# Alkali metal complexes of sterically demanding amino-functionalised secondary phosphanide ligands

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The reaction between $\{(Me_3Si)_2CH\}PCl_2$ (**4**) and one equivalent of either $[C_6H_4\text{-}2\text{-}NMe_2]Li$ or $[2\text{-}C_5H_4N]ZnCl$, followed by *in situ* reduction with $LiAlH_4$ gives the secondary phosphanes $\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}NMe_2)PH$ (**5**) and $\{(Me_3Si)_2CH\}(2\text{-}C_5H_4N)PH$ (**6**) in good yields as colourless oils. Metalation of **5** with $Bu^nLi$ in THF gives the lithium phosphanide $[[\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}NMe_2)P]Li(THF)_2]$ (**7**), which undergoes metathesis with either $NaOBu^t$ or $KOBu^t$ to give the heavier alkali metal derivatives $[[\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}NMe_2)P]Na(tmeda)]$ (**8**) and $[[\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}NMe_2)P]K(pmdeta)]$ (**9**) after recrystallisation in the presence of the corresponding amine co-ligand [tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, pmdeta = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine]. The pyridyl-functionalised phosphane **6** undergoes deprotonation on treatment with $Bu^nLi$ to give a red oil corresponding to the lithium compound $[\{(Me_3Si)_2CH\}(2\text{-}C_5H_4N)P]Li$ (**10**) which could not be crystallised. Treatment of this oil with $NaOBu^t$ gives the sodium derivative $[\{[\{(Me_3Si)_2CH\}(2\text{-}C_5H_4N)P]Na\}_2\cdot(Et_2O)]_2$ (**11**), whilst treatment of **10** with $KOBu^t$, followed by recrystallisation in the presence of pmdeta gives the complex $[[\{(Me_3Si)_2CH\}(2\text{-}C_5H_4N)P]K(pmdeta)]_2$ (**12**). Compounds **5–12** have been characterised by $^1H$, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy and elemental analyses; compounds **7–9**, **11** and **12** have additionally been characterised by X-ray crystallography. Compounds **7–9** crystallise as discrete monomers, whereas **11** crystallises as an unusual dimer of dimers and **12** crystallises as a dimer with bridging pyridyl-phosphanide ligands.

## Introduction

Alkali metal phosphanides are key starting materials for the synthesis of transition metal and main group phosphanides, phosphinidenes and organophosphorus compounds. By far the most common alkali metal phosphanide reagents are the lithium derivatives, (RR′P)Li, due to their ease of preparation and widespread applicability.[1] However, in some circumstances the use of lithium reagents leads to unwanted incorporation of the alkali metal cation in the product. This is particularly true in lanthanide chemistry, where the formation of lithium-containing ate complexes is a major concern.[2] A typical strategy used to avoid the formation of ate complexes is to employ heavier alkali metal compounds, in particular potassium salts, as metathesis reagents.

The low charge/radius ratio of the heavier alkali metal cations and the essentially ionic nature of the M–P bond typically result in highly aggregated heavier alkali metal phosphanides which have low solubilities in non-polar solvents; aggregation states may be reduced and solubilities increased by the use of sterically demanding phosphanide ligands and the judicious choice of co-ligands. Crystallographic studies have revealed a wide array of structural motifs for heavier alkali metal phosphanides, ranging from monomers, dimers, trimers and tetramers to polymeric and lattice structures.[1] As a consequence of this structural diversity and of the need to understand better the relationship between aggregation state and reactivity there has been a growing interest in the structural chemistry of these species.

We have previously shown that a suitable combination of sterically demanding substituents, ligand donor functionality and co-ligands enables the isolation of monomeric heavier alkali metal phosphanides which have excellent solubility, even in hydrocarbon solvents. The complexes $[[\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}CH_2NMe_2)P]ML]$ [ML = $Li(THF)_2$ (**1**), Na(tmeda) (**2**), K(pmdeta) (**3**)] crystallise as discrete monomers in which the phosphanide ligands bind the metal centres *via* their P and N atoms, generating puckered, six-membered chelate rings [tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, pmdeta = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine].[3] We have now extended this study to include related dimethylaminophenyl- and pyridyl-functionalised phosphanide ligands, $[\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}NMe_2)P]^-$ and $[\{(Me_3Si)_2CH\}(2\text{-}C_5H_4N)P]^-$, in order to determine the influence of the amine donor group and the size of the potential chelate ring on the structures of their alkali metal derivatives.

## Results and discussion

The reaction between $\{(Me_3Si)_2CH\}PCl_2$ (**4**) and one equivalent of $[C_6H_4\text{-}2\text{-}NMe_2]Li$ in THF yields the monochlorophosphane $\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}NMe_2)PCl$, which may be reduced *in situ* with $LiAlH_4$ to give the secondary phosphane $\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}NMe_2)PH$ (**5**) as a colourless oil after an aqueous work-up (Scheme 1). In contrast, the reaction

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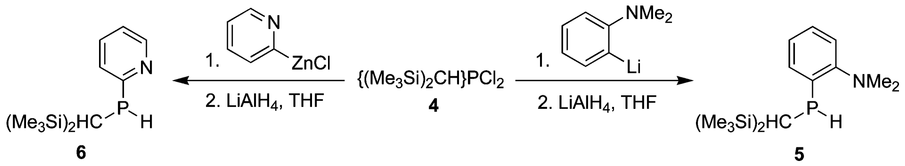


Scheme 1

between **4** and one equivalent of [2-$C_5H_4N$]Li under similar conditions yields an inseparable mixture of products containing unreacted **4**, {$(Me_3Si)_2CH$}(2-$C_5H_4N$)PCl and {$(Me_3Si)_2CH$}(2-$C_5H_4N)_2P$. However, a metathesis reaction between [2-$C_5H_4N$]Li and $ZnCl_2$ gives the less nucleophilic zinc reagent [2-$C_5H_4N$]ZnCl,[4] which reacts cleanly with **4** to give the monochlorophosphane {$(Me_3Si)_2CH$}(2-$C_5H_4N$)PCl as the sole phosphorus-containing product; reduction of this chlorophosphane with $LiAlH_4$ gives the secondary phosphane {$(Me_3Si)_2CH$}(2-$C_5H_4N$)PH (**6**) in reasonable yield as a colourless oil after an aqueous work-up.

The $^1H$, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of **5** and **6** are as expected; in the $^1H$ NMR spectra the two diastereotopic $Me_3Si$ groups give rise to a pair of singlets in each case and the PH protons are observed as a doublet of doublets at 4.41 ppm ($J_{PH} = 214.5$ Hz, $J_{HH} = 6.1$ Hz) and 4.38 ppm ($J_{PH} = 210.2$ Hz, $J_{HH} = 4.9$ Hz) for **5** and **6**, respectively. The $^{31}P\{^1H\}$ spectra of **5** and **6** exhibit singlets at −69.3 and −56.2 ppm, respectively.

