

The synthesis and molecular structures of the crystalline 1-aza-2-phospha(v)allyllithium compounds [Li(LL')(OEt₂)₂] and [Li(LL')]₂ [LL' = CH(SiMe₃)P(Ph)₂=NSiMe₃] and the preparation and characterisation of the new phosphinimines CH(R¹)(R²)P(Ph)₂=NSiMe₃ [R¹ = R² = SiMe₃; R¹ = H, R² = Si(Me)₂NEt₂][†]

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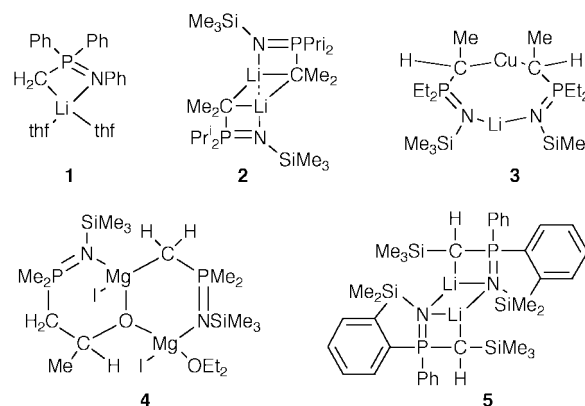
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Reaction of CH₂(SiMe₃)P(Ph)₂=NSiMe₃ (HLL') **I** with LiBuⁿ afforded, after recrystallisation from diethyl ether, [Li{CH(SiMe₃)P(Ph)₂=NSiMe₃}(OEt₂)₂]. Removal of the co-ordinating Et₂O molecules *in vacuo* and subsequent recrystallisation from hexane yielded the solvent-free dimeric lithium complex [Li{CH(SiMe₃)P(Ph)₂=NSiMe₃}]₂. The crystal structures of the crystalline compounds [Li(LL')(OEt₂)₂] and the fused dinuclear [Li(LL')]₂ are reported. Each contains a planar Li(LL') ring. The Li(2)–N bond of the Li(LL') moiety of the latter is also part of a six-membered Li(2)–N–Li(1)–N–P–C ring, planar except for Li(2); the two Li atoms are bridged by a second [LL'][–] ligand, so that the bridgehead lithium atom Li(2) is bound to the allyl carbon of each [LL'][–] ligand, whereas Li(1) is bound to two nitrogen atoms. In toluene-*d*₈, this compound shows singlet ⁷Li-¹H and ³¹P-¹H NMR spectral signals, even at low temperatures. Its reaction with Me₃SiO₃SCF₃ afforded the phosphinimine CH(SiMe₃)P(Ph)₂=NSiMe₃ (HLL'') **II**, a potential precursor for a new 1-aza-2-phospha(v)allyl ligand, as was shown by its straightforward lithiation to yield Li(LL''). The novel phosphinimine CH₂{SiMe₂(NEt₂)}P(Ph)₂=NSiMe₃ (HLL''') **III** was synthesized by reaction of Li[CH₂P(Ph)₂=NSiMe₃] with Et₂NSi(Me)₂Cl and, similar to the lithiation of **II**, reaction of **III** with LiBuⁿ afforded Li(LL''') in high yield.

1-Aza-2-phospha(v)allyl ligands have recently attracted much attention in co-ordination chemistry. In 1995 the crystal structure of [Li{CH₂P(Ph)₂=NPh}(thf)₂] **1** was determined.¹ The compound is monomeric in the solid state with a 4-membered Li–C–P–N ring. MNDO Calculations revealed that (i) this is the preferred conformation, (ii) the C–Li and N–Li bonds are largely ionic and (iii) there is no P–Li bonding or interaction. When the phosphinimine CH₃P(Me)₂=NSiMe₃ was treated with LiBuⁿ the crystalline tetrameric complex [Li{CH₂P(Me)₂=NSiMe₃}]₄ was obtained,² believed to contain relatively polar Li–C bonds. Significantly shorter, and thus more ionic, Li–C bonds were found in crystalline [Li{CMe₂P(Pr)₂=NSiMe₃}]₂ **2**.² Apart from chelating, a 1-aza-2-phospha(v)allyl ligand can also be bridging, as shown by Dehnicke and co-workers³ in 1997, for the crystalline complexes [LiCu{CH(Me)P(Et)₂=NSiMe₃}]₂ **3**, [Zn(Cl){CH(Me)P(Et)₂=NSiMe₃}]₁₂ and [Mg₂I₂{CH₂P(Me)₂=NSiMe₃}]{OCH(Me)CH₂P(Me)₂=NSiMe₃}(OEt₂) **4**.

