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# Reactions of α-lithiated phosphinimines with PhCN; the crystal structure of $[\overline{K\{N(H)C(Ph)C(H)P(Ph)_2{=}N}SiMe_3\}(tmen)]_2$ (tmen = $Me_2NCH_2CH_2NMe_2$)

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Treatment of the α-lithiated phosphinimine $\overline{Li\{CH(R')P(R)_2{=}N}SiMe_3\}$ with benzonitrile yielded (*via* a trimethylsilyl or hydrogen 1,3 C ⟶ N shift) the trimethylsilyliminophosphoranylenamidolithium complex $\overline{Li\{N(R')C(Ph)C(H)P(R)_2{=}N}SiMe_3\}$ (R = Me, R′ = $SiMe_3$ **1**; R = Ph, R′ = $SiMe_3$ **2**; or R = Ph, R′ = H **3**). Complex **2** was transformed into the corresponding potassium complex **4** by an exchange reaction with $KOBu^t$. Crystallisation of **4** from hexane in the presence of $Me_2NCH_2CH_2NMe_2$ (tmen) gave the tmen adduct **5** and a trace of the partially hydrolysed product $[\overline{K\{N(H)C(Ph)C(H)P(Ph)_2{=}N}SiMe_3\}(tmen)]_2$ **6**, which was characterised by a single crystal X-ray diffraction study as a dinuclear complex with each of the two potassium atoms in a different co-ordination environment. Complex **1** or **2** was hydrolysed to form the neutral iminophosphoranylenamine $\overline{N(SiMe_3)C(Ph)C(H)P(R)_2N(SiMe_3)H}$ **7** or **8**, which showed ($^1H$ NMR spectroscopy) the presence of hydrogen bonds.

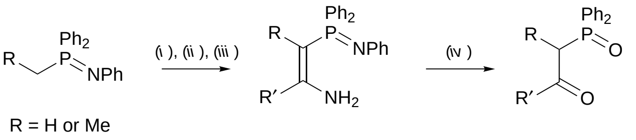
Reactions of α-lithiated phosphinimines with several electrophiles have been explored. Thus, when an α-lithiated phosphinimine was treated with $Me_3SiCl$, $Br_2$ or certain organic electrophiles, a carbon-centred reaction was invariably observed. This was ascribed to the difference in nucleophilicity between the two ylidic positions.[1] Such reactions include alkylation,[2–4] silylation,[4–7] bromination,[3–4] acylation,[2,4,8] α-amino-alkylation[3,9] and α-hydroxyalkylation.[2,10] The reaction of an α-lithiated phosphinimine with an aryl nitrile yielded, after hydrolysis, the iminophosphoranylenamine, which when further hydrolysed by a solution of sulfuric acid led to the β-keto-phosphine oxide (Scheme 1);[2] but no attempt was made to separate the lithiated intermediate.

We report here our investigations of the addition reactions of $\overline{Li\{CH(R')P(R)_2{=}N}SiMe_3\}$ (R = Me, R′ = $SiMe_3$; R = Ph, R′ = $SiMe_3$; or R = Ph, R′ = H) and benzonitrile, the conversion of one of these adducts into the potassium analogue and crystal structural characterisation of $[\overline{K\{N(H)C(Ph)C(H)P(Ph)_2{=}N}SiMe_3\}(tmen)]_2$ (tmen = $Me_2NCH_2CH_2NMe_2$).

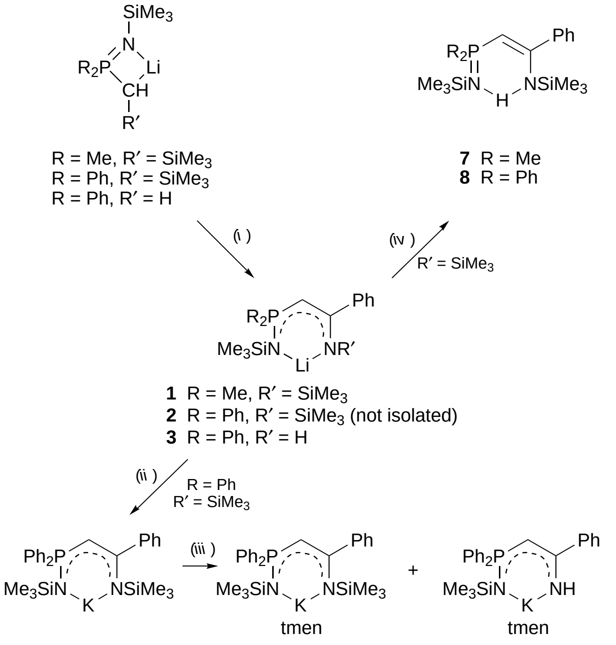
## Results and Discussion

The synthesis and reactions of complexes $\overline{Li\{N(R')C(Ph)C(H)P(R)_2{=}N}SiMe_3\}$ (R = Me, R′ = $SiMe_3$ **1**; R = Ph, R′ = $SiMe_3$ **2**; or R = Ph, R′ = H **3**) are summarised in Scheme 2.

