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Synthesis, structures and reactions of lithium complexes of [(*o*-RCHC$_6$H$_4$)PPh$_2$=NSiMe$_3$]$^-$ (R = H, SiMe$_3$) ligands

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N-Trimethylsilyl *o*-methylphenyldiphenylphosphinimine, (*o*-MeC$_6$H$_4$)PPh$_2$=NSiMe$_3$ (**1**), was prepared by reaction of Ph$_2$P(Br)=NSiMe$_3$ with *o*-methylphenyllithium. Treatment of **1** with LiBu^n and then Me$_3$SiCl afforded (*o*-Me$_3$SiCH$_2$-C$_6$H$_4$)PPh$_2$=NSiMe$_3$ (**2**). Lithiations of both **1** and **2** with LiBu^n in the presence of tmen gave crystalline lithium complexes [Li{CH(R)C$_6$H$_4$(PPh$_2$=NSiMe$_3$)-2}·tmen] (**3**, R = H; **4**, R = SiMe$_3$). From the mother liquor of **4**, traces of the tmen-bridged complex [Li{CH(SiMe$_3$)C$_6$H$_4$(PPh$_2$=NSiMe$_3$)-2}]$_2$(μ-tmen) (**5**) were obtained. Reaction of **2** with LiBu^n in Et$_2$O yielded complex [Li{CH(SiMe$_3$)C$_6$H$_4$(PPh$_2$=NSiMe$_3$)-2}·OEt$_2$] (**6**). Reaction of lithiated **1** with Me$_2$SiCl$_2$ in a 2:1 molar ratio afforded dimethylsilyl-bridged compound Me$_2$Si[CH$_2$C$_6$H$_4$(PPh$_2$=NSiMe$_3$)-2]$_2$ (**7**). Lithiation of **7** with two equivalents of LiBu^n in Et$_2$O yielded [Li$_2${(CHC$_6$H$_4$(PPh$_2$=NSiMe$_3$)-2)$_2$SiMe$_2$}·0.5OEt$_2$] (**8**·0.5OEt$_2$). Treatment of **4** with PhCN formed a lithium enamide complex [Li{N(SiMe$_3$)C(Ph)CHC$_6$H$_4$(PPh$_2$=NSiMe$_3$)-2}·tmen] (**9**). Reaction of two equivalents of **5** with 1,4-dicyanobenzene gave a dilithium complex [{Li(OEt$_2$)$_2$}$_2$(1,4-{C(N(SiMe$_3$)CHC$_6$H$_4$(PPh$_2$=NSiMe$_3$)-2}$_2$C$_6$H$_4$)] (**10**). All compounds were characterised by NMR spectroscopy and elemental analyses. The structures of compounds **2**, **3**, **5**, **6** and **9** have been determined by single crystal X-ray diffraction techniques.

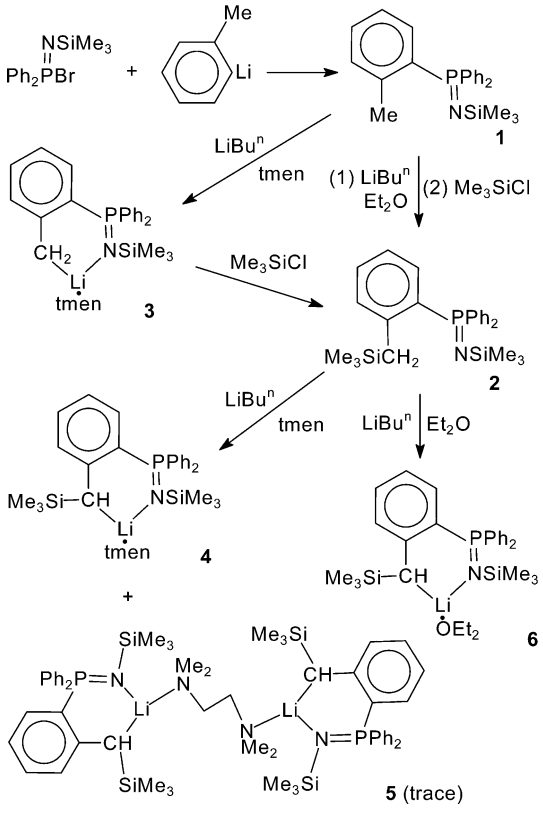
Introduction

Ligands bearing a sidearm donor are widely used in coordination and organometallic chemistry.[1,2] The ligands provide extra stabilisation and structural rigidity and often lead to remarkable reactivity due to intramolecular chelating coordination.[3] The donation functionality has also a strong influence on the reaction selectivity or catalytic activity of the complexes.[4] For example, Kol and coworkers found that the catalytic activity for olefin polymerisation of amine bis(phenolate) complexes of zirconium and hafnium was strongly influenced by an extra donor on a sidearm of the ligand.[4,5] A number of organolithium complexes with chelated structures *via* a sidearm donation have been reported. They were used as ligand transfer reagents and also showed interesting structural features. For example, reactions[6] of [LiC$_6$H$_4$(Ph$_2$P=NSiMe$_3$)-2] with halides of Zn, Cu(I), In(III), Fe(II), Sn(II), and Pb(II) or with Ph$_3$GeCl gave the corresponding aryl complexes.[7] Recently, solution structures and dynamics of amine- and ether-chelated aryllithium complexes were systematically studied. The effects of the chelate ring size and chelating atom on the structural, stereochemical and chemical properties of the lithium complexes were explored.[8] Herein we report the synthesis, structures and reactions of lithium complexes of *C*,*N*-chelating ligands with a Ph$_2$P=NSiMe$_3$ sidearm, [Li·L{CH(R)C$_6$H$_4$(PPh$_2$=NSiMe$_3$)-2}] (R = H or SiMe$_3$; L = Et$_2$O or tmen).