Treatment of **5** with one equivalent of $Bu^nLi$ in THF yields the lithium salt [[{$(Me_3Si)_2CH$}($C_6H_4$-2-$NMe_2$)P]Li$(THF)_2$] (**7**) as orange blocks after crystallisation from cold *n*-hexane containing a few drops of THF. A metathesis reaction between **7** and one equivalent of either $NaOBu^t$ or $KOBu^t$ in diethyl ether yields the corresponding heavier alkali metal derivatives as highly air and moisture sensitive orange powders which may be isolated as the adducts [[{$(Me_3Si)_2CH$}($C_6H_4$-2-$NMe_2$)P]Na(tmeda)] (**8**) and [[{$(Me_3Si)_2CH$}($C_6H_4$-2-$NMe_2$)P]K(pmdeta)] (**9**) after crystallisation from methylcyclohexane in the presence of the corresponding amine co-ligand (Scheme 2). The $^1H$ and $^{13}C\{^1H\}$ NMR spectra of **7**, **8** and **9** are consistent with these formulations and exhibit a single singlet for the two $Me_3Si$ groups in each case, suggesting that P–M cleavage is rapid on the NMR time-scale; a similar phenomenon has been observed for the closely related compounds **1**–**3**.[3] Metalation of the phosphane results in a shift in the $^{31}P\{^1H\}$ signal from −69.3 ppm in **5** to −78.6, −73.1 and −61.3 ppm in **7**, **8**, and **9**, respectively. Compound **7** is soluble in ether solvents and toluene but is insoluble in light petroleum; compounds **8** and **9** are soluble in ether solvents but are insoluble in hydrocarbons.

X-Ray crystallography reveals that **7**, **8**, and **9** crystallise as discrete monomers in which the phosphanide ligands bind the metal ions *via* their P and N centres to give envelope-shaped, five-membered chelate rings in each case with N–M–P bite angles of 80.70(18) and 79.75(17)° (**7**), 70.53(3)° (**8**) and 59.79(5)° (**9**). These angles are significantly smaller than the corresponding angles in **1**, **2** and **3** [93.8(3)/94.5(3), 81.40(4) and 75.53(3)°, respectively],[3] consistent with the smaller chelate ring size in the former compounds. The structures of **7**, **8**, and **9** are shown in Fig. 1, 2 and 3, respectively, and details of selected bond lengths and angles for these compounds are given in Tables 1, 2 and 3.

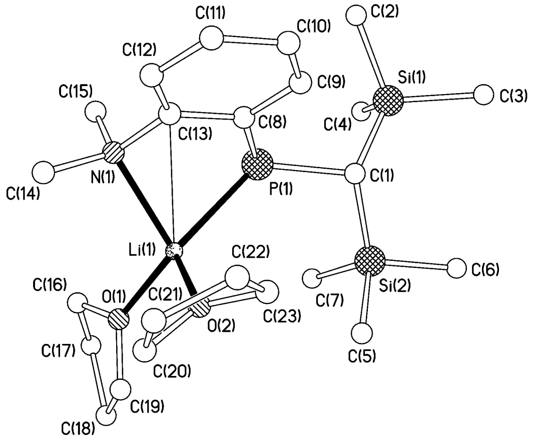
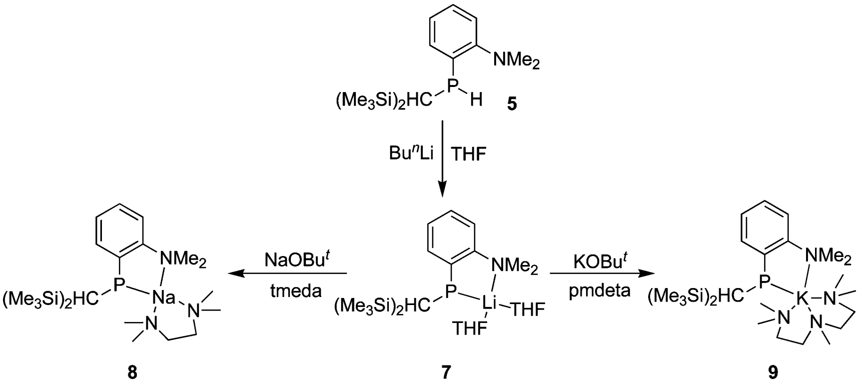


**Fig. 1** Molecular structure of one of the two independent molecules of **7** with H atoms and minor disorder components omitted for clarity.

Compound **7** crystallises with two crystallographically distinct molecules in the asymmetric unit which differ only trivially in their bond lengths and angles. The lithium coordination sphere in **7** is completed by two molecules of THF, conferring a distorted



Scheme 2

**Table 1** Selected bond lengths (Å) and angles (°) for **7**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Molecule 1 | | | | | | | |
| P(1)–Li(1) | 2.489(5) | N(1)–Li(1) | 2.154(6) | O(1)–Li(1) | 1.942(6) | Si(1)–C(1) | 1.883(3) |
| O(2)–Li(1) | 1.933(6) | Li(1)–C(13) | 2.733(6) | P(1)–C(1) | 1.897(3) | Si(2)–C(1) | 1.885(3) |
| P(1)–C(8) | 1.828(3) | | | | | | |
| P(1)–Li(1)–O(1) | 127.4(3) | P(1)–Li(1)–O(2) | 120.1(3) | P(1)–Li(1)–N(1) | 80.70(18) | O(1)–Li(1)–O(2) | 102.3(3) |
| O(1)–Li(1)–N(1) | 111.7(3) | O(2)–Li(1)–N(1) | 112.6(3) | Li(1)–P(1)–C(1) | 126.28(16) | Li(1)–P(1)–C(8) | 80.25(16) |
| C(1)–P(1)–C(8) | 104.46(13) | | | | | | |
| Molecule 2 | | | | | | | |
| P(2)–Li(2) | 2.505(5) | N(2)–Li(2) | 2.159(6) | O(3)–Li(2) | 1.933(5) | Si(3)–C(24) | 1.881(3) |
| O(4)–Li(2) | 1.939(5) | Li(2)–C(36) | 2.700(6) | P(2)–C(24) | 1.896(3) | Si(4)–C(24) | 1.880(3) |
| P(2)–C(31) | 1.830(3) | | | | | | |
| P(2)–Li(2)–O(3) | 117.9(2) | P(2)–Li(2)–O(4) | 124.6(2) | P(2)–Li(2)–N(2) | 79.75(17) | O(3)–Li(2)–O(4) | 107.9(3) |
| O(3)–Li(2)–N(2) | 108.9(3) | O(4)–Li(2)–N(2) | 113.9(3) | Li(2)–P(2)–C(24) | 126.37(15) | Li(2)–P(2)–C(31) | 79.76(15) |
| C(24)–P(2)–C(31) | 103.37(13) | | | | | | |