Treatment of the appropriate compound $\overline{Li\{CH(R')P(R)_2{=}N}SiMe_3\}$ [obtained *in situ* from the phosphinimine $CH_2(R')P(R)_2{=}NSiMe_3$ and $LiBu^n$] with PhCN in $Et_2O$ proceeded readily at room temperature. Complexes **1**–**3** were formed as colourless crystals (**1**), pale yellow solid (**3**) or colourless oil (**2**). A 1,3-trimethylsilyl (when R′ = $SiMe_3$) or hydrogen (when R′ = H) C ⟶ N migration was observed in these reactions. Mixing of **2** with $KOBu^t$ in hexane afforded a white precipitate of the potassium analogue **4**. Crystallisation of **4** with tmen in hexane produced colourless crystals of the tmen adduct **5**. From the mother-liquor of **5**, a few colourless crystals were further separated; a single-crystal X-ray diffraction study showed that these were those of another potassium complex **6**. Formation of the very small amount of complex **6** is assumed to have been the result of partial hydrolysis of



**Scheme 1** *Reagents and conditions:* (*i*) $LiNPr^i_2$ or $LiBu^n$, −30 °C, tetrahydrofuran (thf); (*ii*) R′CN (R′ = Ph or 4-$MeC_6H_4$); (*iii*) $H_2O$; (*iv*) $H_2O$–$H_2SO_4$



**7** R = Me
**8** R = Ph

**1** R = Me, R′ = $SiMe_3$
**2** R = Ph, R′ = $SiMe_3$ (not isolated)
**3** R = Ph, R′ = H

**4** **5** **6**

**Scheme 2** *Reagents and conditions:* (*i*) PhCN, $Et_2O$, −50 °C to *ca.* 20 °C, 3 h; (*ii*) $KOBu^t$, hexane, *ca.* 20 °C, 3 h; (*iii*) tmen, hexane, *ca.* 20 °C; (*iv*) $H_2O$, thf, −20 °C to *ca.* 20 °C, 1 h