Results and discussion

The synthesis and reactions of (*o*-RCH$_2$C$_6$H$_4$)PPh$_2$=NSiMe$_3$ (R = H, SiMe$_3$) are summarised in Scheme 1.

N-Trimethylsilyl-*o*-methylphenyldiphenylphosphinimine, (*o*-MeC$_6$H$_4$)PPh$_2$=NSiMe$_3$ (**1**), was prepared by the reaction of Ph$_2$P(Br)=NSiMe$_3$ with *o*-methylphenyllithium in high yield. Treatment of **1** with LiBu^n in Et$_2$O and subsequent Me$_3$SiCl gave (*o*-Me$_3$SiCH$_2$C$_6$H$_4$)PPh$_2$=NSiMe$_3$ (**2**). Attempts to prepare compounds **1** and **2** by reaction of (*o*-RCH$_2$C$_6$H$_4$)PPh$_2$ (R = H, SiMe$_3$) with Me$_3$SiN$_3$ were unsuccessful. Both **1** and **2** reacted readily with LiBu^n in the presence of tmen to afford lithium complexes **3** and **4**, respectively. From the mother liquor of **4**, a few crystals were further obtained and identified by single crystal X-ray diffraction as **5**. In the molecule two [Li{CH(SiMe$_3$)C$_6$H$_4$(PPh$_2$=NSiMe$_3$)-2}] units were joined by a tmen bridge. tmen generally functions as a chelating bidentate ligand. This bridging coordination mode is relatively rare.[9] Compounds **1** and **2** were also lithiated by treatment with LiBu^n in Et$_2$O, but only the lithiated product of **2** was isolated as yellow–orange crystals (**6**). Complex **6** can be converted to **4** by its recrystallisation with tmen in hexane. Treatment of **1** with LiBu^n in Et$_2$O and then half equivalents of Me$_2$SiCl$_2$ afforded



Scheme 1

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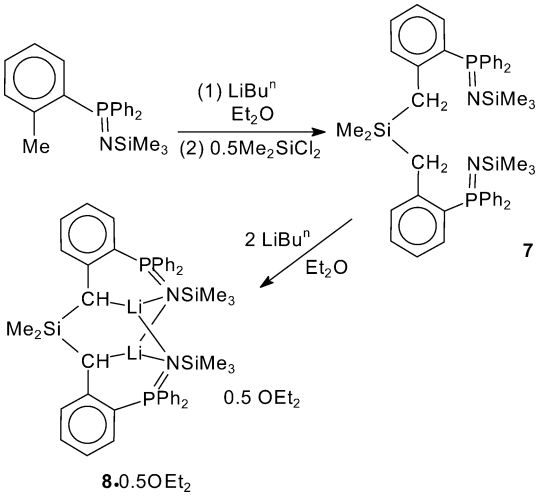
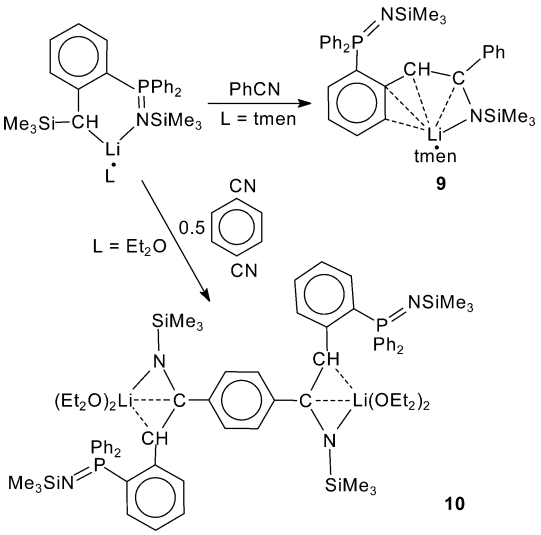
$Me_2Si[CH_2C_6H_4(PPh_2{=}NSiMe_3)\text{-}2]_2$ (**7**) as colourless crystals (Scheme 2). Reaction of compound **7** with two equivalents of $LiBu^n$ in Et_2O gave a dilithium complex, assumed to be **8**·0.5Et_2O, as red crystals. Reaction of complex **4** with PhCN in Et_2O proceeded readily and formed red crystalline complex **9** (Scheme 3). A 1,3-trimethylsilyl C → N migration was observed in the reaction. Similar treatment of two equivalents of **6** with 1,4-dicyanobenzene in hexane afforded dilithium complex **10** in high yield. If the reaction was carried out in Et_2O or thf, a mixture was obtained.



Scheme 2



Scheme 3

The compounds **1–10** were characterised by ^1H, ^{13}C and ^{31}P NMR spectroscopy and elemental analysis. The ^1H NMR spectrum of complex **3** showed that the two protons of CH_2 group were inequivalent, the chemical shifts being at 3.07 and 3.17 ppm, respectively. In complex **8** two Me groups of $SiMe_2$ were inequivalent. However, the ^1H, ^{13}C and ^{31}P NMR spectra showed that the two $[CHC_6H_4(PPh_2{=}NSiMe_3)\text{-}2]$ units in complex **8** had identical chemical environments. For example, its ^1H NMR spectrum gave single CH signal at 2.98 ppm and single $SiMe_3$ signal at 0.35 ppm, the ^{31}P NMR spectrum also gave single resonance signal. The ^1H NMR spectrum of **10** showed that in the molecule the chemical environment of two azaallyl units was identical.

