Novel (silylimino)diarylphosphoranyl(trimethylsilyl)methyl-*C,N* ligands $[CH(SiMe_3)PPh_2{=}NSiMe_3]^-$ ($[LL']^-$) and $[CH(SiMe_3)\{Ph(1,2\text{-}C_6H_4)P{=}NSiMe_2\}]^-$ ($[LL'']^-$) and the structures of $[Li(LL'')]_2$ and $[Pb(LL')_2]$†

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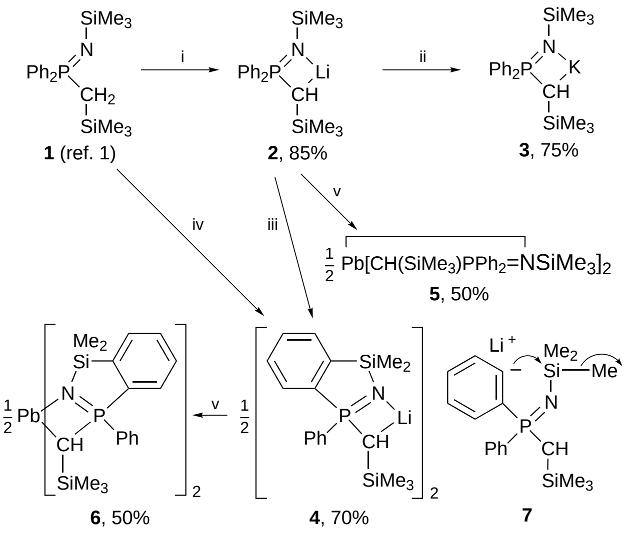
Metal complexes containing the ligands $[CH(SiMe_3)PPh_2{=}NSiMe_3]^-$ {≡$[LL']^-$} and $[CH(SiMe_3)\{Ph(1,2\text{-}C_6H_4)P{=}NSiMe_2\}]^-$ {≡$[LL'']^-$} are reported [from, as initial precursor, $CH_2(SiMe_3)PPh_2{=}NSiMe_3$]: Li(LL′), K(LL′), $[Li(LL'')]_2$ 4, $Pb(LL')_2$ 5 and $Pb(LL'')_2$; mass and multinuclear NMR spectra and single-crystal X-ray diffraction data for 4 (a fused tricyclic complex having a central LiNLiN ring) and 5 are presented.

We report the synthesis and characterisation of five lithium, potassium and lead(II) homoleptic derivatives of two novel *C,N*-centred (iminophosphoranyl)methyl ligands, including the X-ray structures of two of them.

Treatment of the phosphinimine $CH_2(SiMe_3)PPh_2{=}NSiMe_3$ **1**[1] with $LiBu^n$ yielded (Scheme 1, step i) colourless $[Li\{CH(SiMe_3)PPh_2{=}NSiMe_3\}]_2$ {≡$[Li(LL')]_2$} **2**, which with $KOBu^t$ in hexane afforded (Scheme 1, step ii) the insoluble, pale yellow K(LL′) **3**, which was soluble in thf or pyridine. Reacting **2** with $LiBu^n$ gave (Scheme 1, step iii) the colourless *ortho*-silylated product $[Li(CH(SiMe_3)\{Ph(1,2\text{-}C_6H_4)P{=}NSiMe_2\})]_2$ {=$[Li(LL'')]_2$} **4**, which was also accessible (Scheme 1, step iv) from **1** and 1.2 equiv. of $LiBu^n$. The product obtained (Scheme 1, step v) from $PbCl_2$ and either **2** or **4** was the yellow $Pb(LL')_2$ **5** or the colourless $Pb(LL'')_2$ **6**. The yields shown in Scheme 1 refer to isolated, pure, crystalline (or for **3**, powder) **2**–**6**.



Scheme 1 Synthesis of (silylimino)diarylphosphoranyl(trimethylsilyl)methyl-*C,N*]metal complexes **2**–**6**. *Reagents and conditions*: i, $LiBu^n$, hexane, −20 °C to room temp., 3 h; ii, $KOBu^t$, hexane, room temp., 3 h; iii, $LiBu^n$, hexane, reflux, 4 h; iv, 1.2 equiv. $LiBu^n$, hexane, −20 °C to room temp., 5 d; v, 1/2 $PbCl_2$, Et_2O, −45 to *ca.* 20 °C.

The conversion of **2** to **4** (Scheme 1, step iii) probably proceeded *via* an *ortho*-lithiated intermediate, followed by an intramolecular displacement of Me^- at silicon by the aromatic anion, as shown in **7**. In a separate experiment (Scheme 1, step iv) it was shown that the transformation **2** to **4** was effected catalytically using 0.2 mol excess of $LiBu^n$.

