Ca\{N[P(NMe_2)_2NSiMe_3]_2\}_2} + 2\,HN(SiMe_3)_2 \quad (3)$$

However, the 1:1 reaction of $Ca[N(SiMe_3)_2]_2$ with the phosphazene yields **3** together with unreacted calcium bis(trimethylsilyl)amide. In the mechanism of reaction it is assumed that in the first step a low co-ordinated unstable monocyclic species is formed. Further cyclisation takes place in order to enhance the co-ordination number. Complex **3** is a light yellow solid melting at 115 °C. It is highly soluble in organic solvents. By cooling its hexane solution at 0 °C a 60–70% yield of crystallised product is formed.

The ^1H NMR spectra of compounds **1**–**3** show a characteristic resonance pattern for the $N(SiMe_3)$ groups in accordance with the symmetric nature of the ligand. In the ^{31}P NMR spectra of **1** and **2** a high-field chemical shift is observed in comparison to the phosphazene. In contrast compound **3** does not show any appreciable ^{31}P NMR shift from that of the starting phosphazene. The occurrence of only one singlet in the ^{31}P NMR spectra of these compounds at room temperature suggests that the phosphorus centres are equivalent in solution. This occurs even in the spectrum of **1**, for which the solid-state structure has two ^{31}P environments.

Crystal Structures of the Metallated Phosphazenes.—Selected bond lengths and angles are listed in Tables 1–3. Suitable crystals of complex **1** were obtained from a solution of it in pentane. The dimeric contact ion pair adopts C_i symmetry (Fig. 1). The sodium atoms are surrounded by two phosphazene ligands. Only the nitrogen atoms of the phosphazene systems have donor functions, while the dimethylamino groups together with the trimethylsilyl groups form a non-polar surface around the metal centre of the molecule. Each sodium atom is four-co-ordinated. There are two short distances to terminal nitrogen atoms of each ligand [Na(1)–N(1) 238.9(2), Na(1)–N(3a) 243.3(2) pm], which are comparable with Na–N distances in the sodium aminoimino phosphoranate $[Na(thf)_6]Na[(N\text{-}SiMe_3)_2PPh_2]$ (thf = tetrahydrofuran) [Na–N 238.9–242.4 pm],[9] and two longer distances to a central and a terminal nitrogen atom of one ligand [Na(1)–N(2) 266.6(2), Na(1)–N(3) 271.8(2) pm].

The analogous potassium compound has a totally different geometry. Crystals of **2** were obtained by cooling a hot saturated hexane solution to room temperature. The solid-state structure consists of polymeric zigzag chains in which ligands and metal atoms alternate (Fig. 2). Also the nitrogen atoms of the dimethylamino groups take part in the co-ordination. Each

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

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

Na(1)–N(1)	238.9(2)	Na(1)–N(3a)	243.3(2)
Na(1)–N(2)	266.6(2)	Na(1)–N(3)	271.8(2)
Na(1) ··· Na(1a)	327.7(2)	P(1)–N(1)	156.4(2)
P(1)–N(2)	158.4(2)	P(1)–N(5)	168.3(2)
P(1)–N(4)	168.3(2)	P(2)–N(2)	156.4(2)
P(2)–N(3)	157.2(2)	P(2)–N(6)	167.4(2)
P(2)–N(7)	170.2(2)	Si(1)–N(3)	171.0(2)
Si(2)–N(1)	169.2(2)		
N(1)–Na(1)–N(3a)	138.99(7)	N(1)–Na(1)–N(2)	61.78(6)
N(3a)–Na(1)–N(2)	128.66(7)	N(1)–Na(1)–N(3)	114.55(7)
N(3a)–Na(1)–N(3)	101.18(6)	N(2)–Na(1)–N(3)	60.44(6)
N(1)–P(1)–N(2)	111.72(10)	N(1)–P(1)–N(5)	110.72(10)
N(2)–P(1)–N(5)	109.88(10)	N(1)–P(1)–N(4)	116.84(10)
N(2)–P(1)–N(4)	107.55(10)	N(5)–P(1)–N(4)	99.39(10)
N(2)–P(2)–N(3)	119.53(10)	N(2)–P(2)–N(6)	108.67(10)
N(3)–P(2)–N(6)	110.10(10)	N(2)–P(2)–N(7)	103.58(10)
N(3)–P(2)–N(7)	104.55(9)	N(6)–P(2)–N(7)	109.89(10)
P(1)–N(1)–Si(2)	139.51(12)	P(2)–N(2)–P(1)	158.16(14)
P(2)–N(3)–Si(1)	133.74(12)		

Symmetry transformation used to generate equivalent atoms: a $-x + 1, -y, -z + 2$.