The structures of compounds **2**, **3**, **5**, **6** and **9** were further characterised by single crystal X-ray diffraction. The structure of **2** is presented in Fig. 1 along with selected bond lengths

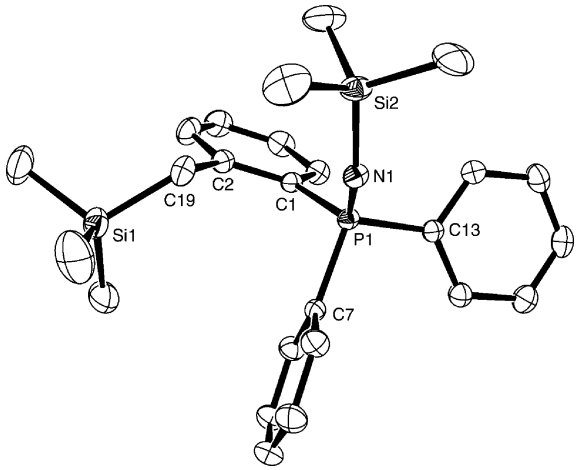


Fig. 1 Molecular structure of **2** shown with 30% thermal ellipsoids. Selected bond lengths (in Å) and angles (in °): P1–N1, 1.539(3); P1–C1, 1.828(3); P1–C7, 1.816(3); P1–C13, 1.822(4); N1–P1–C1, 117.16(15); N1–P1–C7, 111.87(16); C7–P1–C1, 104.86(15).

and angles. Crystalline **2** is monomeric. The P atom is four-coordinate, having a distorted tetrahedral geometry. The P–N bond length of 1.539(3) Å is indicative of a P–N double bond, whereas the P–C distances of 1.816(3)–1.828(3) Å show these to be P–C single bonds.[10]

Complex **3** is a monomer and crystallises with two molecules in the unit cell. An ORTEP representation of the structure of a single molecule is shown in Fig. 2 along with selected bond lengths and angles. The lithium atom lies outside C7–C2–C1 plane. The torsion angle of Li1C7C2C1 is 58.1°. The Li1–C7 distance of 2.300(10) Å is a little longer than those in $[Li\{CH(SiMe_3)PPh_2{=}NSiMe_3\}]_2$ (average 2.156 Å),[11] but shorter than those in $[Li\{CH(PPh_2{=}NSiMe_3)_2\}]_2$ [2.370(9)–2.784(10) Å][12] and $[Li_2\{C(PPh_2{=}NSiMe_3)_2\}]_2$ (average 2.38 Å).[13] The distance of the Li1 ··· C2 contact [2.694(10) Å] is too long to be considered as contributing significantly to the bonding. The 2.103(9) Å of Li1–N1 distance is longer than those in $[LiC_6H_4(Ph_2P{=}NSiMe_3)\text{-}2]$ (average 2.032 Å)[6] and $[Li\{CH(SiMe_3)PPh_2{=}NSiMe_3\}(OEt_2)_2]$ [2.018(5) Å],[11] but still within the normal range as observed for lithium amides[14] and lithium phosphinimines.[11,13,15]

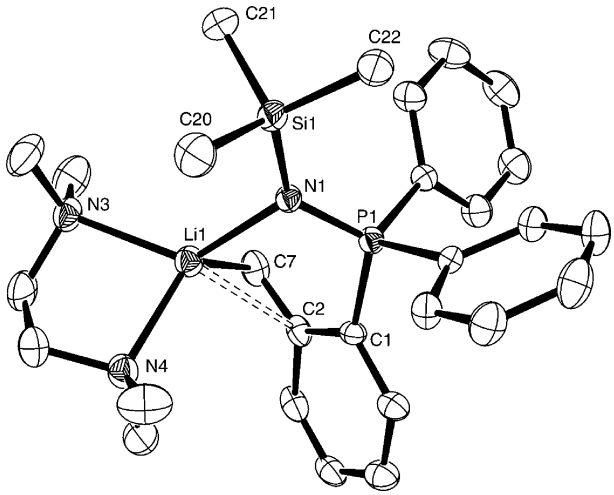


Fig. 2 Molecular structure of **3** shown with 20% thermal ellipsoids. Selected bond lengths (in Å) and angles (in °): Li1–N1, 2.103(9); Li1–C7, 2.300(10); Li1–C2, 2.694(10); Li1–N3, 2.172(9); Li1–N4, 2.165(9); P1–N1, 1.576(4); P1–C1, 1.765(5); C2–C7, 1.376(6); N1–Li1–C7, 93.6(4); N1–Li1–N3, 127.5(4); N3–Li1–C7, 107.5(4); C2–C7–Li1, 90.6(4); P1–N1–Li1, 107.9(3); N1–P1–C1, 113.1(2).

The structure of complex **5** is presented in Fig. 3 along with selected bond lengths and angles. The molecule lies about

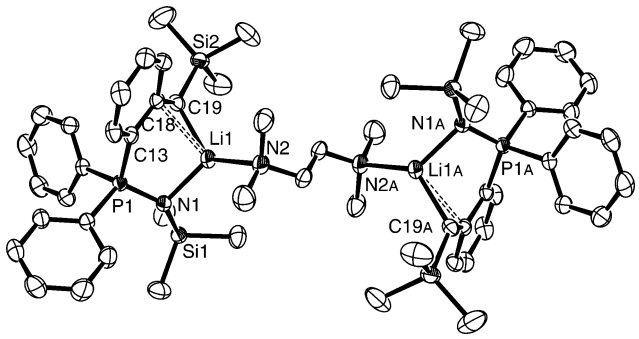


Fig. 3 Molecular structure of **5** shown with 30% thermal ellipsoids. Selected bond lengths (in Å) and angles (in °): Li1–N1, 2.022(5); Li1–N2, 2.104(6); Li1–C19, 2.203(6); Li1–C18, 2.409(5); Li1–C13, 2.636(6); P1–N1, 1.574(2); P1–C13, 1.787(3); C18–C19, 1.421(4); N1–Li1–N2, 129.1(3); N1–Li1–C19, 97.8(2); N2–Li1–C19, 131.5(3); N1–P1–C13, 109.87(12); Li1–C19–C18, 80.2(2); P1–N1–Li1, 102.17(8).

an inversion centre and that the additional letters "A" in the atom labels in Fig. 3 refer to atoms at equivalent position $(2 - x, 1 - y, -z)$. The complex is monomeric in the solid state. In the molecule, tmen bridges two [Li{CH(SiMe$_3$)-C$_6$H$_4$(PPh$_2$=NSiMe$_3$)-2}] units *via* the coordination of the nitrogen atoms to the lithium atoms. The atoms N1, N2, Li1 and C19 are approximately coplanar, the sum of angles at lithium atom being 358.4°. The torsion angle of Li1C19C18C13 is 58.6°, very close to corresponding that in complex **3**. The Li1–C19 distance of 2.203(6) Å is slightly shorter than that in **3** [2.300(10) Å]. The Li1–N1 distance of 2.024(7) Å is also shorter than corresponding that in **3** [2.103(9) Å]. In addition, it is also noted that the distance of Li1–C18 [2.409(5) Å] is apparently shorter than Li1–C2 in **3** [2.694(10) Å]. These are ascribed to lower coordinate number of the lithium atoms in **5** than in **3**.