We recently reported on applications of C,N-centred phosphinimines, such as CH₂(SiMe₃)P(Ph)₂=NSiMe₃ (HLL') **I**,⁴ as ligand precursors in alkali and Group 14 metal chemistry.⁵ Reaction of **I** with LiBuⁿ was believed to yield Li(LL') **6** on the basis of its reactions with (i) KOBu^t affording K(LL')⁵ (ii) ½ PbCl₂ giving the X-ray characterised $\overline{\text{Pb}}(\text{LL}')_2$,⁵ (iii) LiBuⁿ yielding the crystalline *ortho*-silylated derivative [Li{CH(SiMe₃){Ph(1,2-C₆H₄)P=NSiMe₃}] **5**,⁵ and (iv) PhCN and then successively KOBu^t and tmen, furnishing [K{N(SiMe₃)P(Ph)₂C(H)C(Ph)NSiMe₃}(tmen)]⁶.

We now describe the synthesis, characterisation and crystal structures of the crystalline 1-aza-2-phospha(v)allyllithium compounds [Li(LL')(OEt₂)₂] **6** and the solvent-free dimeric analogue [Li(LL')]₂ **7** [LL' = CH(SiMe₃)P(Ph)₂=NSiMe₃]. Furthermore, we report on the synthesis and characterisation

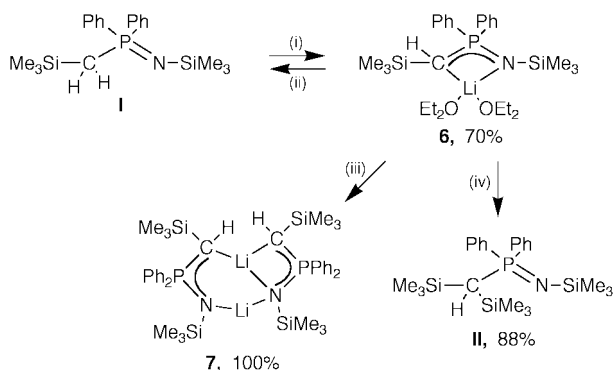


of the new phosphinimines CH(SiMe₃)P(Ph)₂=NSiMe₃ (HLL'') **II** and CH₂{SiMe₂(NEt₂)}P(Ph)₂=NSiMe₃ (HLL''') **III** and their respective lithium complexes Li(LL'') **8** and Li(LL''') **9**.

Results and discussion

The synthesis of the crystalline complexes [Li(LL')(OEt₂)₂] **6** and [Li(LL')]₂ **7** is summarised in Scheme 1. Thus, treatment of **I** with LiBuⁿ in diethyl ether, concentration of the solution and cooling yielded crystalline **6**. The ¹H NMR spectrum, recorded in benzene-*d*₆, showed that only one equivalent of Et₂O was present in solution. Therefore, we suspected that the Et₂O molecules were loosely bound in **6** and this proved to be the case. After exposing [Li(LL')(OEt₂)₂] **6** *in vacuo* at ca. 40 °C, the solvent-free complex [Li(LL')]₂ **7** was obtained. This route proved to be cleaner than that previously reported for the reaction of **I** with LiBuⁿ in hexane.^{5,6} As the Et₂O molecules were easily removed from **6**, no elemental analysis of the complex was carried out.

[†]Supplementary data available: rotatable 3-D crystal structure diagram in CHIME format. See <http://www.rsc.org/suppdata/dt/1999/3413/>

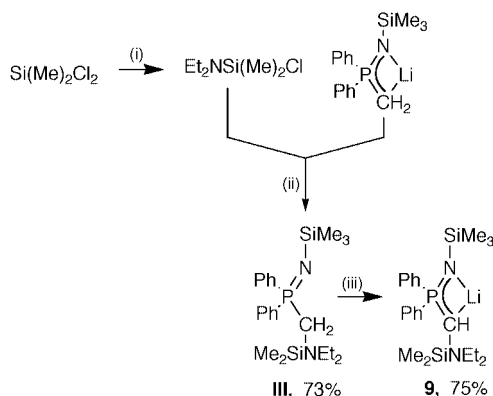


Scheme 1 Preparation of the crystalline 1-aza-2-phospha(v)allyl-lithium compounds [Li(LL')(OEt₂)₂] **6** and [Li(LL'')] **7** and the phosphinimine CH(SiMe₃)₂P(Ph)₂=NSiMe₃ **II**. *Reagents and conditions:* (i) LiBuⁿ in hexane, Et₂O, -40 °C, 1 h; (ii) MeOH in hexane, 0 °C, 0.5 h; (iii) 40 °C/10⁻³ Torr, 3 h; (iv) Me₃SiO₃SCF₃ in hexane, -78 °C, 0.5 h.