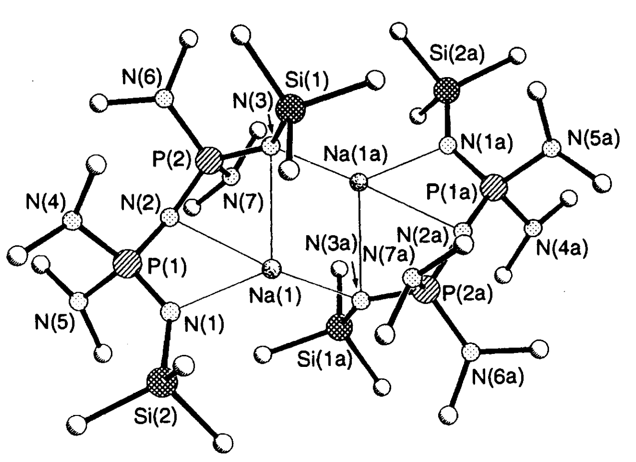

Fig. 1 Molecular structure of complex **1**

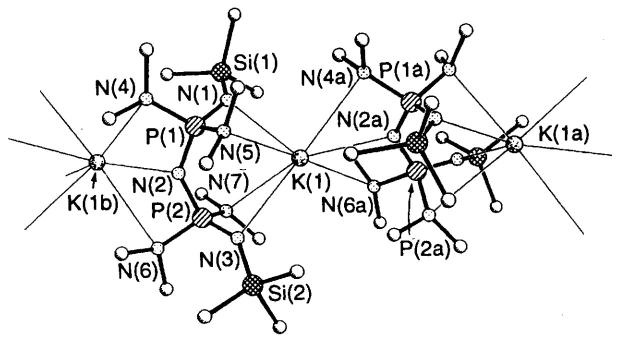

Fig. 2 Molecular structure of complex **2**

potassium atom is surrounded by the back of the last and the front side of the next ligand. Both ligands are twisted with respect to each other by an angle of 89.3°. There are four relatively short potassium–nitrogen distances to N(1) [291.9(2)] N(2a) [298.7(2)], N(5) [303.6(2)] and N(3) [311.4(2) pm] and three longer distances to N(4a) [336.7(2)], N(6a) [339.1(2)] and N(7) [344.7(3) pm].

Keeping a solution of complex **3** in hexane at 0 °C for 7 d yielded suitable crystals for X-ray investigation. The compound is a monomer in the solid state (Fig. 3). Two tridentate phosphazene ligands surround the central calcium atom, which is co-ordinated almost linearly by the central nitrogen atoms of the ligands N(4) and N(11) [N(4)–Ca(1)–N(11) 172.1(1)°] and tetrahedrally by the terminal phosphazene nitrogen atoms [N(1), N(7), N(8) and N(14)]. The calcium atom is almost in a plane with the nitrogen atoms of each ligand. Both ligands are twisted with respect to each other by an angle of 88°. The bonding pattern in **3** has also been found in the analogous barium compound.[8] The metal–nitrogen distances are 30 pm longer than the corresponding distances in **2**.

The phosphorus–nitrogen bond lengths in the phosphazene systems of **1**–**3** are in the range 155–160 pm. This indicates delocalisation of the electron density within the anions. The