The structure of complex **6** is shown in Fig. 4 along with selected bond lengths and angles. Complex **6** is also monomeric in the solid state. The bond parameters of **6** are similar to those of complex **5**. For example, the Li1–C19 distance of 2.216(8) Å in **6** is close to corresponding that in **5** [2.203(6) Å]. The distances of Li1–N1 and Li1–C18 [2.024(7) Å and 2.402(8) Å, respectively] in **6** are almost identical to coresponding those in **5** [2.022(5) Å and 2.409(5) Å, respectively].

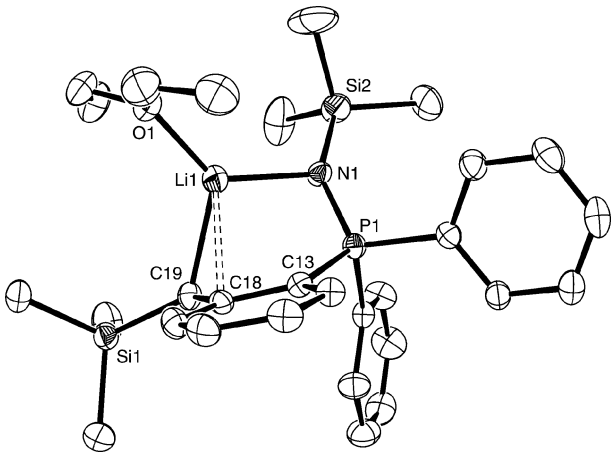


Fig. 4 Molecular structure of **6** shown with 20% thermal ellipsoids. Selected bond lengths (in Å) and angles (in °): Li1–N1, 2.024(7); Li1–C19, 2.216(8); Li1–C18, 2.402(8); Li1–C13, 2.718(8); Li1–O1, 1.925(8); P1–N1, 1.573(3); P1–C13, 1.788(4); C18–C19, 1.416(5); N1–Li1–C19, 102.6(3); N1–Li1–O1, 132.0(4); C19–Li1–O1, 125.3(4); C18–C19–Li1, 79.5(3); P1–N1–Li1, 102.8(2); C13–P1–N1, 109.91(16).

The ORTEP drawing of complex **9** is exhibited in Fig. 5, along with selected bond lengths and angles. Crystalline **9** is monomeric and there is not coordinate interaction between the nitrogen atom of Ph$_2$P=NSiMe$_3$ group and the lithium atom.

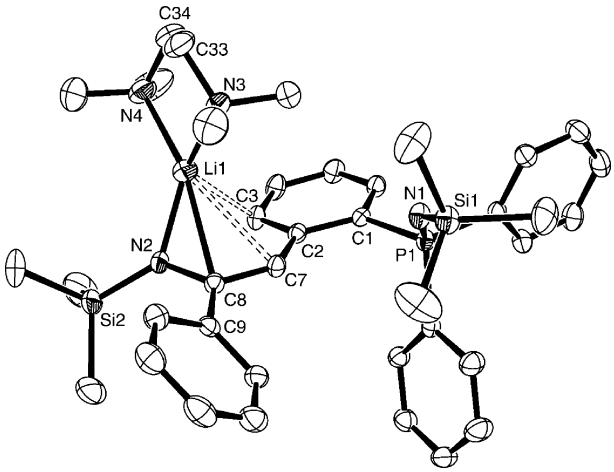


Fig. 5 Molecular structure of **9** shown with 20% thermal ellipsoids. Selected bond lengths (in Å) and angles (in °): Li1–N2, 1.972(6); Li1–N3, 2.083(7); Li1–N4, 2.134(7); Li1–C3, 2.651(7); Li1–C7, 2.752(7); Li1–C8, 2.496(6); N2–C8, 1.360(4); C2–C7, 1.446(4); C7–C8, 1.381(4); P1–N1, 1.545(3); N2–Li1–N3, 131.1(3); N2–Li1–N4, 132.5(4); N3–Li1–N4, 86.2(3); N2–Li1–C8, 32.87(13); N2–Li1–C7, 59.24(18); N2–C8–C7, 125.0(3); C2–C7–C8, 130.3(3).

The Li(tmen) group is positioned above N1C8C7 plane. The Li1–N2 distance of 1.972(6) Å is in the normal range for the Li–N (amide) bonds.[14] The Li1–C8 distance of 2.496(6) Å shows significant bonding interaction, while the distances between Li1 and the C7, C2, and C3 atoms are too long for a bonding interaction. Although the bond distances from the lithium atom to N2, C8, C7, C2 and C3 suggest that some extent of π interaction is present, it is probably more proper to regard **9** as an enamide, rather than an η^3-1-azaallyl.[16] The structure of **9** is similar to those of [Li{N(SiMe$_3$)C(Ph)C(H)Ph}(tmen)][16] and [Li$_2$(tmen)$_2${*o*-, *m*-or *p*-{N(SiMe$_3$)C(R)C(H)}$_2$C$_6$H$_4$}] (R = Bu^t, Ph).[17]

The structure of complex **10** was also determined by single crystal X-ray diffraction techniques. However, the data quality is poor due to the quality of the crystal. Hence, the data is not reported here. Even so, the coordinate mode of the complex can be identified from the data. The structure is similar to that of **9**. Namely, there is no interaction between Ph$_2$P=NSiMe$_3$ groups and the lithium atoms. The Li–N distances are short, while the distances between the lithium atoms and the carbon atoms of the respective azaallyl are rather long.