Compound **6** was cleanly hydrolysed by treatment with MeOH in hexane at 0 °C. Even when an excess of MeOH was used, no cleavage of the N–Si or C–Si bond was observed.

When Me₃SiCl was added to a solution of compound **7** in pentane no reaction occurred. Since the analogue Li[CH₂P(Me)₂=NSiMe₃] was reported to react readily with Me₃SiCl to afford CH₂(SiMe₃)P(Me)₂=NSiMe₃,⁷ the SiMe₃ group on the C atom in **7** evidently provides additional protection of the Li atom. However, a reaction did take place when Me₃SiO₃SCF₃ was used, instead of Me₃SiCl. In this way the phosphinimine CH(SiMe₃)₂P(Ph)₂=NSiMe₃ (HLL'') **II** was obtained in 88% yield (Scheme 1). Incidentally, **II** was not obtained by employment of the synthetic route towards HLL',⁶ because the precursor CH(SiMe₃)₂P(Ph)₂, a product of the reaction between LiCH(SiMe₃)₂ and P(Ph)₂Cl, was not obtained as a pure compound, even after multiple recrystallisations from pentane. Compound **II** was satisfactorily analysed by ¹H and ³¹P-{¹H} NMR spectroscopy. The potential of **II** to act as a new 1-aza-2-phospha(v)allyl ligand is currently under investigation and initial results include the synthesis of its lithium complex Li(LL''') **8**. The [LL''']⁻ ligand is sterically more hindered than its counterpart [LL']⁻ and this might result in the synthesis of metal complexes of enhanced stability.

The phosphinimine CH₂{SiMe₂(NEt₂)}P(Ph)₂=NSiMe₃ (HLL''') **III** was obtained from Et₂NSi(Me)₂Cl and Li[CH₂P(Ph)₂=NSiMe₃] in Et₂O at low temperature (Scheme 2). The



Scheme 2 Preparation of the phosphinimine HLL''' **III** and its lithium complex Li(LL''') **9**. *Reagents and conditions:* (i) LiNEt₂, Et₂O, -50 °C, 3 h; (ii) hexane, Et₂O, -78 °C, 16 h; (iii) LiBuⁿ in hexane, -20 °C, 3 h.

chlorosilane was prepared similarly to the reported procedure for the *in situ* synthesis of Me₂NSi(Me)₂Cl,⁸ and Li[CH₂P(Ph)₂=NSiMe₃] from the phosphinimine CH₃P(Ph)₂=NSiMe₃⁹ and

Table 1 Selected bond distances (Å) and angles (°) for compound **6**

Li–O(1)	1.949(5)	Li⋯P	2.593(5)
Li–O(2)	1.978(5)	P–N	1.592(2)
Li–N	2.018(5)	P–C(1)	1.702(3)
Li–C(1)	2.289(6)		
C(1)–P–N	110.18(13)	Li–N–P	91.1(2)
Li–C(1)–P	79.6(2)	C(1)–Li–N	77.4(2)

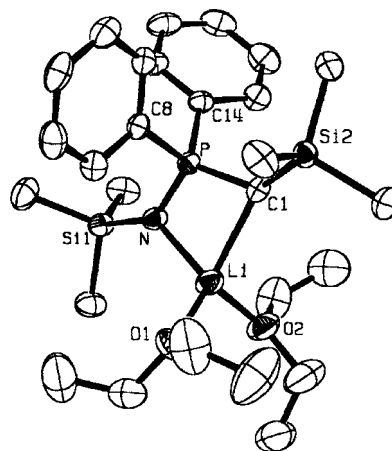
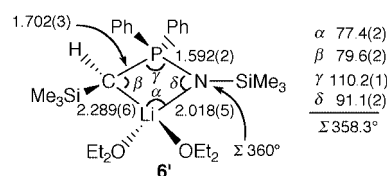


Fig. 1 The molecular structure of crystalline complex **6**.