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

K(1)–N(1)	291.9(2)	K(1)–N(2a)	298.7(2)
K(1)–N(5)	303.6(2)	K(1)–N(3)	311.4(2)
K(1)–N(4a)	336.7(2)	K(1)–N(6a)	339.1(2)
K(1)–N(7)	344.7(3)	P(1)–N(1)	155.8(2)
P(1)–N(2)	159.1(2)	P(1)–N(4)	169.6(2)
P(1)–N(5)	170.0(2)	P(2)–N(3)	155.1(2)
P(2)–N(2)	160.0(2)	P(2)–N(7)	168.4(2)
P(2)–N(6)	170.0(2)	Si(1)–N(1)	168.8(2)
Si(2)–N(3)	168.3(2)		
N(1)–K(1)–N(2a)	125.51(5)	N(1)–K(1)–N(5)	51.35(5)
N(2a)–K(1)–N(5)	136.63(5)	N(1)–K(1)–N(3)	92.77(5)
N(2a)–K(1)–N(3)	141.37(5)	N(5)–K(1)–N(3)	69.34(5)
N(1)–K(1)–N(4a)	90.55(5)	N(2a)–K(1)–N(4a)	46.96(5)
N(5)–K(1)–N(4a)	91.28(5)	N(3)–K(1)–N(4a)	151.60(5)
N(1)–K(1)–N(6a)	126.83(5)	N(2a)–K(1)–N(6a)	46.09(5)
N(5)–K(1)–N(6a)	177.05(5)	N(3)–K(1)–N(6a)	109.11(5)
N(4a)–K(1)–N(6a)	91.06(5)	N(1)–K(1)–N(7)	72.14(5)
N(2a)–K(1)–N(7)	134.47(5)	N(5)–K(1)–N(7)	88.36(5)
N(3)–K(1)–N(7)	46.31(5)	N(4a)–K(1)–N(7)	157.97(5)
N(6a)–K(1)–N(7)	88.79(5)	N(1)–P(1)–N(2)	120.81(9)
N(1)–P(1)–N(4)	111.39(9)	N(2)–P(1)–N(4)	102.03(9)
N(1)–P(1)–N(5)	104.78(9)	N(2)–P(1)–N(5)	108.19(9)
N(4)–P(1)–N(5)	109.37(9)	N(3)–P(2)–N(2)	119.54(10)
N(3)–P(2)–N(7)	106.76(10)	N(2)–P(2)–N(7)	108.25(9)
N(3)–P(2)–N(6)	117.60(10)	N(2)–P(2)–N(6)	99.79(9)
N(7)–P(2)–N(6)	103.59(10)	P(1)–N(1)–Si(1)	135.39(11)
P(1)–N(2)–P(2)	134.45(11)	P(2)–N(3)–Si(2)	144.73(12)

Symmetry transformation used to generate equivalent atoms: a $x, -y + \frac{1}{2}, z + \frac{1}{2}$.

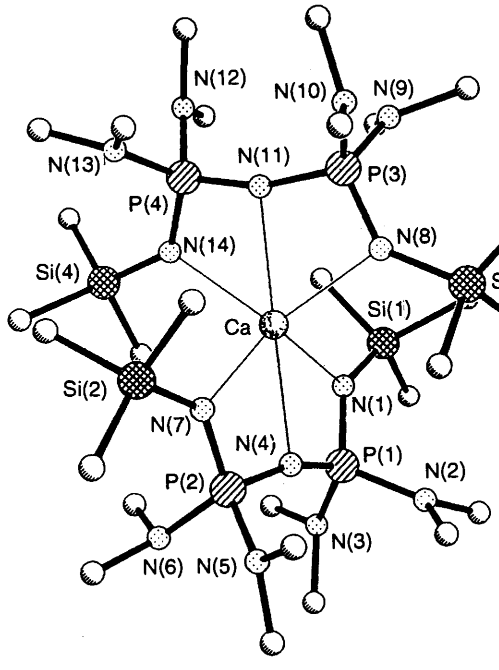

Fig. 3 Molecular structure of complex **3**

central P–N–P angle increases in the sequence **2** [134.45(11)], **1** [158.2(1)], **3** [161.4(2) and 162.0(2)°], showing the high flexibility of the ligand.

Experimental

The complexes described are moisture and air sensitive. Therefore, all syntheses and subsequent manipulations were conducted under nitrogen using Schlenk, vacuum-line and glovebox techniques. Solvents were dried prior to use and kept under dry nitrogen. The phosphazene[10] and Ca[N(SiMe$_3$)$_2$]$_2$·2thf[11] were prepared as previously described; NaH and KH (Aldrich) were used as received. The IR spectra were recorded on a Bio-Rad FTS 7 spectrophotometer, and NMR spectra on a Bruker AM 250 spectrometer using SiMe$_4$ and 85% H$_3$PO$_4$ as external references, respectively. Analyses were obtained from the analytical laboratory, Institut für anorganische Chemie, Universität Göttingen.