**Table 2** Selected bond lengths (Å) and angles (°) for **8**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Na–P | 2.8189(8) | Na–N(1) | 2.4758(13) | Na–N(2) | 2.4582(13) | Si(1)–C(1) | 1.8794(14) |
| Na–N(3) | 2.4900(14) | Na–C(8) | 3.0072(14) | Na–C(13) | 2.8792(14) | Si(2)–C(1) | 1.8813(15) |
| P–C(1) | 1.8967(13) | P–C(8) | 1.8257(13) | | | | |
| P–Na–N(3) | 123.52(4) | N(1)–Na–N(2) | 128.96(5) | P–Na–N(1) | 70.53(3) | P–Na–N(2) | 148.88(4) |
| Na–P–C(1) | 126.06(5) | Na–P–C(8) | 77.45(4) | N(1)–Na–N(3) | 109.32(4) | N(2)–Na–N(3) | 76.74(4) |
| C(1)–P–C(8) | 103.91(6) | | | | | | |

**Table 3** Selected bond lengths (Å) and angles (°) for **9**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| K–P | 3.2198(10) | K–N(1) | 2.869(3) | K–N(2) | 2.830(3) | K–C(21) | 3.324(6) |
| K–N(3) | 2.866(3) | K–N(4) | 2.797(3) | K–C(13) | 2.990(3) | K–C(23) | 3.344(2) |
| K–C(8) | 3.117(3) | K–C(14) | 3.371(4) | K–C(24) | 3.277(6) | P–C(1) | 1.899(3) |
| P–C(8) | 1.812(3) | Si(1)–C(1) | 1.867(3) | Si(2)–C(1) | 1.862(3) | | |
| N(1)–K–P | 59.79(5) | N(2)–K–N(1) | 138.62(8) | N(2)–K–N(3) | 64.43(9) | N(4)–K–N(2) | 114.16(9) |
| N(3)–K–N(1) | 116.39(8) | N(4)–K–N(1) | 100.23(9) | N(4)–K–N(3) | 64.09(9) | N(2)–K–P | 125.05(7) |
| N(3)–K–P | 169.90(7) | N(4)–K–P | 106.59(7) | C(8)–P–K | 70.29(9) | C(1)–P–K | 118.59(10) |
| C(8)–P–C(1) | 103.70(12) | | | | | | |

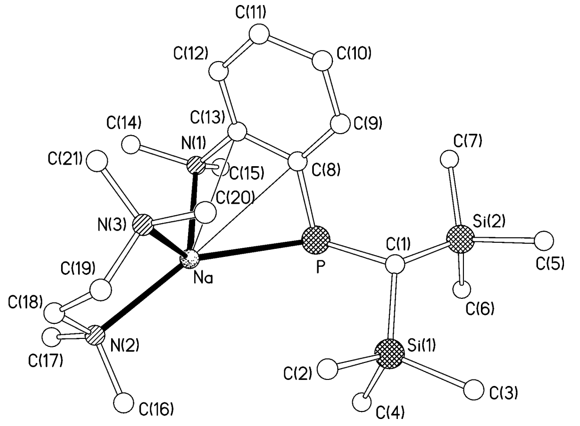


**Fig. 2** Molecular structure of **8** with H atoms omitted for clarity.

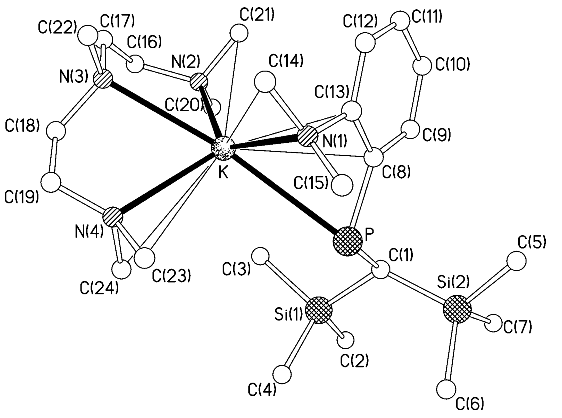


**Fig. 3** Molecular structure of **9** with H atoms and minor disorder components omitted for clarity.

tetrahedral geometry on the lithium ion. In addition, there is a close contact between the lithium ion and the *ipso*-carbon atom directly bonded to nitrogen [Li(1) $\cdots$ C(13) 2.733(6), Li(2) $\cdots$ C(36) 2.700(6) Å]. The Li–P distances of 2.498(5) and 2.505(5) Å are similar to the corresponding distances in **1** [2.535(8) and 2.535(7) Å][3] and other lithium phosphanides; for example, the Li–P distances in $[(Ph_2P)Li(DME)]_\infty$ are 2.563(3) and 2.541(3) Å,[5] whereas the Li–P distances in $[\{([Me_3Si]_2CH)_2P\}Li]_2$ are 2.481(10) and 2.473(9) Å.[6] The Li–N distances also fall in the range typically exhibited by tertiary amine-complexed organolithiums.[7]

The sodium ion in **8** is also formally four-coordinate with a distorted tetrahedral geometry, its coordination sphere being completed by the two nitrogen atoms of a chelating tmeda ligand. Once again, the Na–P and Na–N(1) distances to the phosphanide ligand of 2.8189(8) and 2.4758(13) Å, respectively, are similar to the corresponding distances in **2** [Na–P 2.8396(9), Na–N 2.4689(18) Å].[3] The Na–P distance in **8** is at the shorter end of the typical range of such distances;[1] for example, the Na–P distances in $[(CyPH)Na(tmeda)]_2$ are 2.884(8) and 2.936(7),[8] whereas the Na–P distances in $[EtSi\{P(Na)(SiPr^i_3)\}_3]_2\cdot(PhMe)_2$ range from 2.778(2) to 3.357(2) Å.[9] In addition to these Na–P and Na–N contacts the sodium atom has close contacts with both of the *ipso*-carbon atoms of the aromatic ring [Na · · · C(8) 3.0072(14), Na · · · C(13) 2.8792(14) Å]; these distances are within the typical range of $\eta^2$-arene–sodium contacts [2.57–3.00 Å].[10]

The potassium compound **9** crystallises as a discrete monomer in which the K–P and K–N contacts to the phosphanide ligand are supplemented through coordination by the three nitrogen atoms of a pmdeta ligand. The K–P distance of 3.2198(10) Å is similar to the corresponding distance in **3** and related potassium phosphanides;[1,3] for example the K–P distances in $[\{(\text{mes}^*)\text{PH}\}\text{K}]_\infty$ are 3.181(2), 3.271(2) and 3.357(2) Å [mes* = 2,4,6-$\text{Bu}^t_3$-$C_6H_2$].[11] The K–N distances in **9** [2.797(3)–2.869(3) Å] are also similar to the K–N distances in **3** [2.8008(16)–2.8725(17) Å][3] and related tertiary amine-complexed organopotassium complexes.[12] Once again, the potassium ion has short contacts to the two *ipso*-carbon atoms of the aromatic ring [K · · · C(8) 3.117(3), K · · · C(13) 2.990(3) Å]. In addition to these short K · · · C contacts the potassium atom has short, agostic-type K · · · Me contacts to one NMe group on the phosphanide ligand and three methyl groups on the triamine co-ligand [K · · · C(14) 3.371(4), K · · · C(21) 3.324(6), K · · · C(23) 3.344(2), K · · · C(24) 3.277(6) Å]. The increasing tendency towards M · · · Me agostic interactions and M · · · arene contacts for the heavier alkali metal cations is consistent with the larger ionic radius of $K^+$ compared to $Li^+$ and $Na^+$. The K · · · C(aryl) distances are typical for this type of contact, whereas the K · · · C(Me) distances in **9** are at the longer end of the range of typical K · · · C(Me) distances [3.20–3.30 Å].[10]