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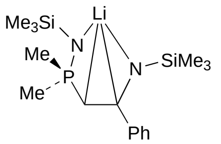
**Table 1** Selected intramolecular distances (Å) and angles (°) for complex **6**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| K(1)–N(1) | 3.137(8) | K(1)–N(2) | 2.874(9) | K(2)–N(7) | 3.028(10) | K(2)–N(8) | 2.852(11) |
| K(1)–N(3) | 3.033(8) | K(1)–N(4) | 3.020(8) | P(1)–N(1) | 1.568(8) | P(1)–C(1) | 1.712(9) |
| K(1)–N(5) | 2.973(11) | K(1)–C(1) | 3.209(10) | P(2)–N(3) | 1.593(8) | P(2)–C(24) | 1.741(9) |
| K(1)–C(2) | 3.072(9) | K(1)–C(24) | 3.251(10) | Si(2)–N(3) | 1.669(8) | Si(1)–N(1) | 1.701(8) |
| K(1)–C(25) | 3.116(9) | K(2)–N(1) | 2.978(8) | N(2)–C(2) | 1.302(11) | N(4)–C(25) | 1.315(11) |
| K(2)–N(2) | 2.858(8) | K(2)–N(4) | 2.745(8) | C(1)–C(2) | 1.418(12) | C(24)–C(25) | 1.368(12) |
| | | | | | | | |
| N(2)–K(1)–N(5) | 144.4(3) | N(2)–K(1)–N(4) | 77.7(2) | C(2)–K(1)–C(24) | 143.3(2) | C(25)–K(1)–C(24) | 24.7(2) |
| N(5)–K(1)–N(4) | 137.8(3) | N(2)–K(1)–N(3) | 93.1(2) | N(1)–K(1)–C(24) | 118.9(2) | C(1)–K(1)–C(24) | 163.3(3) |
| N(5)–K(1)–N(3) | 99.0(3) | N(4)–K(1)–N(3) | 67.4(2) | N(4)–K(2)–N(8) | 99.2(3) | N(4)–K(2)–N(2) | 82.7(2) |
| N(2)–K(1)–C(2) | 25.0(2) | N(5)–K(1)–C(2) | 119.4(3) | N(8)–K(2)–N(2) | 87.3(3) | N(4)–K(2)–N(1) | 98.9(2) |
| N(4)–K(1)–C(2) | 102.8(2) | N(3)–K(1)–C(2) | 102.8(2) | N(8)–K(2)–N(1) | 150.6(3) | N(2)–K(2)–N(1) | 72.3(2) |
| N(2)–K(1)–C(25) | 102.4(2) | N(5)–K(1)–C(25) | 113.2(3) | N(4)–K(2)–N(7) | 114.0(3) | N(8)–K(2)–N(7) | 61.2(3) |
| N(4)–K(1)–C(25) | 24.7(2) | N(3)–K(1)–C(25) | 66.7(2) | N(2)–K(2)–N(7) | 145.5(3) | N(1)–K(2)–N(7) | 129.6(3) |
| C(2)–K(1)–C(25) | 127.4(3) | N(2)–K(1)–N(1) | 69.7(2) | P(1)–N(1)–Si(1) | 134.6(5) | P(1)–N(1)–K(2) | 101.1(3) |
| N(5)–K(1)–N(1) | 106.0(3) | N(4)–K(1)–N(1) | 89.9(2) | Si(1)–N(1)–K(2) | 108.8(4) | P(1)–N(1)–K(1) | 97.9(4) |
| N(3)–K(1)–N(1) | 154.4(2) | C(2)–K(1)–N(1) | 69.7(2) | Si(1)–N(1)–K(1) | 121.5(4) | K(2)–N(1)–K(1) | 76.4(2) |
| C(25)–K(1)–N(1) | 97.7(2) | N(2)–K(1)–C(1) | 45.6(2) | C(2)–N(2)–K(2) | 137.7(6) | C(2)–N(2)–K(1) | 86.0(6) |
| N(5)–K(1)–C(1) | 102.5(3) | N(4)–K(1)–C(1) | 117.7(2) | K(2)–N(2)–K(1) | 82.6(2) | P(2)–N(3)–Si(2) | 134.1(5) |
| N(3)–K(1)–C(1) | 127.3(2) | C(2)–K(1)–C(1) | 26.0(2) | P(2)–N(3)–K(1) | 99.8(3) | Si(2)–N(3)–K(1) | 126.0(4) |
| C(25)–K(1)–C(1) | 139.3(3) | N(1)–K(1)–C(1) | 52/4(2) | C(25)–N(4)–K(2) | 132.7(6) | C(25)–N(4)–K(1) | 81.8(5) |
| N(2)–K(1)–C(24) | 120.0(2) | N(5)–K(1)–C(24) | 93.5(3) | K(2)–N(4)–K(1) | 81.9(2) | C(2)–C(1)–P(1) | 122.9(7) |
| N(4)–K(1)–C(24) | 45.7(2) | N(3)–K(1)–C(24) | 52.8(2) | N(2)–C(2)–C(1) | 122.0(8) | C(25)–C(24)–P(2) | 126.1(7) |



**1**

complex **5**. The anionic ligand of **6** is identical to that in **3**. However, attempts to prepare **6** by reaction of **3** with $KOBu^t$ in hexane or benzene and then to crystallise it as a tmen complex were unsuccessful; instead, an unidentified yellow, crystalline compound was obtained. Treatment of complex **1** or **2** with 1 equivalent of $H_2O$ in thf gave in high yield $N(SiMe_3)C(Ph)C(H)P(R)_2N(SiMe_3)H$ as colourless crystals **7** (R = Me) or pale yellow oil **8** (R = Ph).

The oily complex **2** was characterised solely by its conversion into the potassium analogue **4**, while each of the crystalline complexes **1** and **3** gave satisfactory microanalytical data as well as $^1H$, $^{13}C$-{$^1H$}, $^{31}P$-{$^1H$} and $^7Li$-{$^1H$} NMR spectra. The $^1H$ NMR spectrum of $Li\{N(SiMe_3)C(Ph)C(H)P(Me)_2{=}NSiMe_3\}$ **1** showed two sets of broad signals for the phosphorus-bound methyl groups. A variable-temperature $^1H$ NMR study showed that the two sets of signals observed at 291 K coalesced to a sharp singlet when the temperature was raised to 348 K. This is ascribed to the fact that at the lower temperature the lithium atom is firmly attached to the ligand giving rise to distinct axial and equatorial *P*-methyl groups, while at the higher temperature rapid inversion occurs. The $^{13}C$-{$^1H$} NMR spectrum of **1** provided evidence for the migration of the trimethylsilyl group. In the $^{13}C$-{$^1H$} NMR spectra of $Li\{CH(SiMe_3)P(Ph)_2{=}NSiMe_3\}$ or $K\{CH(SiMe_3)P(Me)_2{=}NSiMe_3\}$, P–$SiMe_3$ coupling was observed for both trimethylsilyl groups, each appearing as a doublet.[11] However, in the $^{13}C$-{$^1H$} NMR spectrum of **1**, only one silylmethyl signal was a doublet, the other a singlet. Such 1,3-trimethylsilyl migrations from carbon to nitrogen have previously been observed in the reaction of $MCH(R)SiMe_3$ (M = Li or K; R = Ph or $SiMe_3$) with a nitrile ($Bu^tCN$ or PhCN), giving rise to $M\{N(SiMe_3)C(Bu^t)CHR\}$[12] or $M\{N(SiMe_3)C(Ph)C(H)C(Ph)NSiMe_3\}$.[13] However, for $Li\{CH(SiMe_3)P(R)_2{=}NSiMe_3\}$, no reaction with $Bu^tCN$ occurred, even under reflux in thf; this is attributed to a steric effect.