Table 3 Selected bond lengths (pm) and angles (°) for complex **3**

Ca–N(11)	246.1(3)	Ca–N(4)	246.8(3)
Ca–N(8)	256.1(3)	Ca–N(7)	256.5(3)
Ca–N(1)	258.3(3)	Ca–N(14)	263.1(3)
N(1)–P(1)	157.0(3)	N(1)–Si(1)	169.7(3)
P(1)–N(4)	158.1(3)	P(1)–N(2)	166.4(3)
P(1)–N(3)	166.5(3)	N(4)–P(2)	158.3(3)
P(2)–N(7)	157.0(3)	P(2)–N(5)	165.2(3)
P(2)–N(6)	167.7(3)	N(7)–Si(2)	170.1(3)
N(8)–P(3)	157.1(3)	N(8)–Si(3)	170.4(3)
P(3)–N(11)	158.1(3)	P(3)–N(9)	165.9(3)
P(3)–N(10)	166.2(3)	N(11)–P(4)	158.3(3)
P(4)–N(14)	157.2(3)	P(4)–N(13)	166.0(3)
P(4)–N(12)	166.5(3)	N(14)–Si(4)	170.4(3)
N(11)–Ca–N(4)	172.08(11)	N(11)–Ca–N(8)	60.39(10)
N(4)–Ca–N(8)	114.31(10)	N(11)–Ca–N(7)	114.39(10)
N(4)–Ca–N(7)	60.05(10)	N(8)–Ca–N(7)	104.70(10)
N(11)–Ca–N(1)	125.54(10)	N(4)–Ca–N(1)	60.41(10)
N(8)–Ca–N(1)	104.81(10)	N(7)–Ca–N(1)	120.06(10)
N(11)–Ca–N(14)	59.77(10)	N(4)–Ca–N(14)	126.17(10)
N(8)–Ca–N(14)	119.44(10)	N(7)–Ca–N(14)	107.02(10)
N(1)–Ca–N(14)	101.77(10)	P(1)–N(1)–Si(1)	138.9(2)
N(1)–P(1)–N(4)	107.6(2)	N(1)–P(1)–N(2)	115.4(2)
N(4)–P(1)–N(2)	106.0(2)	N(1)–P(1)–N(3)	110.4(2)
N(4)–P(1)–N(3)	115.4(2)	N(2)–P(1)–N(3)	102.1(2)
P(1)–N(4)–P(2)	162.0(2)	N(7)–P(2)–N(4)	106.1(2)
N(7)–P(2)–N(5)	112.3(2)	N(4)–P(2)–N(5)	115.0(2)
N(7)–P(2)–N(6)	117.2(2)	N(4)–P(2)–N(6)	106.8(2)
N(5)–P(2)–N(6)	99.6(2)	P(2)–N(7)–Si(2)	136.8(2)
P(3)–N(8)–Si(3)	137.6(2)	N(8)–P(3)–N(11)	106.6(2)
N(8)–P(3)–N(9)	117.2(2)	N(11)–P(3)–N(9)	107.0(2)
N(8)–P(3)–N(10)	111.7(2)	N(11)–P(3)–N(10)	114.6(2)
N(9)–P(3)–N(10)	100.0(2)	P(3)–N(11)–P(4)	161.4(2)
N(14)–P(4)–N(11)	107.4(2)	N(14)–P(4)–N(13)	115.3(2)
N(11)–P(4)–N(13)	105.8(2)	N(14)–P(4)–N(12)	110.8(2)
N(11)–P(4)–N(12)	116.1(2)	N(13)–P(4)–N(12)	101.6(2)
P(4)–N(14)–Si(4)	134.4(2)		