Treatment of a diethyl ether solution of the colourless, pyridyl-functionalised secondary phosphane **6** with $\text{Bu}^n\text{Li}$ gives a deep red solution, strongly suggesting conversion of the phosphane to the lithium phosphanide $[\{(\text{Me}_3\text{Si})_2\text{CH}\}(2\text{-}C_5H_4N)\text{P}]\text{Li}$ (**10**). However, attempts to isolate this material in a suitable state for analysis were unsuccessful; this compound was consistently isolated as a deep red oil. The successful formation of **10** was confirmed by its conversion into the corresponding sodium and potassium salts. A metathesis reaction between *in situ* prepared **10** and $\text{NaOBu}^t$ in diethyl ether, followed by the removal of solvent *in vacuo* and extraction of the $\text{LiOBu}^t$ side-product into light petroleum gives a sticky, deep red solid, which may be crystallised from hot *n*-hexane as deep red blocks of the sodium derivative $[\{[\{(\text{Me}_3\text{Si})_2\text{CH}\}(2\text{-}C_5H_4N)\text{P}]\text{Na}\}_2.(\text{Et}_2\text{O})]_2$ (**11**) (Scheme 3).

Although in the solid state there are two distinct sodium environments and two distinct phosphanide ligand environments (see below), the room temperature $^1$H, $^{13}$C{$^1$H} and $^{31}$P{$^1$H} NMR spectra of **11** all exhibit a single, rather broad, set of peaks for the phosphanide ligands; the $^1$H and $^{13}$C{$^1$H} NMR spectra exhibit a single signal for the two $\text{SiMe}_3$ groups, indicating that P–Na cleavage is rapid on the NMR time-scale. The NMR spectra of **11** suggest either that the tetranuclear structure observed in the solid state de-aggregates in solution or else that **11** is subject to a dynamic exchange process which rapidly interconverts the two ligand environments on the NMR time-scale. A variable temperature $^1$H NMR study of **11** was uninformative: the phosphanide signals merely broaden as the temperature is reduced and de-coalescence was not observed even at −80 °C. In contrast, the single, broad signal observed in the $^{31}$P{$^1$H} NMR spectrum of **11** de-coalesces as the temperature is reduced, until at −80 °C the spectrum consists of numerous, broad, overlapping signals in the range −40 to −75 ppm, suggesting that **11** is subject to complex dynamic equilibria between several species in toluene solution.

X-Ray crystallography shows that **11** crystallises as an unusual "dimer of dimers" with a crystallographic inversion centre; the molecular structure of **11** is shown in Fig. 4 and details of

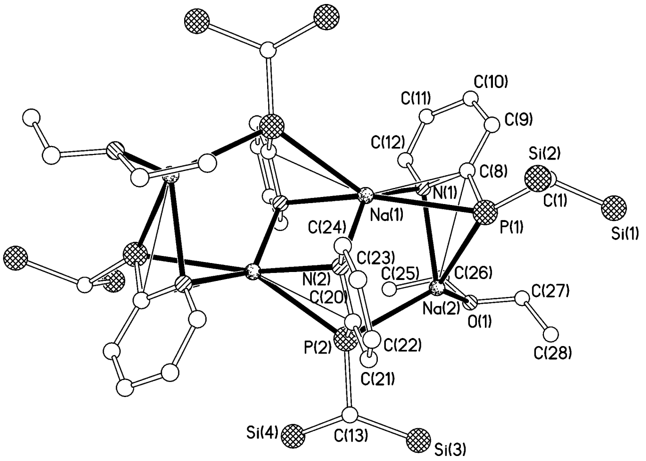
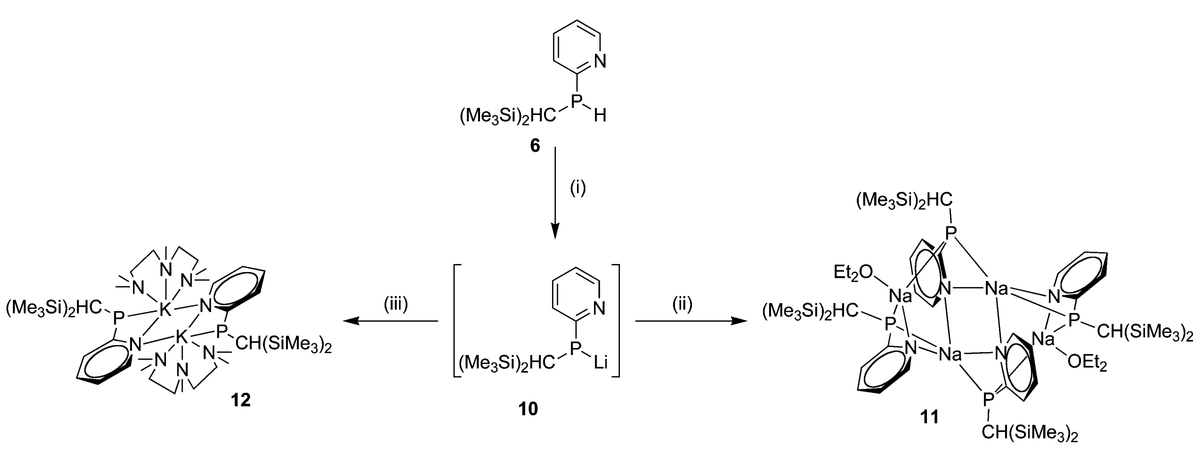


**Fig. 4** Molecular structure of **11** with C atoms of $\text{Me}_3\text{Si}$ groups and all H atoms omitted for clarity.



**Scheme 3** Reagents and conditions: (i) $\text{Bu}^n\text{Li}$, $\text{Et}_2\text{O}$; (ii) $\text{NaOBu}^t$, $\text{Et}_2\text{O}$; (iii) $\text{KOBu}^t$, $\text{Et}_2\text{O}$, pmdeta.