Experimental

All experiments were performed under nitrogen using standard Schlenk and vacuum line techniques. Solvents were distilled under nitrogen over sodium (toluene), sodium–benzophenone (benzene, thf, Et$_2$O and n-hexane) and degassed prior to use. C$_6$D$_6$ were purchased from Acros Organics and stored over Na/K alloy and degassed prior to use. CDCl$_3$, Ph$_2$PCl and 1,4-dicyanobenzene were purchased from Acros Organics and used as obtained. LiBu^n was purchased from Acros Organics and Alfa Acesar and used as received. tmen was purchased from Acros Organics, dried with sodium and distilled prior to use. Ph$_2$P(Br)=NSiMe$_3$[18] and *o*-MeC$_6$H$_4$Li[19] were prepared according to the literature. NMR spectra were recorded on a Bruker av400 or av300 spectrometer at ambient temperature. The chemical shifts of ^{1}H and ^{13}C{^{1}H} NMR spectra are referenced to internal solvent resonances; the ^{31}P{^{1}H} NMR spectra are referenced to external 85% H$_3$PO$_4$. Elemental analyses were performed by the Analytical Centre of University of Science and Technology of China and the Analytical Laboratory of Shanghai Institute of Organic Chemistry. Melting points were uncorrected.

Preparations

(*o*-MeC$_6$H$_4$)PPh$_2$=NSiMe$_3$ (1). To a diethyl ether solution of Ph$_2$P(Br)=NSiMe$_3$ prepared from Ph$_2$PN(SiMe$_3$)$_2$ (7.53 g, 21.79 mmol) and Br$_2$ (1.12 cm^3, 21.79 mmol) was added a diethyl ether solution of LiC$_6$H$_4$Me-2 (prepared from 2-BrC$_6$H$_4$Me and Li) at about −80 °C. The mixture was allowed to warm to room temperature and stirred overnight. Solvent was removed and the residue was extracted with benzene (30 cm^3 × 2). The mixture was filtered and distilled *in vacuo* to dry to give white solid. The solid was recrystallised from hexane to afford colourless crystals (4.76 g, 60%), mp 81–83 °C (Found: C, 72.63; H, 7.25; N, 3.77%. C$_{22}$H$_{26}$NPSi requires C, 72.69; H, 7.21; N, 3.85%). ^{1}H NMR (CDCl$_3$): δ −0.01 (s, 9H, SiMe$_3$), 2.25 (s, 3H, Me), 7.04–7.15 (m, 3H, Ph + C$_6$H$_4$), 7.28–7.38 (m, 7H, Ph + C$_6$H$_4$), 7.62–7.70 (m, 4H, Ph + C$_6$H$_4$). ^{13}C NMR (CDCl$_3$): δ 4.32, 22.05, 125.46 (d, J = 12.4 Hz), 128.52, 130.75, 131.17, 132.06 (d, J = 10.2 Hz), 132.31, 133.31 (d, J = 12.7 Hz), 133.80, 135.10, 135.84, 137.22, 142.64 (d, J = 8.1 Hz). ^{31}P NMR (CDCl$_3$): δ 1.65.

(*o*-Me$_3$SiCH$_2$C$_6$H$_4$)PPh$_2$=NSiMe$_3$ (2). To a solution of **1** (2.34 g, 6.44 mmol) and tmen (1 cm^3, 6.63 mmol) in hexane (30 cm^3) at about −30 °C was added dropwise LiBu^n (2.9 cm^3, 2.25 M solution in hexanes, 6.53 mmol) with stirring. The solution was warmed to room temperature and stirred for 6 h. Volatiles were removed *in vacuo* and the residue was dissolved in Et$_2$O (30 cm^3). To the solution was added Me$_3$SiCl (0.9 cm^3, 7.04 mmol) at about −80 °C. The mixture was stirred overnight at room temperature and then filtered. The filtrate was distilled *in vacuo* to remove solvent and tmen. The residual solid was recrystallised from hexane to give colourless crystals (2.66 g, 95%), mp 122–124 °C (Found: 68.07; H, 7.66; N, 2.91%. C$_{25}$H$_{34}$NPSi$_2$ requires C, 68.92; H, 7.87; N, 3.21%). ^{1}H NMR (CDCl$_3$): δ −0.14 (s, 9H, SiMe$_3$), −0.03 (s, 9H, SiMe$_3$), 2.60 (s, 2H, CH$_2$), 6.98–7.15 (m, 3H, Ph + C$_6$H$_4$), 7.25–7.30 (m, 1H, Ph + C$_6$H$_4$), 7.40–7.46 (m, 6H, Ph + C$_6$H$_4$), 7.55–7.62 (m, 4H, Ph + C$_6$H$_4$). ^{13}C NMR (CDCl$_3$): δ −0.66, 4.04 (d, J = 3.1 Hz), 24.66 (d, J = 4.1 Hz), 123.45, 128.33 (d, J = 11.9 Hz), 130.63, 130.66, 130.72, 132.14 (d, J = 10.1 Hz), 133.76, 133.83 (d, J = 13.5 Hz), 137.06, 146.77 (d, J = 7.7 Hz). ^{31}P NMR (CDCl$_3$): δ 4.06.

Compound **2** was also prepared by lithiation of **1** in Et$_2$O and then treatment with Me$_3$SiCl.