The $^1H$ NMR spectrum of $Li\{N(H)C(Ph)C(H)P(Ph)_2{=}NSiMe_3\}$ **3** showed two equal intensity signals at δ 4.16 and δ 4.43. The former was a doublet, $J(^1H–^{31}P)$ 24.3 Hz, and the latter a singlet (NH). This clearly shows that one of the $CH_2$ protons had migrated from carbon to nitrogen in the course of the reaction of $Li\{CH_2P(Ph)_2{=}NSiMe_3\}$ with PhCN. The $^{13}C$-{$^1H$} NMR spectrum showed the silylmethyl signal as a doublet. This imples that the trimethylsilyl group lies on the nitrogen atom attached to the phosphorus, rather than on the more remote nitrogen atom. The $^1H$, $^{13}C$-{$^1H$} and $^{31}P$-{$^1H$} NMR spectra of the potassium compounds **4** and **5** were consistent with the structures shown in Scheme 2. Their $^{13}C$-{H} NMR spectra showed a similar feature to that in complex **1**, in that only one silylmethyl was split by $^{31}P$ coupling.

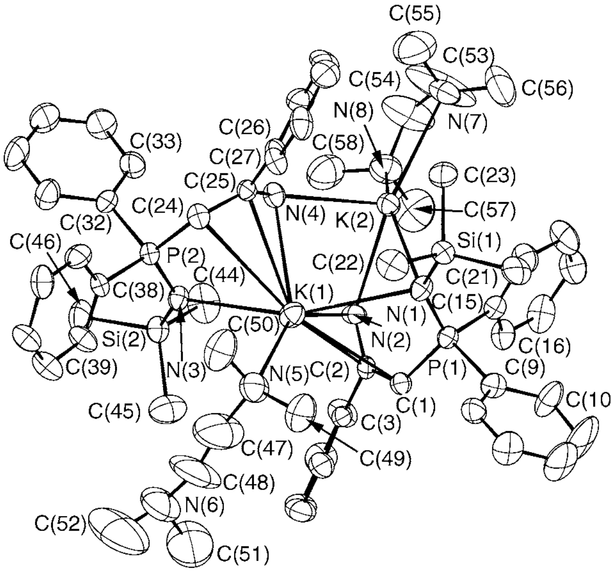


**Fig. 1** Molecular structure of $[K\{N(H)C(Ph)C(H)P(Ph)_2{=}NSiMe_3\}(tmen)]_2$ **6** with the atom numbering scheme

Compounds **7** and **8** are neutral iminophosphoranylenamines. Their $^1H$ NMR spectra showed that the NH signals appeared at δ 8.39 (**7**) and 8.29 (**8**). The high frequency chemical shifts indicate the presence of hydrogen bonds in both molecules.

The molecular structure and the atom numbering scheme of $[K\{N(H)C(Ph)C(H)P(Ph)_2{=}NSiMe_3\}(tmen)]_2$ **6** are shown in Fig. 1. Selected bond distances and angles are presented in Table 1.