Each of the compounds **2**–**6** (except **3**), were hydrocarbon-soluble, gave satisfactory microanalytical, as well as ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^7Li\{^1H\}$ (**2** and **4**) and $^{207}Pb\{^1H\}$ (**5** and **6**) NMR‡ and EI mass spectra {which showed as the highest ion $[M - Li\ (or\ K) + 1]^+$ (*ca.* 30% for **2** or **3**), $[M - Li]^+$ (58% for **4**) and M^+ (1% for **5** and 5% for **6**)} (thf = OC_4H_8, M = the mononuclear molecular ion). Single-crystal X-ray diffraction data§ established the molecular structures of **4** (Fig. 1), **5** (Fig. 2) and **6**; the structure of **6** will be presented in the full paper.

Noteworthy features of the NMR spectra‡ include the demonstration of (*i*) long-range phosphorus–silylmethyl coupling in the $^{13}C\{^1H\}$ NMR spectrum of **2**, $^3J(^{13}C\text{–}^{31}P)$ 3.5, 4.6

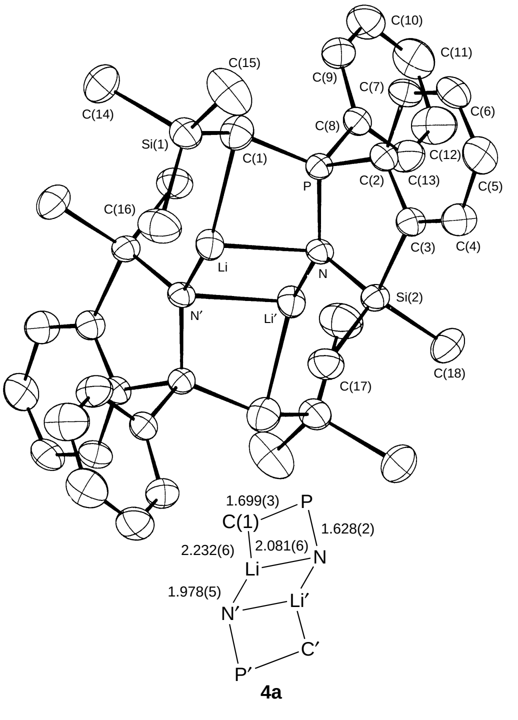
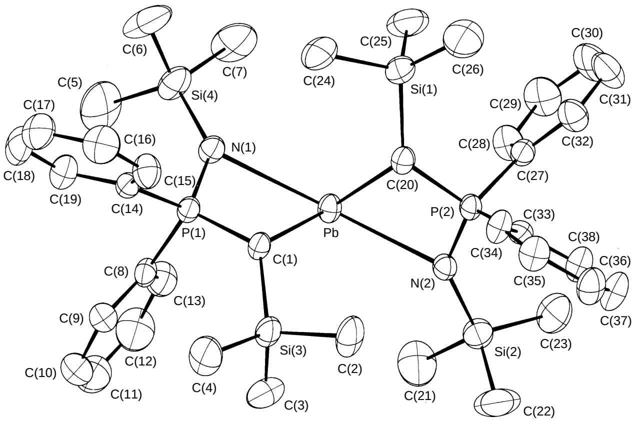


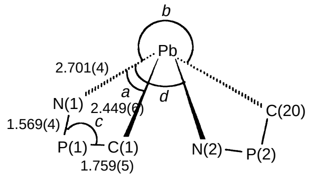
Fig. 1 The molecular structure of crystalline complex **4**. Selected bond lengths (Å) (see also **4a**) and angles (°): N–Li–C(1) 80.1(2), N–Li–N′ 103.8(2), N′–Li–C(1) 135.0(3), N–P–C(1) 113.18(14), P–N–Li 86.2(2), P–N–Li′ 126.4(2), P–C(1)–Li 79.9(2), Li–N-Li′ 76.2(2).

Hz for the two $SiMe_3$ groups; (*ii*) separate (axial and equatorial) Si–Me ^1H signals due to the endocyclic $SiMe_2$ group in **4** and **6**; and (*iii*) $^2J(^{31}P–^{207}Pb)$ and $^2J(^{207}Pb–^{31}P)$ in **5** and **6**.