Table 5 Atomic coordinates (× 10^4) for complex **1**

Atom	*x*	*y*	*z*
Na(1)	4 874(1)	366(1)	11 130(1)
P(1)	3 903(1)	1 622(1)	11 221(1)
P(2)	4 630(1)	1 095(1)	9 043(1)
Si(1)	7 458(1)	704(1)	9 575(1)
Si(2)	4 336(1)	1 160(1)	13 555(1)
N(1)	4 281(2)	1 186(1)	12 179(1)
N(2)	3 986(2)	1 323(1)	10 069(1)
N(3)	5 800(2)	643(1)	9 192(1)
N(4)	4 763(2)	2 250(1)	11 226(2)
N(5)	2 375(2)	1 894(1)	11 304(2)
N(6)	5 068(2)	1 669(1)	8 316(2)
N(7)	3 378(2)	723(1)	8 333(1)
C(1)	6 112(3)	2 224(1)	10 909(2)
C(2)	4 683(3)	2 642(1)	12 155(2)
C(3)	1 353(2)	1 496(1)	11 611(2)
C(4)	1 858(3)	2 297(1)	10 443(2)
C(5)	4 334(3)	2 219(1)	8 303(3)
C(6)	5 756(3)	1 597(1)	7 339(2)
C(7)	2 028(2)	940(1)	8 346(2)
C(8)	3 613(3)	536(1)	7 230(2)
C(9)	8 273(3)	50(1)	9 034(2)
C(10)	8 341(3)	1 355(1)	9 072(2)
C(11)	7 793(3)	696(1)	11 096(2)
C(12)	3 425(3)	1 756(1)	14 224(2)
C(13)	3 583(3)	457(1)	13 969(2)
C(14)	6 086(3)	1 169(2)	14 161(2)
C(61)	−249(14)	1 154(4)	4 509(10)
C(62)	−86(19)	670(4)	5 357(10)
C(63)	−179(14)	89(3)	4 791(11)
C(64)	290(14)	−398(3)	5 539(12)
C(65)	127(20)	−970(4)	4 908(13)

Table 4 Crystal data for compounds **1**–**3**

Compound	**1**	**2**	**3**
Colour	Colourless	Colourless	Colourless
Formula	$C_{28}H_{84}Na_2N_{14}P_4Si_4$	$C_{14}H_{42}KN_7P_2Si_2$	$C_{28}H_{84}CaN_{14}P_4Si_4$
Formula weight	899.2	465.8	893.4
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/pm	1014.7(1)	1121.1(3)	1997.5(2)
b/pm	2290.6(2)	1894.3(5)	1255.5(2)
c/pm	1231.1(2)	1291.8(3)	2057.4(3)
β/°	95.30(2)	112.04(2)	104.30(1)
U/nm^3	2.892(6)	2.543(1)	5.000(1)
Z	2	4	4
F(000)	1060	1008	1944
D_c/g cm^{-3}	1.132	1.217	1.187
Crystal size/mm	0.5 × 0.4 × 0.3	0.4 × 0.3 × 0.3	0.4 × 0.3 × 0.3
μ/mm^{-1}	0.269	0.443	0.386
No. data measured	4907	4906	6813
No. unique data	3737	4548	6498
2θ range/°	8–45	8–50	8–45
$R [I > 2\sigma(I)]$*	0.0330	0.0340	0.0443
R'	0.0846	0.0918	0.1075
g_1	0.0332	0.0427	0.0322
g_2	2.2368	1.7685	8.0907
ρ/e nm^{-3}	261	347	325

* $R = \Sigma|F_o - F_c|/\Sigma F_o$ and $R' = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{\frac{1}{2}}$.

Syntheses.—$\{NaN[P(NMe_2)_2NSiMe_3]_2\}_2$ **1**. The phosphazene (3.5 g, 8.2 mmol) and NaH (0.2 g, 8.3 mmol) were refluxed in toluene (25 cm^3) until the liberation of hydrogen gas ceased. A homogeneous solution was obtained along with some undissolved NaH which was filtered off. All volatiles were evaporated under reduced pressure. The crude product can be purified by recrystallisation from hexane solution at −30 °C (1.6 g, 43%), m.p. 102 °C (Found: C, 37.4; H, 9.4; N, 21.8%; *M* 449. $C_{14}H_{42}N_7NaP_2Si_2$ requires C, 37.1; H, 9.1; N, 21.8%; *M* 449); $\tilde{\nu}/cm^{-1}$(Nujol) 1330s, 1254vs, 1241vs, 1210vs, 1183vs, 972vs, 861s and 827vs; $\delta_H(C_6D_6)$ 0.30 (18 H, s, $SiMe_3$) and 2.63 (24 H, m, NMe_2); $\delta_C(C_6D_6)$ 5.1 (s, $SiMe_3$) and 39.0 (s, NMe_2); $\delta_{Si}(C_6D_6)$ −16.2 (m); $\delta_P(C_6D_6)$ 9.8 (s); *m/z* 449 (M^+, 78) and 362 ($M - 2NMe_2 + H$, 100%).