**Table 4** Selected bond lengths (Å) and angles (°) for **11**[a]

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Na(1)–P(1) | 2.9638(13) | Na(1)–N(1) | 2.485(3) | Na(1)–N(2A) | 2.654(2) | Na(1)–C(20A) | 3.029(3) |
| Na(1)–P(2A) | 2.8701(13) | Na(1)–N(2) | 2.425(2) | Na(1)–C(8) | 2.944(3) | Na(2)–P(1) | 2.8195(13) |
| Na(2)–O(1) | 2.346(2) | Na(2)–N(1) | 2.619(3) | Na(2)–C(8) | 3.104(3) | Na(2)–P(2) | 2.9356(13) |
| P(1)–C(1) | 1.870(2) | P(1)–C(8) | 1.786(3) | Si(1)–C(1) | 1.868(3) | Si(4)–C(13) | 1.880(3) |
| Si(2)–C(1) | 1.878(3) | P(2)–C(13) | 1.885(3) | Si(3)–C(13) | 1.870(3) | | |
| P(1)–Na(1)–P(2A) | 150.01(4) | P(1)–Na(1)–N(2) | 96.59(6) | N(1)–Na(1)–N(2A) | 92.56(8) | N(2)–Na(1)–N(2A) | 97.41(8) |
| P(1)–Na(1)–N(1) | 57.11(6) | P(1)–Na(1)–N(2A) | 145.84(7) | P(1)–Na(2)–P(2) | 108.17(4) | P(1)–Na(2)–O(1) | 121.72(7) |
| P(2A)–Na(1)–N(1) | 122.46(7) | P(2A)–Na(1)–N(2) | 96.94(6) | P(1)–Na(2)–N(1) | 57.90(5) | P(2)–Na(2)–O(1) | 130.05(7) |
| P(2A)–Na(1)–N(2A) | 57.56(5) | N(1)–Na(1)–N(2) | 137.91(9) | P(2)–Na(2)–N(1) | 111.31(7) | O(1)–Na(2)–N(1) | 97.72(8) |

[a] Symmetry operation: (A) $-x, -y, -z$.

selected bond lengths and angles are given in Table 4. The solid state structure of compound **11** contains two distinct sodium environments and two distinct ligand environments; Na(2) is coordinated by the phosphorus and nitrogen atoms of ligand 1 and by the phosphorus atom of ligand 2. In addition, Na(2) is bound by the oxygen atom of a molecule of diethyl ether and has a short contact with the *ipso*-carbon of ligand 1. In contrast, Na(1) is coordinated by the nitrogen and phosphorus atoms of ligand 1 and by the nitrogen atom of ligand 2. In addition, Na(1) is coordinated by the nitrogen and phosphorus atoms of a symmetry equivalent of ligand 2, and has short contacts with the *ipso*-carbon atoms of both ligand 1 and ligand 2. Thus, ligand 1 bridges Na(1) and Na(2) in a $\mu_2$-P,$\mu_2$-N mode; ligand 2 bridges Na(1) and a symmetry equivalent of Na(2) in a $\mu_2$-P mode and bridges Na(1) and its symmetry equivalent in a $\mu_2$-N mode. The Na–P distances are 2.8195(13), 2.8701(13), 2.9356(13) and 2.9638(13) Å and are similar to the corresponding distances in **2** and **8** (see above).[3] The Na–N distances range from 2.425(2) to 2.654(2) Å and fall in the range of Na–N distances observed in complexes where two sodium ions are $\mu_2$-bridged by a pyridyl ligand; for example, the Na–N distances in $[\{(2\text{-}C_5H_4N)N(SiMe_3)\}Na(THF)_{0.5}]_\infty$ range from 2.494(4) to 2.624(5) Å.[13]

A metathesis reaction between **6** and KOBu$^t$ in diethyl ether gives the corresponding potassium phosphanide, which may be crystallized as the pmdeta adduct $[[\{(Me_3Si)_2CH\}(2\text{-}C_5H_4N)P]K(pmdeta)]_2$ (**12**) as deep red blocks (Scheme 3); we were unable to crystallise the potassium salt in the absence of co-ligands. The molecular structure of **12** is shown in Fig. 5 and details of selected bond lengths and angles are given in Table 5. The $^1$H, $^{13}$C{$^1$H} and $^{31}$P{$^1$H} NMR spectra of **12** are as expected and contain sharp resonances, suggesting that **12** is not subject to the same dynamic behaviour in solution as **11**; once again in the $^1$H NMR spectrum a single singlet is observed for the two SiMe$_3$ groups.

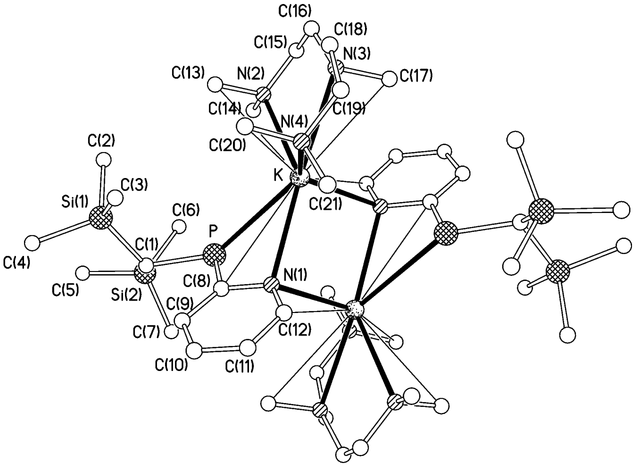


**Fig. 5** Molecular structure of **12** with minor disorder components and H atoms omitted for clarity.

In contrast to monomeric **9**, which contains the same co-ligand (pmdeta), compound **12** crystallises from *n*-hexane as a centrosymmetric dimer. Each potassium ion is coordinated by the three nitrogen atoms of a molecule of pmdeta, by the nitrogen atom of a bridging phosphanide ligand and by the nitrogen and phosphorus atoms of a second symmetry equivalent phosphanide ligand. Thus, each phosphanide ligand chelates one potassium ion, whilst simultaneously bridging the two potassium ions in the dimer *via* its pyridyl nitrogen atom. These contacts are supplemented by short K–C(aryl) contacts and short, agostic-type interactions with one methyl group on each of the three pmdeta nitrogen atoms. The K–P distance of 3.3605(7) Å is somewhat longer than the corresponding distance in **9**, but falls in the typical range of K–P distances in potassium phosphanide complexes (see above). The K–N(pyridyl) distances of 2.8029(17)

**Table 5** Selected bond lengths (Å) and angles (°) for **12**[a]

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| K–P | 3.3605(7) | K–N(1) | 2.8737(16) | K–N(1A) | 2.8029(17) | P–C(8) | 1.7807(19) |
| K–N(2) | 2.9023(19) | K–N(3) | 2.9382(17) | K–N(4) | 2.8305(19) | Si(1)–C(1) | 1.872(2) |
| K–C(8) | 3.4721(18) | K–C(12A) | 3.324(2) | K–C(13) | 3.392(4) | Si(2)–C(1) | 1.879(2) |
| K–C(17) | 3.371(3) | K–C(20) | 3.459(4) | P–C(1) | 1.8858(19) | | |
| N(1A)–K–N(4) | 128.79(5) | N(1A)–K–N(1) | 93.79(4) | N(1A)–K–P | 96.08(4) | N(4)–K–P | 125.73(4) |
| N(4)–K–N(1) | 93.17(5) | N(1A)–K–N(2) | 97.97(5) | N(1)–K–P | 49.75(3) | N(2)–K–P | 90.23(4) |
| N(4)–K–N(2) | 108.70(5) | N(1)–K–N(2) | 139.34(5) | N(3)–K–P | 149.09(5) | C(8)–P–C(1) | 103.13(9) |
| N(1A)–K–N(3) | 97.92(5) | N(4)–K–N(3) | 62.26(5) | C(8)–P–K | 78.39(6) | C(1)–P–K | 145.17(6) |
| N(1)–K–N(3) | 154.88(5) | N(2)–K–N(3) | 60.63(5) | | | | |

[a] Symmetry operation: (A) $1 - x, 1 - y, 1 - z$.

and 2.8737(16) Å are similar to the corresponding distances in other pyridyl-bridged potassium complexes; for example, the K–N distances in $[\{(2\text{-}C_5H_4N)N(SiMe_3)\}K(12\text{-crown-}4)]_2\cdot(PhMe)_2$ are 2.853(2) and 2.858(2) Å.[14] The remaining K–N distances are as expected.