Crystalline **6** is a dinuclear molecule with each of the two potassium atoms in a different co-ordination environment. The atom K(1) has co-ordination number nine taking the N(H)C(Ph)C(H)-moiety to occupy three co-ordination sites and K(2) co-ordination number five. As a result of the very crowded environment around K(1), only one nitrogen atom of tmen is co-ordinated to this potasium atom. Unlike K(1), K(2) is bonded to a chelating tmen. It is also noteworthy that the ligand co-ordination is not $\eta^5$, there being no P−K bond. It seems that there is a combination of $\eta^3$-azaallyl and phosphinimine co-ordination, the latter bonding to the potassium through the free-electron pair on nitrogen. The K−C bond lengths are in the range 3.072(9)–3.251(10) Å, but the K−N bond lengths vary rather more widely, from 2.745(8) to 3.137(8) Å. The P atom has a slightly disorted tetrahedral geometry. The mean P−N bond length of 1.58 Å is indicative of a double bond.[14–16] The P(1)−C(1) bond length [1.712(9) Å] is close to that of P(2)−C(24) [1.741(9) Å] and shows that the P−C bond is in between a formal single (1.83 Å)[14,15] and double (1.57 Å)[14] bond. There are no short K···H contacts in the vacant site *trans* to N(4). Intermolecular approach at this site is blocked by the phenyl group C(15)−C(20), and the shortest K(2)···C contacts to this group are K(2)···C(15) 3.48 and K(2)···C(20) 3.45 Å.

## Experimental

All reactions were performed under argon using standard Schlenk techniques. The thf and diethyl ether were dried using sodium–benzophenone; hexane and pentane were dried using sodium–potassium alloy. The NMR spectra were recorded on AC-P250, WM-360 or AMX-500 instruments, and the solvent resonances were used as the internal references for $^{1}$H and $^{13}$C spectra; $H_3PO_4$ (85% aqueous solution) and LiCl (1 mol dm$^{-3}$ aqueous solution) were the external references for $^{31}$P and $^{7}$Li NMR spectra, respectively. Infrared spectra were recorded on a Perkin-Elmer 1720 FT spectrometer as liquid films or Nujol mulls using KBr windows, and elemental analyses were carried out by Medac Ltd, Brunel University. Melting points were determined under argon in sealed capillaries on an electrothermal apparatus and were uncorrected.

### Preparations

**The phosphinimines $CH_2(R)P(Ph)_2{=}NSiMe_3$.** (*a*) *R* = *H*. A mixture of methyl(diphenyl)phosphine (10.0 g, 0.05 mmol) and trimethylsilyl azide (6.6 cm$^3$, 0.05 mmol) was heated at 130 °C for 6 h with stirring. The unreacted starting materials were removed at 25 °C (10$^{-5}$ Torr) leaving $CH_3P(Ph)_2{=}NSiMe_3$ (13.6 g, 95%), as a colourless oil. $^{1}$H NMR (298 K, $CDCl_3$): δ 0.02 (s, 9 H, $SiMe_3$), 1.96 [d, 3 H, $^{2}J(^{1}H{-}^{31}P) = 12.7$ Hz, $CH_3$], 7.46 (s, 6 H, Ph), 7.65–7.75 (m, 4 H, Ph).

(*b*) *R* = *SiMe*$_3$. A solution of $LiCH_2SiMe_3$ (50 cm$^3$ of a 1 mol dm$^{-3}$ solution in pentane, 0.05 mol) was added dropwise to a solution diphenylphosphorus(III) chloride (11.0 g, 0.05 mol) in tetrahydrofuran (50 cm$^3$) at −78 °C with stirring. The mixture was allowed to warm to room temperature with stirring during 15 h. The precipitate was filtered off and solvent was removed from the filtrate *in vacuo*. The residue was distilled to yield $CH_2(SiMe_3)PPh_2$ (10.7 g, 78%), b.p. 99–101 °C (0.02 Torr). $^{1}$H NMR (298 K, $CDCl_3$): δ 0.01 (s, 9 H, $SiMe_3$), 1.43 [d, 2 H, $^{2}J(^{1}H{-}^{31}P) = 10.0$ Hz, $CH_2$], 7.34–7.36 (m, 6 H, Ph), 7.51–7.54 (m, 4 H, Ph). A mixture of $CH_2(SiMe_3)PPh_2$ (10.7 g, 0.039 mol) and trimethylsilyl azide (5.2 cm$^3$, 0.039 mol) was heated at 130 °C for 6 h with stirring. The unreacted starting materials were removed at 25 °C (10$^{-5}$ Torr), leaving a residue of $CH_2(SiMe_3)P(Ph)_2{=}NSiMe_3$ (13.7 g, 97.5%). $^{1}$H NMR (298 K, $CDCl_3$): δ −0.02 (s, 9 H, $SiMe_3$), −0.01 (s, 9 H, $SiMe_3$), 1.69 [d, 2 H, $^{2}J(^{1}H{-}^{31}P) = 15.3$ Hz, $CH_2$], 7.39–7.42 (m, 6 H, Ph), 7.64–7.70 (m, 4 H, Ph).