$KN[P(NMe_2)_2NSiMe_3]_2$ **2** The phosphazene (2.0 g, 4.7 mmol) and KH (0.2 g, 5.0 mmol) were refluxed in toluene (25 cm^3) as above. A homogeneous solution was obtained along with some undissolved KH which was filtered off from the hot hexane solution. Complex **2** crystallises upon cooling the solution to room temperature (1.2 g, 55%), m.p. 165 °C (Found: C, 36.1; H, 9.1; N, 21.1%; *M* 465. $C_{14}H_{42}KN_7P_2Si_2$ requires C, 35.1; H, 9.2; N, 21.6%; *M* 465); $\tilde{\nu}/cm^{-1}$(Nujol) 1261vs, 1227vs, 1196vs, 1170vs, 963vs, 951vs, 860s and 825vs; $\delta_H(C_6D_6)$ 0.34 (18 H, s, $SiMe_3$) and 2.79 (24 H, m, NMe_2); $\delta_C(C_6D_6)$ 5.1 (s, $SiMe_3$) and 39.0 (s, NMe_2); $\delta_{Si}(C_6D_6)$ −20.1 (m); $\delta_P(C_6D_6)$ 6.4 (s); *m/z* 465 (M^+, 100%).

$Ca\{N[P(NMe_2)_2NSiMe_3]_2\}_2$ **3**. The compound $Ca[N(SiMe_3)_2]_2\cdot 2thf$ (1.2 g, 2.4 mmol) was dissolved in hexane (20 cm^3) in a 100 cm^3 flask. A solution of the phosphazene (2.0 g, 4.7 mmol) in hexane was added slowly dropwise at room temperature. The reaction mixture was stirred for 16 h at room temperature. Evaporation of all volatiles and drying overnight in vacuum yielded a light yellow solid product, 2.0 g (98%). This is sufficiently spectroscopically pure but can be further purified by recrystallisation from hexane at 0 °C (Found: C, 37.4; H, 9.2; N, 21.9%; *M* 892. $C_{28}H_{84}CaN_{14}P_4Si_4$ requires C, 37.7; H, 9.4; N, 22.0%; *M* 892); $\tilde{\nu}/cm^{-1}$(Nujol) 1919m(br), 1404s, 1310s, 1255m(br), 1191(br), 1145(br), 1064s, 993s, 973vs, 858s, 829s, 778m, 751m, 720m, 612s, 564s, and 506vs; $\delta_H(CDCl_3)$ 0.04 (s, 18 H, $SiMe_3$) and 2.5–2.6 (d, 24 H, NMe_2); $\delta_P(CDCl_3)$ 19.0 (s); *m/z* 892 (M^+, 28) and 820 ($M - 2\,SiMe_3 + H$, 100%).

Crystallography.—The intensities for all structures were measured on a Stoe-Siemens AED diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Data were collected from oil-coated rapidly cooled crystals at 153 K with a profile-fitting method.[12] Crystal data are listed in Table 4. All structures were solved by direct methods[13] and were refined by full-matrix least squares against F^2.[14] Non-H atoms were refined with anisotropic displacement parameters and H atoms were set geometrically. A weighting scheme of the form $w^{-1} = \sigma(F_o^2) + (g_1P)^2 + g_2P$ with $P = (F_o^2 + 2F_c^2)/3$ was introduced for each structure. In **1** there is also an unco-ordinated