In summary, amino-functionalised phosphanes **5** and **6** and their alkali metal derivatives are readily accessible. The solid state structures of the lithium, sodium and potassium phosphanides are dependent upon the nature of the amine donor group, the size of the alkali metal cation and the presence of co-ligands: whilst the *N*,*N*-dimethylaminophenyl substituent in **5** favours monomeric species, the pyridyl substituent in **6** favours the formation of dimers or higher aggregates.

## Experimental

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Diethyl ether, THF, *n*-hexane, methylcyclohexane and light petroleum (bp 40–60 °C) were distilled under nitrogen from potassium or sodium–potassium alloy; pyridine was distilled under nitrogen from $CaH_2$. THF and pyridine were stored over activated 4A molecular sieves; light petroleum, methylcyclohexane, *n*-hexane and diethyl ether were stored over a potassium film. Deuterated THF, toluene and $C_6D_6$ were distilled from potassium and $CDCl_3$ was distilled from $CaH_2$; all NMR solvents were deoxygenated by three freeze–pump–thaw cycles and were stored over activated 4A molecular sieves. tmeda and pmdeta were dried over $CaH_2$ and purified by distillation. *n*-Butyllithium was purchased from Aldrich as a 2.5 M solution in hexanes and was used as supplied. $ZnCl_2$ was treated with $Me_3SiCl$ and dried *in vacuo* prior to use; $NaOBu^t$ and $KOBu^t$ were dried *in vacuo* at 100 °C for 2 h prior to use. The compounds $\{(Me_3Si)_2CH\}PCl_2$,[15] and $[C_6H_4\text{-}2\text{-}NMe_2]Li$[16] were prepared by previously published procedures. All other compounds were used as supplied by the manufacturer.

$^1H$ and $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL Lambda500 spectrometer operating at 500.16 and 125.65 MHz, respectively, or a Bruker Avance300 spectrometer operating at 300.15 and 75.47 MHz, respectively; chemical shifts are quoted in ppm relative to tetramethylsilane. $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL Lambda500 spectrometer operating at 202.35 MHz and chemical shifts are quoted in ppm relative to external 85% $H_3PO_4$. Elemental analyses were obtained by the Elemental Analysis Service of London Metropolitan University.

### $\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}NMe_2)PH$ (5)

A solution of $[C_6H_4\text{-}2\text{-}NMe_2]Li$ (2.56 g, 20.2 mmol) in THF (30 ml) was added, dropwise, to a cold (−78 °C) solution of $\{(Me_3Si)_2CH\}PCl_2$ (5.28 g, 20.2 mmol) in THF (20 ml). The reaction mixture was allowed to warm to room temperature and was stirred overnight. Solid $LiAlH_4$ (0.76 g, 20.2 mmol) was cautiously added and the reaction mixture was heated under reflux for 2 h. The reaction mixture was allowed to cool to room temperature and excess $LiAlH_4$ was quenched by the careful addition of deoxygenated water (30 ml). The organic layer was decanted and the aqueous layer was extracted into diethyl ether (3 × 20 ml). The combined organic extracts were dried over 4Å molecular sieves. The solution was filtered and the solvent removed *in vacuo* from the filtrate to give **5** as a colourless oil. Yield 4.11 g, 64.9%. $\delta_H$ ($CDCl_3$): 0.01 (9H, s, $SiMe_3$), 0.16 (9H, s, $SiMe_3$), 0.45 [1H, dd, $^3J_{HH} = 6.1$ Hz, $J_{PH} = 3.1$ Hz, CHP], 2.72 (6H, s, $NMe_2$), 4.41 [1H, dd, $^3J_{HH} = 6.1$ Hz, $J_{PH} = 214.5$ Hz, PH], 7.01–7.41 (4H, m, ArH). $\delta_C$ ($CDCl_3$): 0.88 ($SiMe_3$), 5.70 [d, $J_{PC} = 41.7$ Hz, CHP], 44.98 ($NMe_2$), 119.44, 123.43, 128.40, 133.41 (ArH), 134.88 [d, $J_{PC} = 21.9$ Hz, Ar], 156.51 [d, $J_{PC} = 9.8$ Hz, Ar]. $\delta_P$ ($CDCl_3$): −69.3 [d, $J_{PH} = 214.5$ Hz].

### $[[\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}NMe_2)P]Li(THF)_2]$ (7)

To a stirred solution of **5** (0.92 g, 2.94 mmol) in diethyl ether (20 ml) was added $Bu^nLi$ (1.17 ml, 2.94 mmol) and this mixture was stirred at room temperature for 1 h. The solvent was removed *in vacuo* giving an orange, viscous oil which was crystallised from cold (−30 °C) *n*-hexane containing a few drops of THF as yellow blocks of **7** suitable for X-ray crystallography. Yield 0.68 g, 72.6%. Found: C, 59.96; H, 9.86; N, 3.14%. $C_{23}H_{45}LiNO_2PSi_2$ requires C, 59.87; H, 9.76; N, 3.04%. $\delta_H$ ($C_6D_6$): 0.49 (18H, s, $SiMe_3$), 0.63 (1H, s, CHP), 1.28 (8H, m, THF), 2.61 (6H, s, $NMe_2$), 3.36 (8H, m, THF), 6.70–7.44 (4H, m, ArH). $\delta_C$ ($C_6D_6$): 2.40 ($SiMe_3$), 4.95 [d, $J_{PC} = 64.6$ Hz, CHP], 26.06 (THF), 45.02 ($NMe_2$), 69.12 (THF), 115.55, 116.19, 125.33, 127.72 (Ar), 148.14 [d, $J_{PC} = 21.1$ Hz, Ar] 158.37 [d, $J_{PC} = 65.6$ Hz, Ar]. $\delta_P$ ($C_6D_6$): −78.6.