**$Li\{N(SiMe_3)C(Ph)C(H)P(Me)_2{=}NSiMe_3\}$ 1.** Benzonitrile (0.58 cm$^3$, 5.69 mmol) was added dropwise to a stirred solution of $Li\{CH(SiMe_3)P(Me)_2{=}NSiMe_3\}$ [from $CH_2(SiMe_3)P(Me)_2{=}NSiMe_3$[16] (1.33 g, 5.68 mmol) and LiBu$^n$ (3.6 cm$^3$ of a 1.6 mol dm$^{-3}$ solution in hexane, 5.68 mmol)] (1.37 g, 5.68 mmol) in diethyl ether (30 cm$^3$) at *ca.* 20 °C. The solution was stirred for 4 h and the solvent was then removed *in vacuo*. The resultant solid was recrystallised from pentane to yield the colourless crystalline compound **1** (1.4 g, 72%) (Found: C, 56.5; H, 8.95; N, 7.7. $C_{16}H_{30}LiN_2PSi_2$ requires C, 55.8; H, 8.8; N, 8.15%), m.p. 115–126 °C. NMR (298 K, $C_6D_6$): $^{1}$H, δ 0.17 (s, 9 H, $SiMe_3$); 0.34 (s, 9 H, $SiMe_3$); 0.84–1.05 (br, 3 H, PMe); 1.42–1.60 (br, 3 H, PMe); 3.69 (d, 1 H, CH, *J* = 26.3 Hz); 7.15 (s, 3 H), 7.47 (s, 2 H) (Ph). $^{13}$C-{$^{1}$H}, δ 3.80 (s), 4.06 (d, *J* = 3.5) ($SiMe_3$); 16.21 (d, *J* = 45), 19.58 (d, *J* = 60) (PMe); 77.55 (d, CH, *J* = 118.1); 127.68 (s), 128.65 (s), 128.76 (s), 147.42 (d, *J* = 14.4 Hz) (Ph); 178.91 (s, Ph*C*). $^{31}$P-{$^{1}$H}, δ 17.61. $^{7}$Li-{$^{1}$H}, δ 0.67.

**$Li\{N(H)C(Ph)C(H)P(Ph)_2{=}NSiMe_3\}$ 3.** Benzonitrile (0.4 cm$^3$, 3.92 mmol) was added dropwise at *ca.* −50 °C to a diethyl ether (*ca.* 30 cm$^3$) solution of $Li\{CH_2P(Ph)_2{=}NSiMe_3\}$, prepared from $CH_3P(Ph)_2{=}NSiMe_3$ (1.09 g, 3.80 mmol) and LiBu$^n$ (2.4 cm$^3$ of a 1.6 mol dm$^{-3}$ solution in hexane, 3.84 mmol). The mixture was allowed to warm to room temperature and was stirred overnight, then filtered to remove some yellow precipitate. Volatiles were removed from the filtrate *in vacuo* and the solid residue was washed with pentane (2 × 15 cm$^3$). Drying *in vacuo* yielded the free-flowing, pale yellow powder **3** (1.26 g, 84%) (Found: C, 69.7; H, 6.65; N, 6.95. $C_{23}H_{26}LiN_2PSi$ requires C, 69.7; H, 6.6; N, 7.05%), m.p. 206–208 °C. NMR (298 K, $C_6D_6$ + 10% [$^{2}H_8$]thf): $^{1}$H, δ 0.00 (s, 9 H, $SiMe_3$); 4.16 (d, 1 H, CH, *J* = 24.3 Hz); 4.43 (s, 1 H, NH); 7.08 (s), 7.22 (s), 7.79 (s), 7.84 (s) (Ph). $^{13}$C-{$^{1}$H}, δ 4.32 (d, $SiMe_3$, *J* = 3.8); 67.93 (d, CH, *J* = 78.1); 126.47 (s), 128.07 (d, *J* = 11.3), 128.26 (s), 130.14 (d, *J* = 2.6), 132.44 (d, *J* = 9.9), 139.59 (d, *J* = 93.5), 148.53 (d, *J* = 11.8 Hz) (Ph); 175.88 (s, Ph*C*). $^{31}$P-{$^{1}$H}, δ 14.84. $^{7}$Li-{$^{1}$H}, δ 0.68.