Table 6 Atomic coordinates (× 10^4) for complex **2**

Atom	*x*	*y*	*z*
K(1)	8 300(1)	2 424(1)	4 880(1)
P(1)	9 695(1)	2 268(1)	3 024(1)
P(2)	6 949(1)	1 895(1)	2 053(1)
Si(1)	9 970(1)	3 836(1)	3 375(1)
Si(2)	6 050(1)	668(1)	3 151(1)
N(1)	9 828(2)	2 978(1)	3 665(1)
N(2)	8 364(2)	2 045(1)	2 078(1)
N(3)	6 773(2)	1 404(1)	2 947(2)
N(4)	10 715(2)	2 233(1)	2 331(1)
N(5)	10 114(2)	1 637(1)	4 034(1)
N(6)	6 196(2)	1 663(1)	690(1)
N(7)	6 269(2)	2 674(1)	2 141(2)
C(1)	9 864(3)	3 993(1)	1 908(2)
C(2)	11 544(3)	4 222(1)	4 313(2)
C(3)	8 705(3)	4 382(1)	3 605(2)
C(4)	6 902(3)	319(1)	4 593(2)
C(5)	4 343(2)	827(2)	3 011(3)
C(6)	6 023(3)	−90(2)	2 211(3)
C(7)	10 738(2)	1 605(1)	1 681(2)
C(8)	12 002(2)	2 540(1)	2 846(2)
C(9)	9 867(2)	894(1)	3 714(2)
C(10)	11 404(2)	1 718(1)	4 905(2)
C(11)	6 757(2)	1 085(1)	271(2)
C(12)	4 796(2)	1 602(2)	277(2)
C(13)	6 277(3)	3 236(1)	1 375(2)
C(14)	5 162(2)	2 714(1)	2 476(2)

Table 7 Atomic coordinates (× 10^4) for complex **3**

Atom	*x*	*y*	*z*
Ca	2514.1(4)	4792.4(6)	2023.6(4)
N(1)	2150(2)	2834(2)	1760.0(15)
Si(1)	1517.5(6)	2397.4(10)	1103.7(5)
C(1)	1770(3)	2554(4)	296(2)
C(2)	1255(2)	962(4)	1116(3)
C(3)	719(2)	3180(4)	1077(2)
P(1)	2796.0(5)	2379.8(8)	2284.5(5)
N(2)	3379(2)	1769(3)	1961(2)
C(4)	3197(2)	787(4)	1590(2)
C(5)	4108(2)	1999(4)	2119(2)
N(3)	2559(2)	1412(3)	2734(2)
C(6)	3090(2)	870(4)	3241(2)
C(7)	1884(2)	1353(4)	2875(2)
N(4)	3184(2)	3352(2)	2702.4(15)
P(2)	3602.2(5)	4059.0(8)	3303.4(5)
N(5)	4433(2)	3774(3)	3559(2)
C(8)	4666(2)	2758(3)	3886(2)
C(9)	4966(2)	4326(4)	3324(2)
N(6)	3344(2)	3693(3)	3987.2(15)
C(10)	3686(2)	4191(4)	4626(2)
C(11)	2610(2)	3571(4)	3921(2)
N(7)	3472.5(15)	5247(2)	3068.8(14)
Si(2)	3739.5(6)	6470.7(9)	3384.0(5)
C(12)	4500(2)	6515(4)	4134(2)
C(13)	3982(2)	7261(3)	2711(2)
C(14)	3028(2)	7179(4)	3644(2)
N(8)	2988(2)	5398(2)	1035.4(14)
Si(3)	3670.0(6)	4889.5(9)	777.1(5)
C(15)	4437(2)	4886(4)	1510(2)
C(16)	3929(2)	5616(4)	78(2)
C(17)	3512(2)	3486(3)	491(2)
P(3)	2406.7(5)	6254.0(8)	788.6(5)
N(9)	1826(2)	6007(3)	76(2)
C(18)	1201(2)	5447(5)	27(2)
C(19)	2054(3)	5922(5)	−545(2)
N(10)	2729(2)	7395(3)	590(2)
C(20)	2267(2)	8268(3)	297(2)
C(21)	3417(2)	7761(3)	903(2)
N(11)	2001(2)	6348(2)	1355.7(15)
P(4)	1416.7(5)	6614.0(8)	1728.8(5)
N(12)	644(2)	6915(3)	1239(2)
C(22)	560(2)	7884(4)	835(2)
C(23)	91(2)	6160(4)	1004(2)
N(13)	1646(2)	7760(2)	2123(2)
C(24)	1182(2)	8284(3)	2465(2)
C(25)	2216(2)	8423(3)	2059(2)
N(14)	1365.1(15)	5641(2)	2194.5(15)
Si(4)	902.5(6)	5384.8(9)	2770.9(5)
C(26)	1304(3)	5981(4)	3611(2)
C(27)	−18(2)	5852(4)	2553(3)
C(28)	853(2)	3918(3)	2883(2)

and disordered pentane molecule on an inversion centre. Final atomic coordinates are given in Tables 5–7.

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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