[LiCH$_2$C$_6$H$_4${(PPh$_2$=NSiMe$_3$)-2}(tmen)] (3). To a solution of **1** (0.968 g, 2.66 mmol) and tmen (0.4 cm^3, 2.65 mmol) in hexane (25 cm^3) at about −30 °C was added dropwise LiBu^n (1.2 cm^3, 2.25 M solution in hexanes, 2.7 mmol) with stirring. The solution was stirred at room temperature for 6 h and then filtered. Concentration of the filtrate gave red crystals (1.05 g, 81%), mp 129–131 °C (Found: C, 68.91; H, 8.24; N, 8.33%. C$_{28}$H$_{41}$N$_3$PliSi requires C, 69.25; H, 8.51; N, 8.65%). ^{1}H NMR (C$_6$D$_6$): δ 0.25 (s, 9H, SiMe$_3$), 1.88 (s, 4H, tmen), 2.08 (s, 12H, tmen), 3.07 (s, 1H, CH$_2$), 3.17 (s, 1H, CH$_2$), 5.63–5.68 (m, 1H, Ph + C$_6$H$_4$), 6.41–6.49 (m, 1H, Ph + C$_6$H$_4$), 6.61 (t, J = 6.3 Hz, 1H, Ph + C$_6$H$_4$), 6.75 (t, J = 7.8 Hz, 1H, Ph + C$_6$H$_4$), 7.13–7.19 (m, 6H, Ph + C$_6$H$_4$), 7.60–8.35 (b, 4H, Ph + C$_6$H$_4$). ^{13}C NMR (C$_6$D$_6$): δ 5.20, 46.71, 57.38, 59.09, 96.35, 98.04, 101.96 (d, J = 14.6 Hz), 122.65 (d, J = 10.6 Hz), 127.16, 128.16, 130.66 (d, J = 7.2 Hz), 133.48 (d, J = 9.7 Hz), 135.26 (d, J = 14.3 Hz), 136.21, 153.64 (d, J = 10.7 Hz). ^{31}P NMR (C$_6$D$_6$): δ 23.46.

[LiCH(SiMe$_3$)C$_6$H$_4${(PPh$_2$=NSiMe$_3$)-2}(tmen)] (4). To a solution of **2** (1.90 g, 4.36 mmol) and tmen (0.66 cm^3, 4.37 mmol) in hexane (35 cm^3) at about −30 °C was added dropwise LiBu^n (2 cm^3, 2.25 M solution in hexanes, 2.7 mmol) with stirring. The solution was stirred at room temperature for 6 h and then filtered. Concentration of the filtrate gave red crystals (2.15 g, 88%), mp 136–138 °C (Found: C, 66.44; H, 8.60; N, 7.10%. C$_{31}$H$_{49}$N$_3$PLiSi$_2$ requires C, 66.75; H, 8.85; N, 7.53%). ^{1}H NMR (C$_6$D$_6$): δ 0.25 (s, 9H, SiMe$_3$), 0.31 (s, 9H, SiMe$_3$), 1.90 (s, 4H, tmen), 2.08 (s, 12H, tmen), 2.88 (s, 1H, CH), 5.88–5.95 (m, 1H, Ph + C$_6$H$_4$), 6.55–6.63 (m, 1H, Ph + C$_6$H$_4$), 6.88–6.95 (m, 2H, Ph + C$_6$H$_4$), 7.10–7.20 (m, 6H, Ph + C$_6$H$_4$), 7.65–8.25 (b, 4H, Ph + C$_6$H$_4$). ^{13}C NMR (C$_6$D$_6$): δ 1.90, 5.10 (d, J = 4 Hz), 46.49, 57.71, 60.21, 105.51, 123.85 (d, J = 10.8 Hz), 130.66 (d, J = 2.8 Hz), 132.30, 132.44, 133.30 (d, J = 9.7 Hz), 134.92, 137.63, 159.25. ^{31}P NMR (C$_6$D$_6$): δ 23.50.

The mother liquor was further concentrated to afford several crystals identified by single crystal X-ray diffraction techniques as complex **5**.

[LiCH(SiMe$_3$)C$_6$H$_4${(PPh$_2$=NSiMe$_3$)-2}(OEt$_2$)] (6). To a solution of **2** (0.375 g, 0.86 mmol) in Et$_2$O (10 cm^3) at about −30 °C was added dropwise LiBu^n (0.35 cm^3, 2.5 M solution in hexanes, 0.87 mmol) with stirring. The solution was stirred at room temperature for 6 h and then filtered. Concentration of the filtrate gave yellow–orange crystals (0.40 g, 90%). mp 95–97 °C (Found: C, 67.88; H, 8.17; N, 2.63%. C$_{29}$H$_{43}$NOPLiSi$_2$ requires C, 67.54; H, 8.40; N, 2.72%). ^{1}H NMR (C$_6$D$_6$): δ 0.20 (s, 9H, SiMe$_3$), 0.30 (s, 9H, SiMe$_3$), 1.08 (t, J = 7.0 Hz, 6H, Et$_2$O), 2.97 (s, 1H, CH), 3.23 (q, J = 7.0 Hz, 4H, Et$_2$O), 5.94–6.02 (m, 1H, Ph + C$_6$H$_4$), 6.56–6.64 (m, 1H, Ph + C$_6$H$_4$), 6.98 (t, J = 7.5 Hz, 6H, Ph + C$_6$H$_4$), 7.10–7.24 (m, 7H, Ph + C$_6$H$_4$), 7.50–8.20 (b, 4H, Ph + C$_6$H$_4$). ^{13}C NMR (C$_6$D$_6$): δ 2.02, 4.05 (d, J = 3.8 Hz), 14.78, 59.15, 66.32, 106.99,(d, J = 14.6 Hz), 123.33 (d, J = 10.0 Hz), 128.26, 130.74, 131.06, 131.44, 132.37 (d, J = 10.1 Hz), 133.19 (d, J = 10.3 Hz), 134.90 (d, J = 14.9 Hz), 157.21 (d, J = 10.4 Hz). ^{31}P NMR (C$_6$D$_6$): δ 20.74.