The structures of crystalline $[Li\{CH_2PMe_2{=}NSiMe_3\}]_4$ **8** and $[Li\{CMe_2PPr^i{}_2{=}NSiMe_3\}]_2$ **9** have the lithium atoms bridged by carbon.[2] It is surprising, therefore, that the dinuclear crystalline **4** (Fig. 1) has the imido nitrogen atoms bridging the lithium atoms, the skeletal structure being ladder-shaped, **4a**. The central LiNLi′N′ ring is planar, with the angle at N narrower [76.2(2)°] than that at Li, 103.8(2)°. The terminal LiNPC rings are puckered, Li lying 0.26 Å out of the NPC plane. The bond angles at the three-coordinate Li range from 80.1(2) [N–Li–C(1)] to 135.0(3)° [N′–Li–C(1)], the sum of the angles at Li being *ca.* 319°. The six bond angles at N (av. 108°) vary from 76.2(2) to 129.6(2)° [Si(2)–N–Li]. The Li–N and Li–C bond lengths are unexceptional,[3] while the Li···P contact of 2.556(5) Å is similar to the 2.56 (av.), 2.58 (av.) or 2.520(9) Å found in $[\{Li(thf)_2\}_2\{PhPCH_2CH_2PPh\}]$,[4] $[\{Li(tmen)\}_2\text{-}C_6H_4(PPh)_2\text{-}1,2\}]$,[5] or $Li(thf)_2[\{N(SiMe_3)\}_2PPh_2]$,[6] respectively [tmen = $(Me_2NCH_2)_2$]. The average Li–N and Li–C distances are 2.03 (**8**) and 1.928 (**9**), and 2.39 (**8**) and 2.27 (**9**), respectively.[2] The X-ray structure of $[Li\{2\text{-}C_6H_4PPh_2{=}NSiMe_3\}_2Li(OEt)_2]$ is available.[7]

Crystalline **5** is mononuclear, Fig. 2. The four-coordinate lead has a stereochemically active lone pair of electrons. The phosphorus approximates to its having tetrahedral geometry. A simplified bonding pattern is shown in **5a**. The P–N bond length of 1.569(4) Å indicates a double bond, while the mean endocyclic P–C distance of 1.757(6) Å is slightly shorter than usual for a P^V–C single bond. The average Pb–N distance of 2.678 Å is much longer than in anionic nitrogen-centred lead(II) compounds, *e.g.*, 2.24(2) Å in $Pb[N(SiMe_3)_2]_2$,[8] or 2.465 Å (av.) in $Pb[\{N(SiMe_3)\}_2PPh_2]_2$,[9] while the mean Pb–C(sp^3) bond length of 2.448 Å in **5** may be compared with the Pb–C(sp^2) distance of 2.336 Å in $Pb[C_6H_2(CF_3)_3\text{-}2,4,6]_2$.[10]





5a [*a*, 62.52(14); *b*, 107.6(2); *c*, 107.2(2); *d*, 167.27(11)°]

Fig. 2 The molecular structure of crystalline complex **5**. Selected bond lengths (Å) and angles (°) (see also **5a**): Pb–C(20) 2.447(5), Pb–N(2) 2.654(4), P(2)–C(20) 1.756(5), P(2)–N(2) 1.569(4); C(20)–Pb–C(1) 88.2(2), C(20)–Pb–N(2) 63.6(2), C(1)–Pb–N(2) 106.69(14), C(20)–Pb–N(1) 107.6(2), N(2)–Pb–N(1) 167.27(11), N(2)–P(2)–C(20) 108.1(2).

The new ligands $[LL']^-$ and $[LL'']^-$ should have an extensive coordination chemistry. Using Li(LL′) **2** or Li(LL″) **4**, we have made *inter alia* $Sn(LL')_2$, $Sn(LL'')_2$, $[Sn(LL')]_2$, $Pb(LL'')_2$ and $[Fe(LL')_3]$, as well as some analogues of Li, K, Sn^{II}, Fe^{II} and Co^{II}.

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Footnotes

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† No reprints available.