**$K\{N(SiMe_3)C(Ph)C(H)P(Ph)_2{=}NSiMe_3\}$ 4.** Benzonitrile (0.28 cm$^3$, 2.75 mmol) was added dropwise to a stirred solution of $Li\{CH(SiMe_3)P(Ph)_2{=}NSiMe_3]$ (see synthesis of **1**) (1.0 g, 2.74 mmol) in diethyl ether (30 cm$^3$) at −50 °C. The solution was allowed to warm to room temperature and was stirred for 4 h. The solvent was removed *in vacuo* and the resultant red-brown oil was redissolved in hexane (30 cm$^3$). Solid KOBu$^t$ (0.31 g, 2.77 mmol) was added with stirring at room temperature. After further stirring for 3 h, the mixture was filtered. The white precipitate was washed with hexane (2 × 20 cm$^3$), then dried *in vacuo* leaving the white complex **4** (1.15 g, 84%) (Found: C, 61.4; H, 6.8; N, 5.25. $C_{26}H_{34}KN_2PSi_2$ requires C, 62.4; H, 6.85; N, 5.6%), m.p. 174–177 °C. NMR (298 K, $C_5D_5N$): $^{1}$N, δ −0.17 (s, 9 H, $SiMe_3$); 0.12 (s, 9 H, $SiMe_3$); 4.42 (d, 1 H, CH, *J* = 25.8 Hz); 7.18–7.57 (m), 8.14–8.19 (m) (Ph). $^{13}$C-{$^{1}$H}, δ 3.69 (s), 4.68 (d, *J* = 3.7) ($SiMe_3$); 76.31 (d, CH, *J* = 129); 126.51 (s), 127.59 (d, *J* = 5.4), 127.98 (d, *J* = 11.0), 129.29 (s), 132.06 (d, *J* = 9.4), 141.59 (d, *J* = 95.1), 151.04 (d, *J* = 16.9 Hz) (Ph); 176.10 (s, Ph*C*). $^{31}$P-{$^{1}$H}, δ 5.90.

**$K\{N(SiMe_3)C(Ph)C(H)P(Ph)_2{=}NSiMe_3\}$(tmen) 5.** Tetramethylethylenediamine (0.9 cm$^3$, 5.97 mmol) was added dropwise to a stirred suspension of **4** (1.2 g, 2.4 mmol) in hexane (*ca.* 30 cm$^3$) at room temperature. The solid dissolved gradually, yielding a pale yellow solution, which was concentrated to *ca.* 3 cm$^3$ and set aside for several hours at room temperature to yield colourless crystals of compound **5** (1.19 g, 80%) (Found: C, 61.9; H, 8.0; N, 9.1. $C_{32}H_{50}KN_4PSi_2$ requires C, 62.3; H, 8.15; N, 9.1%), m.p. 111–113 °C. NMR (298 K, $C_6D_6$): $^{1}$H, δ −0.12 (s, 9

H, SiMe$_3$); 0.19 (s, 9 H, SiMe$_3$); 1.91 (s, 12 H, tmen), 1.92 (s, 4 H, tmen); 4.40 (d, 1 H, CH, $J = 25.7$ Hz); 7.13–7.23 (m), 7.56–7.59 (m), 7.99–8.05 (m) (Ph). $^{13}$C-{$^1$H}, δ 3.70 (s), 4.68 (d, $J = 3.9$ Hz) (SiMe$_3$); 45.47 (s), 57.36 (s) (tmen); 76.38 (d, CH, $J = 126.6$); 126.94 (s), 127.68 (d, $J = 6.1$), 128.05 (d, $J = 11.3$), 129.49 (d, $J = 2.6$), 131.91 (d, $J = 9.7$), 140.84 (d, $J = 95.7$), 150.44 (d, $J = 16.8$) (Ph); 176.72 (d, Ph*C*, $J = 3.9$ Hz). $^{31}$P-{$^1$H}, δ 7.02.

**N(SiMe$_3$)C(Ph)C(H)P(Me)$_2$N(SiMe$_3$)H 7.** Water (0.2 cm$^3$, 11.11 mmol) was added at −20 °C with stirring to a solution of Li{N(SiMe$_3$)C(Ph)C(H)P(Me)$_2$=NSiMe$_3$} **1** (3.54 g, 10.03 mmol) in thf (20 cm$^3$). The mixture was stirred for 30 min at room temperature. The thf was removed *in vacuo* and the residue was extracted with diethyl ether. The extract was filtered and the filtrate was concentrated *in vacuo*. Crystallisation of the residue from pentane yielded colourless crystals of **7** (2.87 g, 85%) (Found: C, 56.6; H, 9.15; N, 8.25. $C_{16}H_{31}N_2PSi_2$ requires C, 56.8; H, 9.25; N, 8.25%), m.p. 116–118 °C. NMR (298 K, CDCl$_3$): $^1$H, δ −0.08 (s, 9 H, SiMe$_3$); 0.09 (s, 9 H, SiMe$_3$); 1.45 (d, 6 H, PMe$_2$, $J = 12.5$); 3.83 (d, 1 H, CH, $J = 24.6$ Hz); 7.29–7.38 (m, Ph); 8.39 (s, 1 H, NH). $^{13}$C-{$^1$H}, δ −0.02 (s), 2.80 (d, $J = 4.0$) (SiMe$_3$); 20.47 (d, PMe, $J = 64.3$); 86.74 (d, CH, $J = 114.3$); 126.53 (s), 126.59 (s), 127.20 (s), 140.45 (d, $J = 15.1$) (Ph); 162.81 (d, Ph*C*, $J = 10.0$ Hz). $^{31}$P-{$^1$H}, δ 6.46. IR (Nujol): $\nu_{max}$(cm$^{-1}$) 3300–3650 (br) (NH), 1590s, 1609s (C=C, Ph), 1251s (P=N).