Me$_2$Si[CH$_2$C$_6$H$_4$(PPh$_2$=NSiMe$_3$)-2]$_2$ (7). To a solution of **1** (2.215 g, 6.09 mmol) in Et$_2$O (30 cm^3) at about −30 °C was added dropwise LiBu^n (2.44 cm^3, 2.5 M solution in hexanes, 6.1 mmol) with stirring. The solution was stirred at room temperature for 5 h. The resulting solution was cooled to about −80 °C and Me$_2$SiCl$_2$ (0.37 cm^3, 3.04 mmol) was added. The mixture was stirred overnight at room temperature and then filtered. Solvent was removed from the filtrate to give white solid. Recrystallisation of the solid from hexane afforded compound **7** (1.67 g, 70%), mp 100–106 °C (Found: C, 70.67; H, 7.49; N, 3.57%. C$_{46}$H$_{56}$N$_2$P$_2$Si$_3$ requires C, 70.55; H, 7.21; N, 3.58%). ^{1}H NMR (CDCl$_3$): δ −0.38 (s, 6H, SiMe$_2$), −0.06 (s, 18H, SiMe$_3$), 2.55 (s, 4H, CH$_2$), 6.93–7.00 (m, 4H, Ph + C$_6$H$_4$), 7.07–7.13 (m, 2H, Ph + C$_6$H$_4$), 7.20–7.26 (m, 2H, Ph + C$_6$H$_4$), 7.36–7.46 (m, 12H, Ph + C$_6$H$_4$), 7.54–7.61 (m, 8H, Ph + C$_6$H$_4$). ^{13}C NMR (CDCl$_3$): δ −2.11, 4.10, 24.33, 123.34 (d, J = 13.2 Hz), 128.23 (d, J = 11.8 Hz), 130.59, 130.65 (d, J = 2.6 Hz), 131.03 (d, J = 10.1 Hz), 131.20, 132.15 (d, J = 10.0 Hz), 132.64, 133.84 (d, J = 14.0 Hz), 135.63, 136.94, 146.43 (d, J = 8.1 Hz). ^{31}P NMR (C$_6$D$_6$): δ 2.62.

[Li$_2${CHC$_6$H$_4$(PPh$_2$=NSiMe$_3$)-2}$_2$SiMe$_2$·(0.5OEt$_2$)] (8·0.5-OEt$_2$). To a stirred solution of **7** (0.345 g, 0.44 mmol) in Et$_2$O (20 cm^3) at about −80 °C was added dropwise LiBu^n (0.36 cm^3, 2.5 M solution in hexane, 0.9 mmol). The mixture was allowed to warm to room temperature and stirred overnight. The red solution was filtered and the filtrate was concentrated to give yellow orange crystals identified by NMR spectra as **8**·0.5Et$_2$O (0.268 g, 73%), mp 70–74 °C (Found: C, 69.57; H, 6.49; N, 3.27%. C$_{46}$H$_{54}$N$_2$P$_2$Si$_3$Li$_2$·0.5Et$_2$O requires C, 69.29; H, 7.15; N, 3.37%.). ^{1}H NMR (C$_6$D$_6$): δ 0.06 (s, 3H, SiMe), 0.13 (s, 3H, SiMe), 0.35 (s, 18 H, SiMe$_3$), 2.98 (s, 2H, CH), 1.11 (t, J = 7.0 Hz, 3H, Et$_2$O), 3.26 (q, J = 7.0 Hz, 2H, Et$_2$O), 6.73–6.78 (m, 2H, Ph + C$_6$H$_4$), 7.03–7.07 (m, 16H, Ph + C$_6$H$_4$), 7.20–7.27 (m, 2H, Ph + C$_6$H$_4$), 7.63–7.72 (m, 6H, Ph + C$_6$H$_4$), 7.78–7.87 (m, 2H, Ph + C$_6$H$_4$). ^{13}C NMR (C$_6$D$_6$): δ 4.31 (d, J = 3 Hz), 4.61 (d, J = 3.2 Hz), 15.57, 24.76 (d, J = 3.9 Hz), 65.92, 123.57 (d, J = 13.3 Hz), 128.83 (d, J = 7.4 Hz), 130.76 (d, J = 2.6 Hz), 132.07 (d, J = 10.1 Hz), 132.42 (d, J = 10 Hz), 133.26 (d, J = 10.2 Hz), 134.18 (d, J = 14 Hz), 136.27, 137.56, 147.14 (d, J = 7.9 Hz). ^{31}P NMR (C$_6$D$_6$): δ 4.80.

Reaction of complex 4 with PhCN. To the solution of complex **4** (0.762 g, 1.366 mmol) in Et$_2$O (15 cm^3) was added

Table 1 Details of the X-ray structure determinations of compounds **2**, **3**, **5**, **6** and **9**