### $[[\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}NMe_2)P]Na(tmeda)]$ (8)

To a solution of **5** (1.51 g, 3.29 mmol) in diethyl ether (20 ml) was added $Bu^nLi$ (1.32 ml, 3.30 mmol) and this mixture was stirred for 1 h. The resulting solution was added to a slurry of $NaOBu^t$ (0.31 g, 3.29 mmol) in diethyl ether (20 ml) and this mixture was stirred at room temperature for 1 h. The solvent was removed *in vacuo* giving a sticky yellow solid which was washed with light petroleum (3 × 20 ml) and dried *in vacuo*, yielding a yellow, pyrophoric solid. Crystals of **8** suitable for an X-ray crystallographic study were obtained from cold (−30 °C) methylcyclohexane containing one equivalent of tmeda. Yield 0.56 g, 50.8%. Found: C, 55.91; H, 9.85; N, 9.09%. $C_{21}H_{45}NaN_3PSi_2$ requires C, 56.03; H, 10.00; N, 9.34%. $\delta_H$ ($d_8$-THF): 0.07 (18H, s, $SiMe_3$), 0.19 [1H, d, $J_{PH} = 2.2$ Hz, CHP], 2.14 (12H, s, $CH_2N\mathit{Me}_2$), 2.30 (4H, s, $CH_2N$), 2.74 (6H, s, $NMe_2$), 6.14–6.85 (4H, m, ArH). $\delta_C$ ($d_8$-THF): 1.63 ($SiMe_3$), 4.57 [d, $J_{PC} = 67.85$ Hz, CHP], 44.12 ($NMe_2$), 46.16 ($CH_2N\mathit{Me}_2$), 58.88 ($CH_2N$), 113.67, 115.08, 123.17, 126.65 (Ar), 148.78 [d, $J_{PC} = 21.2$ Hz, Ar], 158.47 [d, $J_{PC} = 69.1$ Hz, Ar]. $\delta_P$ ($d_8$-THF): −73.1.

### $[[\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}NMe_2)P]K(pmdeta)]$ (9)

To a solution of **5** (0.96 g, 3.07 mmol) in diethyl ether (20 ml) was added $Bu^nLi$ (1.22 ml, 3.07 mmol) and this mixture was stirred at room temperature for 1 h. The resulting solution was added to a solution of $KOBu^t$ (0.34 g, 3.07 mmol) in diethyl ether (20 ml) and this mixture was stirred at room temperature for 1 h. Solvent was removed *in vacuo* to give a sticky brown solid which was washed with light petroleum (3 × 20 ml) and dried *in vacuo*, yielding a yellow-orange, pyrophoric solid. Crystals of **9** suitable for an X-ray crystallographic study were obtained from hot methylcyclohexane containing one equivalent of pmdeta. Yield 0.64 g, 59.5%. Found: C, 55.19; H, 10.00; N, 10.77%. $C_{24}H_{52}KN_4PSi_2$ requires C, 55.07; H, 9.94; N, 10.71%. $\delta_H$ ($d_8$-THF): 0.06 (18H, s, $SiMe_3$), 0.15 [1H, d, $J_{PH} = 3.0$ Hz, CHP], 2.14 (12H, s, $CH_2N\mathit{Me}_2$), 2.20 (3H, s, NMe), 2.31 (4H, m, $CH_2N$), 2.40 (4H, m, $CH_2N$), 2.73 (6H, s, $NMe_2$), 6.03–6.77 (4H, m, ArH). $\delta_C$ ($d_8$-THF): 1.47 ($SiMe_3$), 5.17 [d, $J_{PC}$ = 69.1 Hz, CHP], 43.13 ($CH_2N\mathit{Me}_2$), 43.46 (NMe), 46.03 ($NMe_2$), 57.20 ($CH_2N$), 58.67 ($CH_2N$), 112.36, 115.15, 122.89, 125.96 (Ar), 148.62 [d, $J_{PC}$ = 23.9 Hz, Ar], 159.7 [d, $J_{PC}$ = 75.3 Hz, Ar]. $\delta_P$ ($d_8$-THF): −61.3.

### {$(Me_3Si)_2CH$}(2-$C_5H_4N$)PH (6)

A solution of bromopyridine (2.2 ml, 22.08 mmol) in diethyl ether (10 ml) was added to a cold (−40 °C) solution of Bu$^n$Li (8.8 ml, 22.08 mmol) in diethyl ether (20 ml). The reaction mixture was allowed to warm to −15 °C for 15 min and then re-cooled to −40 °C. A slurry of freshly prepared anhydrous $ZnCl_2$ (2.98 g, 22.08 mmol) in a mixture of THF–pyridine (40 ml : 10 ml) was added to the reaction mixture. The reaction was allowed to warm to room temperature whilst stirring overnight. The resulting white precipitate was isolated by filtration and a mixture of THF–pyridine (40 ml : 10 ml) was added to the resulting solid to form a slurry. The slurry was cooled to −40 °C and added to a cold (−40 °C) solution of {$(Me_3Si)_2CH$}$PCl_2$ (5.76 g, 22.08 mmol) in pyridine (10 ml) and this mixture was allowed to warm to room temperature overnight. The solution was filtered and the solvent removed *in vacuo* from the filtrate to give a colourless oil. This oil was dissolved in THF (30 ml), solid $LiAlH_4$ (0.83 g, 22.08 mmol) was added and the reaction mixture was heated under reflux for 2 h. The mixture was cooled to room temperature and excess $LiAlH_4$ was quenched by the careful addition of deoxygenated water. The organic layer was decanted and the aqueous layer was extracted into diethyl ether (3 × 20 ml). The combined organic extracts were dried over 4Å molecular sieves, the solution was filtered and the solvent removed *in vacuo* from the filtrate to give **6** as a colourless oil. Yield 1.83 g, 30.8%. $\delta_H$ ($CDCl_3$): 0.03 (9H, s, $SiMe_3$), 0.09 (9H, s, $SiMe_3$), 0.92 [1H, dd, $^3J_{HH}$ = 4.0 Hz, $J_{PH}$ = 8.9 Hz, CHP], 4.38 [1H, dd, $^3J_{HH}$ = 4.0 Hz, $J_{PH}$ = 210.2 Hz, PH], 7.07–8.60 (4H, m, ArH). $\delta_C$ ($CDCl_3$): 0.79 ($SiMe_3$), 3.82 [d, $J_{PC}$ = 40.1 Hz, CHP], 121.56, 127.85, 134.69, 149.93 (Ar), 163.96 [d, $J_{PC}$ = 9.80 Hz, Ar]. $\delta_P$ ($CDCl_3$): −56.2 [d, $J_{PH}$ = 210.2 Hz].