**N(SiMe$_3$)C(Ph)C(H)P(Ph)$_2$N(SiMe$_3$)H 8.** Similarly, as for **7**, Li{N(SiMe$_3$)C(Ph)C(H)P(Ph)$_2$=NSiMe$_3$} **2**, prepared from Li{CH(SiMe$_3$)P(Ph)$_2$=NSiMe$_3$} (1.32 g, 3.62 mmol) and PhCN (0.37 cm$^3$, 3.63 mmol), was treated with H$_2$O (0.07 cm$^3$, 3.89 mmol) to yield the pale yellow oil **8** (1.46 g, 87%) (Found: C, 67.2; H, 7.5; N, 5.4. $C_{26}H_{35}N_2PSi_2$ requires C, 67.5; H, 7.6; N, 6.05%). NMR (298 K, CDCl$_3$): $^1$H, δ −0.08 (s, 9 H, SiMe$_3$); −0.05 (s, 9 H, SiMe$_3$); 4.32 (d, 1 H, CH, $J = 23.2$ Hz); 7.33–7.48 (m), 7.67–7.73 (m) (Ph); 8.29 (s, 1 H, NH). $^{13}$C-{$^1$H}, δ 0.00 (s), 2.51 (d, $J = 3.9$) (SiMe$_3$); 85.77 (d, CH, $J = 118.5$); 126.96 (d, $J = 4.4$), 127.44 (s), 129.00 (s), 129.77 (d, $J = 4.6$), 131.17 (d, $J = 19.5$), 136.33 (d, $J = 94.8$), 140.45 (d, $J = 15.0$ Hz) (Ph); 163.83 (s, Ph*C*). $^{31}$P-{$^1$H}, δ 3.99. IR (liquid film): $\nu_{max}$(cm$^{-1}$) 3300–3500 (br) (NH), 1567vs, 1588vs (C=C, Ph), 1256vs (P=N).

### Crystallography

Crystallographic details are given in Table 2. Single crystals of complex **6** were mounted in Lindemann capillaries under argon. Data were collected on an Enraf-Nonius CAD4 diffractometer in the θ–2θ mode with monochromated Mo-Kα radiation (λ = 0.710 73 Å). The structure was solved by direct methods (SHELXS 86)[17] and refined by full-matrix least squares on all $F^2$ (SHELXL 93).[18] All non-H atoms were anisotropic. The H atoms on N(2) and N(4) were located on a difference map and refined with $U_{iso}(H) = 1.5\ U_{eq}(N)$ and the N–H bond lengths restrained to 0.89 Å. Other H atoms were included in riding mode with $U_{iso}$(H) equal to 1.2 $U_{eq}$(C) or 1.5 $U_{eq}$(C) for methyl groups.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/482.

**Table 2** Crystal data and refinement for complex **6**

| | |
|---|---|
| Formula | $C_{58}H_{84}K_2N_8P_2Si_2$ |
| $M$ | 1089.6 |
| Crystal system | Triclinic |
| Space group | $P1$ (no. 1) |
| $a$/Å | 11.310(3) |
| $b$/Å | 11.856(5) |
| $c$/Å | 13.263(4) |
| α/° | 70.51(3) |
| β/° | 70.83(3) |
| γ/° | 83.59(3) |
| $U$/Å$^3$ | 1583.6(9) |
| $Z$ | 1 |
| $D$/g cm$^{-3}$ | 1.14 |
| Crystal size/mm | 0.2 × 0.2 × 0.2 |
| Radiation λ/Å | 0.710 73 |
| $F$(000) | 584 |
| μ(Mo-Kα)/mm$^{-1}$ | 0.28 |
| Temperature/K | 293(2) |
| Total reflections | 5553 |
| Independent reflections | 5553 |
| Reflections with $I > 2\sigma(I)$ | 3319 |
| $R1$ [$I > 2\sigma(I)$][a] | 0.067 |
| $wR2$ (all data)[b] | 0.174 |

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{\frac{1}{2}}$.

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