	2	**3**	**5**	**6**	**9**
Empirical formula	$C_{25}H_{34}NPSi_2$	$C_{28}H_{41}LiN_3PSi$	$C_{56}H_{82}Li_2N_4P_2Si_4$	$C_{29}H_{43}LiNOPSi_2$	$C_{38}H_{54}LiN_4PSi_2$
Formula weight/u	435.68	485.64	999.44	515.73	660.94
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$Pbca$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a/Å	8.677(2)	19.514(4)	10.679(3)	10.780(5)	10.430(3)
b/Å	11.776(3)	16.239(3)	11.054(3)	20.347(9)	15.305(5)
c/Å	26.127(7)	37.215(6)	15.246(4)	14.692(6)	25.749(6)
α/°	90	90	87.212(5)	90	90
β/°	94.496(6)	90	77.795(5)	92.382(9)	90.376(8)
γ/°	90	90	61.351(5)	90	90
V/Å^3	2661.4(12)	11793(4)	1540.7(8)	3220(2)	4110(2)
Z	4	16	1	4	4
D_c/g cm^{-3}	1.087	1.094	1.077	1.064	1.068
$F(000)$	936	4192	538	1112	1424
μ/mm^{-1}	0.204	0.153	0.184	0.179	0.154
θ range for data collection/°	1.56 to 25.02	1.51 to 22.50	2.10 to 26.35	2.00 to 25.00	1.55 to 26.42
No. reflns. collected	10812	38788	8812	16380	23237
No. indep. reflns. (R_{int})	4698 (0.0784)	7718 (0.1595)	6183 (0.0347)	5663 (0.0867)	8397 (0.1010)
No. data/restraints/params	4698/0/268	7718/248/704	6183/0/316	5663/0/324	8397/0/426
Goodness of fit on F^2	0.963	0.992	1.009	0.978	0.927
Final R indices[a] [$I > 2\sigma(I)$]	$R_1 = 0.0529$	$R_1 = 0.0647$	$R_1 = 0.0538$	$R_1 = 0.0605$	$R_1 = 0.0561$
	$wR_2 = 0.1027$	$wR_2 = 0.1134$	$wR_2 = 0.1215$	$wR_2 = 0.1258$	$wR_2 = 0.1068$
R indices (all data)	$R_1 = 0.1292$	$R_1 = 0.1572$	$R_1 = 0.1047$	$R_1 = 0.1529$	$R_1 = 0.1571$
	$wR_2 = 0.1401$	$wR_2 = 0.1430$	$wR_2 = 0.1439$	$wR_2 = 0.1594$	$wR_2 = 0.1472$
Largest diff peak and hole/e Å^{-3}	0.274 and −0.268	0.238 and −0.234	0.398 and −0.376	0.220 and −0.289	0.244 and −0.245

[a] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$.

PhCN (0.14 cm^3, 1.37 mmol) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. The red solution was filtered and the filtrate concentrated to give yellow–orange crystals of complex **9** (0.81 g, 90%), mp 138–140 °C (Found: C, 69.19; H, 7.94; N, 8.93%. $C_{38}H_{54}N_4PLiSi_2$ requires C, 69.05; H, 8.23; N, 8.48%). ^{1}H NMR (C_6D_6): δ 0.31 (s, 9H, $SiMe_3$), 0.36 (s, 9H, $SiMe_3$), 1.61 (s, 4H, tmen), 1.86 (s, 12H, tmen), 6.09 (s, 1H, CH), 6.77 (t, J = 6.9 Hz, 1H, Ph + C_6H_4), 7.16 (s, 6H, Ph + C_6H_4), 7.26–7.29 (m, 6H, Ph + C_6H_4), 7.68–7.76 (m, 1H, Ph + C_6H_4), 7.88–7.95 (m, 4H, Ph + C_6H_4), 9.86 (t, J = 6.6 Hz, Ph + C_6H_4). ^{13}C NMR (C_6D_6): δ 4.44, 4.66, 45.45, 56.57, 100.94, 118.43 (d, J = 14.0 Hz), 119.64, 124.54, 126.07, 127.41, 128.56, 130.26, 131.90, 132.74 (d, J = 10.0 Hz), 135.81 (d, J = 13.0 Hz), 136.33, 137.60, 147.33 (d, J = 7.8 Hz), 150.02, 166.19. ^{31}P NMR (C_6D_6): δ 4.79.

Reaction of complex 6 with 1,4-dicyanobenzene. To the solution of complex **6** (0.672 g, 1.303 mmol) in hexane (20 cm^3) was added 1,4-dicyanobenzene (0.083 g, 0.648 mmol) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. A deep red precipitate was formed. The mixture was filtered and the residual solid was dissolved in Et_2O. Filtration of the solution and concentration of the filtrate gave red–orange crystalline **10** (0.655 g, 87%) (Found: C, 68.42; H, 8.31; N, 4.74%. $C_{66}H_{90}N_4P_2O_2Li_2Si_4$ requires C, 68.36; H, 7.82; N, 4.83%). ^{1}H NMR (C_6D_6): δ 0.08 (s, 18H, $SiMe_3$), 0.52 (s, 18H, $SiMe_3$), 1.26 (t, J = 7 Hz, 24H, Et_2O), 3.41 (q, J = 7 Hz, 16H, Et_2O), 6.16 (s, 2H CH), 7.09–7.35 (m, 19H, Ph + C_6H_4), 7.65–7.72 (m, 2H, Ph + C_6H_4), 7.87–7.93 (m, 1H, Ph + C_6H_4), 7.95–8.09 (m, 10H, Ph + C_6H_4). ^{13}C NMR (C_6D_6): δ 1.91, 5.11 (d, J = 4.1 Hz), 46.68, 57.69, 60.20, 105.40 (d, J = 14.7 Hz), 106.02, 107.68, 123.84 (d, J = 10.3 Hz), 128.24, 128.56, 130.66–130.77 (m), 130.86–130.95 (m), 132.18 (d, J = 10.1 Hz), 132.37 (d, J = 10.1 Hz), 133.29 (d, J = 10.0 Hz), 135.01 (d, J = 14.9 Hz), 137.15, 159.18 (d, J = 10.9 Hz). ^{31}P NMR (C_6D_6): δ 21.65.

X-Ray crystallography

The crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on a Siemens CCD area detector at 293(2) K with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). A semi-empirical absorption correction was applied to the data of **2** and **6**. The structures were solved by direct methods using SHELXS-97[20] and refined against F^2 by full-matrix least-squares using SHELXL-97.[21] For complex **3** the carbon atoms of trimethylsilyl and tmen are disordered in one of the two molecules in the asymmetric unit and the ordered molecule is shown in Fig. 2. Crystal data and experimental details of the structure determinations are listed in Table 1.

CCDC reference numbers 257913-257917. See http://www.rsc.org/suppdata/dt/b4/b418389d/ for crystallographic data in CIF or other electronic format.

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