### [{[{$(Me_3Si)_2CH$}(2-$C_5H_4N$)P]Na}$_2$.($Et_2O$)]$_2$ (11)

To a solution of **6** (0.83 g, 3.08 mmol) in diethyl ether (20 ml) was added Bu$^n$Li (1.2 ml, 3.08 mmol) and this mixture was stirred at room temperature for 1 h. The resulting deep red solution was added to a solution of NaOBu$^t$ (0.29 g, 3.08 mmol) in diethyl ether (20 ml) and this mixture was stirred at room temperature for 1 h. The solvent was removed *in vacuo* to give a sticky, deep red solid which was washed with light petroleum (3 × 20 ml) and dried *in vacuo*. The solid was recrystallised from hot *n*-hexane (10 ml) to give **11** as red blocks. Yield 0.56 g, 62.4%. Found: C, 50.90; H, 8.41; N, 4.32%. $C_{56}H_{112}Na_4O_2N_4P_4Si_8$ requires C, 51.14; H, 8.52; N, 4.26%. $\delta_H$ ($d_8$-toluene): 0.20 (18H, s, $SiMe_3$), 0.23 [1H, d, $J_{PH}$ = 4.0 Hz, CHP], 0.93 [3H, t, $^3J_{HH}$ = 7.1 Hz, $Et_2O$], 3.08 [2H, q, $^3J_{HH}$ = 7.1 Hz, $Et_2O$], 5.96–7.63 (4H, m, ArH). $\delta_C$ ($d_8$-toluene): 2.32 ($SiMe_3$), 5.07 [d, $J_{PC}$ = 59.9 Hz, CHP], 16.03 ($Et_2O$), 66.83 ($Et_2O$), 111.02, 122.24, 135.09 (Ar), 150.27 [d, $J_{PC}$ = 15.5 Hz, Ar], 192.94 [d, $J_{PC}$ = 43.9 Hz, Ar]. $\delta_P$ ($d_8$-toluene): −45.6.

### [[{$(Me_3Si)_2CH$}(2-$C_5H_4N$)P]K(pmdeta)]$_2$ (12)

To a solution of **6** (1.03 g, 3.83 mmol) in diethyl ether (20 ml) was added Bu$^n$Li (1.5 ml, 3.83 mmol) and this mixture was stirred at room temperature for 1 h. This solution was added to a solution of KOBu$^t$ (0.42 g, 3.83 mmol) in diethyl ether (20 ml) and the mixture was stirred at room temperature for 1 h. The solvent was removed *in vacuo* to give a sticky, deep red solid which was washed with light petroleum (3 × 20 ml) and dried *in vacuo*, yielding a red, pyrophoric solid. Crystals of **12** suitable for an X-ray crystallographic study were grown from cold (−30 °C) *n*-hexane containing one equivalent of pmdeta. Yield 0.67 g, 56.9%.

**Table 6** Crystallographic data for **7**, **8**, **9**, **11** and **12**

| Compound | **7** | **8** | **9** | **11** | **12** |
|---|---|---|---|---|---|
| Formula | $C_{23}H_{45}LiNO_2PSi_2$ | $C_{21}H_{45}N_3NaPSi_2$ | $C_{24}H_{52}KN_4PSi_2$ | $C_{56}H_{112}N_4Na_4O_2P_4Si_8$ | $C_{42}H_{92}K_2N_8P_2Si_4$ |
| $M$ | 461.7 | 449.7 | 523.0 | 1314.1 | 961.7 |
| Crystal system | Triclinic | Triclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P2_1/c$ | $P\bar{1}$ | $P2_1/c$ |
| $a$/Å | 11.358(2) | 9.8078(15) | 14.4291(19) | 11.1503(15) | 14.603(2) |
| $b$/Å | 14.476(3) | 11.4689(16) | 11.2424(15) | 13.5201(18) | 10.0903(14) |
| $c$/Å | 17.519(3) | 13.6466(9) | 19.576(3) | 15.406(2) | 23.551(3) |
| $\alpha$/° | 86.512(12) | 90.930(9) | | 109.582(2) | |
| $\beta$/° | 89.130(12) | 103.882(9) | 93.555(2) | 97.502(2) | 122.270(6) |
| $\gamma$/° | 82.367(17) | 103.782(15) | | 110.175(2) | |
| $V$/Å$^3$ | 2849.6(9) | 1442.9(3) | 3198.5(7) | 1972.7(5) | 2934.2(7) |
| $Z$ | 4 | 2 | 4 | 1 | 2 |
| $\mu$/mm$^{-1}$ | 0.198 | 0.204 | 0.308 | 0.276 | 0.331 |
| Data collected | 62419 | 31788 | 22885 | 14338 | 25376 |
| Unique data | 9984 | 6595 | 5630 | 6865 | 7075 |
| $R_{int}$ | 0.056 | 0.036 | 0.031 | 0.025 | 0.028 |
| Data with $F^2 > 2\sigma$ | 7887 | 5236 | 4544 | 5944 | 5611 |
| Refined parameters | 605 | 265 | 311 | 366 | 302 |
| $R$ (on $F$, $F^2 > 2\sigma$) | 0.055 | 0.034 | 0.053 | 0.054 | 0.047 |
| $R_w$ (on $F^2$, all data) | 0.154 | 0.094 | 0.149 | 0.112 | 0.118 |
| Goodness of fit on $F^2$ | 1.197 | 1.072 | 1.094 | 1.257 | 1.107 |
| min, max electron density/e Å$^{-3}$ | 0.36, −0.38 | 0.26, −0.27 | 1.29, −0.54 | 0.38, −0.27 | 0.45, −0.33 |

Found: C, 52.36; H, 9.56; N, 11.58%. $C_{42}H_{92}K_2N_8P_2Si_4$ requires C, 52.45; H, 9.64; N, 11.65%. $\delta_H$ ($d_8$-THF): 0.12 (18H, s, $SiMe_3$), 0.16 (1H, s, CHP), 2.19 (12H, s, $NMe_2$), 2.23 (3H, s, NMe), 2.35 (4H, m, $CH_2N$), 2.45 (4H, m, $CH_2N$), 5.74–7.74 (4H, m, ArH). $\delta_C$ ($d_8$-THF): 0.63 ($SiMe_3$), 4.94 [d, $J_{PC}$ = 65.3 Hz, CHP], 42.33 (NMe), 45.30 ($NMe_2$), 56.49 ($CH_2N$), 57.89 ($CH_2N$), 105.76, 119.46, 131.36 (Ar), 147.79 [d, $J_{PC}$ = 14.4 Hz, Ar], 192.70 [d, $J_{PC}$ = 49.9 Hz, Ar]. $\delta_P$ ($d_8$-THF): −31.9.

### Crystal structure determinations of 7–9, 11 and 12

Measurements were made at 150 K on Bruker AXS SMART CCD and Nonius KappaCCD diffractometers using graphite-monochromated Mo-Kα radiation ($\lambda$ = 0.71073 Å). For all compounds cell parameters were refined from the observed positions of all strong reflections in each data set. Intensities were corrected semi-empirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods or Patterson synthesis and were refined on $F^2$ values for all unique data; Table 6 gives further details. All non-hydrogen atoms were refined anisotropically, and H atoms were constrained with a riding model; $U$(H) was set at 1.2 (1.5 for methyl groups) times $U_{eq}$ for the parent atom. Disorder was resolved and successfully modeled for one THF ligand in **7**, for one of the NMe groups of the pmdeta ligand in **9**, and for one of the NMe groups and two of the backbone carbons of the pmdeta ligand in **12**. Programs were Bruker AXS SMART (control) and SAINT (integration), Nonius COLLECT and associated programmes, and SIR97 and SHELXTL for structure solution, refinement, and molecular graphics.[17]

CCDC reference numbers 622825–622829.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b614373c

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