‡ *Selected NMR data* [^1H 360.1, $^7Li\{^1H\}$ 97.3, $^{31}P\{^1H\}$ 101.3, $^{207}Pb\{^1H\}$ 52.1 MHz; 298 K; C_5D_5N for **3**, C_6D_6 for **2** and **4–6**; *J*, Hz]. **2**: ^1H δ 0.10 (s, 9 H, $SiMe_3$), 0.13 (s, 9 H, $SiMe_3$), 0.17 (d, 1 H, CH, *J* 13.8), 7.19 (s, Ph), 7.21 (s, Ph), 7.84–7.89 (m, Ph); $^7Li\{^1H\}$ δ 2.23; $^{31}P\{^1H\}$ δ 33.32. **3**: ^1H δ 0.26 (s, 9 H, $SiMe_3$), 0.29 (s, 9 H, $SiMe_3$), 7.20–7.58 (m, Ph), 8.18–8.22 (m, Ph); $^{31}P\{^1H\}$ δ 20.23. **4**: ^1H δ −0.02 (s, 9 H, $SiMe_3$), 0.32 (s, 3 H, SiMe), 0.59 (s, 3 H, SiMe), 0.92 (d, 1 H, CH, *J* 4.9), 7.03–7.15 (m, 5 H, Ph), 7.44–7.56 (m, 2 H, C_6H_4), 7.77–7.83 (m, 2 H, C_6H_4); $^7Li\{^1H\}$ δ 2.05; $^{31}P\{^1H\}$ δ 48.70. **5**: ^1H δ −0.01 (s, 18 H, $SiMe_3$), 0.20 (s, 18 H, $SiMe_3$), 1.37 (d, 2 H, CH, *J* 15.8), 7.00–7.05 (m, Ph), 7.15–7.22 (m, Ph), 7.64–7.69 (m, Ph), 7.79–7.85 (m, Ph); $^{31}P\{^1H\}$ δ 19.52 (s, with satellite peaks, *J* 308); $^{207}Pb\{^1H\}$ δ 2787.63 (t, *J* 306). **6**: ^1H δ 0.31 (s, 18 H, $SiMe_3$), 0.53 (s, 6 H, SiMe), 0.69 (s, 6 H, SiMe), 1.43 (d, 2 H, CH, *J* 9.5), 7.06–7.25 (m, Ph + C_6H_4), 7.54–7.65 (m, Ph + C_6H_4); $^{31}P\{^1H\}$ δ 40.27 (s, with satellite peaks, *J* 311.8); $^{207}Pb\{^1H\}$ δ 1998.26 (t, *J* 313.3).

§ *Crystal data*: **4**, $C_{36}H_{50}Li_2N_2P_2Si_4$: $M = 699.0$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.904(1)$, $b = 10.259(3)$, $c = 11.175(1)$ Å, $\alpha = 109.10(2)$, $\beta = 95.79(1)$, $\gamma = 104.44(2)°$, $U = 1018.2(2)$ Å^3, $F(000) = 372$; $Z = 1$, $D_c = 1.14$ g cm^{-3}, specimen 0.3 × 0.3 × 0.3 mm, 3578 independent reflections, 2706 reflections with $[|F^2| > 2\sigma(F^2)]$; $R_1 = 0.054$, $wR_2 = 0.152$ (for all data). **5**, $C_{38}H_{58}N_2P_2PbSi_4$: $M = 924.4$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.767(2)$, $b = 14.091(2)$, $c = 16.775(2)$ Å, $\alpha = 87.07(1)$, $\beta = 72.01(1)$, $\gamma = 69.77(1)°$, $U = 2266.9(6)$ Å^3, $F(000) = 936$; $Z = 2$, $D_c = 1.35$ g cm^{-3}, specimen 0.3 × 0.3 × 0.1 mm, 13179 independent reflections, 7752 reflections with $[|F^2| > 2\sigma(F^2)]$; $R_1 = 0.056$, $wR_2 = 0.102$ (for all data).

Intensities were measured to θ_{max} 25° (for **4**) or 30° (for **5**) on an Enraf-Nonius CAD4 diffractometer using monochromated Mo-Kα (μ = 0.25 mm **4**, 3.92 mm **5**) radiation (λ = 0.71073 Å); absorption correction from ψ scan for **5**. Structure refinements were by SHELXL-93, with H atoms in riding mode. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/455.

References

1 J. C. Wilburn and R. H. Neilson, *Inorg. Chem.*, 1979, **18**, 347.
2 A. Müller, B. Neumüller and K. Dehnicke, *Chem. Ber.*, 1996, **129**, 253.
3 *cf.* K. Gregory, P. v. R. Schleyer and R. Snaith, *Adv. Inorg. Chem.*, 1991, **37**, 47; W. N. Setzer and P. v. R. Schleyer, *Adv. Organomet. Chem.*, 1985, **24**, 353.
4 D. M. Anderson, P. B. Hitchcock, M. F. Lappert and I. Moss, *Inorg. Chim. Acta*, 1988, **141**, 157.
5 D.M. Anderson, P. B. Hitchcock, M. F. Lappert, W.-P. Leung and J. A. Zora, *J. Organomet. Chem.*, 1987, **333**, C13.
6 A. Steiner and D. Stalke, *Inorg. Chem.*, 1993, **32**, 1977.
7 A. Steiner and D. Stalke, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1752.
8 T. Fjeldberg, H. Hope, M. F. Lappert, P. P. Power and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1983, 639.
9 U. Kilimann, M. Noltemeyer and F. T. Edelmann, *J. Organomet. Chem.*, 1993, **443**, 35.
10 S. Brooker, J.-K. Buijink and F. T. Edelmann, *Organometallics*, 1991, **10**, 25.

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