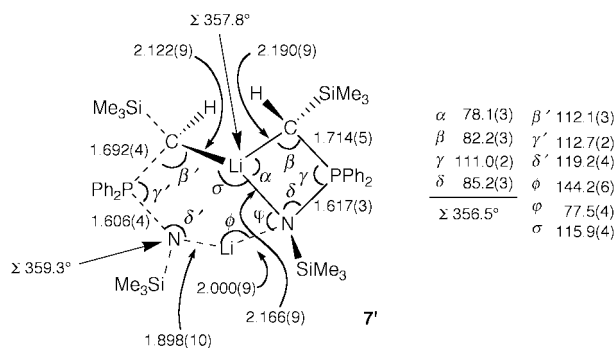
LiBuⁿ at low temperature. Compound **III**, satisfactorily analysed by multinuclear NMR spectroscopy and elemental analysis, was readily lithiated with LiBuⁿ in hexane at -20 °C to yield Li(LL''') **9**. The ⁷Li-{¹H} NMR spectral chemical shift of **9** (δ -0.76) was at significantly lower frequency than that of **7** (δ 1.85). This may be due to the co-ordination of the NEt₂ group to the lithium atom in **9**. We regard [LL''']⁻ as an interesting alternative to the [LL']⁻ ligand, because the former can provide additional stabilisation through co-ordination of the NEt₂ group.



The crystalline lithium complex **6** had not previously been characterised.^{5,6} Suitable single crystals of it were obtained after cooling a solution of **6** in a mixture of diethyl ether and hexane to -25 °C. An ORTEP representation¹⁰ of the molecular structure of **6** is shown in Fig. 1, endocyclic bond lengths and angles are sketched in Table 1. The crystalline molecule is monomeric and the lithium atom is four-co-ordinate with a distorted tetrahedral geometry. The Li–C(1)–P–N ring is approximately planar (sum of angles: 358.3°), a feature also observed in the related complexes **1**,¹ **2**² and **5**,⁵ containing a chelating 1-aza-2-phospha(v)allyl ligand. The two Et₂O molecules in **6** are situated almost equidistant from the Li atom, with unexceptional bond lengths of 1.949(5) and 1.978(5) Å. The Li–N bond distance of 2.018(5) Å is similar to that in **1** [2.00(1) Å]¹ or [Li{CH₂P(Me)₂=NSiMe₃}]₄ (average 2.03 Å),² but is slightly shorter than in the neutral donor-free complex **5** [2.081(6) Å].⁵ The Li–C(1) bond distance in **6** at 2.289(6) Å is slightly longer than in the less hindered analogue **1**, 2.23(1) Å,¹ but it is shorter than in [Li₂C{P(Ph)₂=NSiMe₃}₂], average 2.38(1) Å,¹¹ a complex bearing a dianionic 1-aza-2-phospha(v)allyl ligand with an additional Ph₂P=NSiMe₃ group on the carbon atom. The Li–C(1) bond distance is unexceptional when compared to those in

dimers or higher aggregates of related lithium complexes.^{2,3a} The P–N bond distance in **6** of 1.592(2) Å is significantly shorter than is appropriate for a P–N single bond (1.77 Å).^{12,13} It is similar to P–N bond lengths in related complexes, such as **3** [1.596(2) Å],^{3a} $\text{Pb}[\text{CH}(\text{SiMe}_3)\text{P}(\text{Ph})_2=\text{NSiMe}_3]_2$ [1.568(4) Å],⁶ or $\text{Li}[(\text{NSiMe}_3)_2\text{PPh}_2](\text{thf})_2$, 1.579(4),¹⁴ but slightly shorter than in $[\text{Rh}\{\text{CH}_2\text{P}(\text{Ph})_2=\text{NC}_6\text{H}_4\text{Me}-4\}(\text{COD})]$, 1.624(2) Å.¹⁵ The P–N bond distance in **6** falls in the range of 1.588(5)–1.616(5) Å reported for $[\text{NP}(\text{CH}_2\text{SiMe}_3)_2]_3$ ¹⁶ and other cyclophosphazenes, compounds which have a delocalised π system.¹³ Combining these data with the fact that the P–C(1) bond length of 1.702(3) Å is similar to the P–C bond distances found in ylides (1.71–1.74 Å),¹³ we conclude that the electrons in the C(1)–P–N fragment of the ligand are partly delocalised, a view also supported by the planarity of the Li–C(1)–P–N ring. The Li \cdots P distance of 2.593(5) Å is shorter than the sum of the van der Waals radii (3.68 Å),¹⁷ but falls in the range of 2.38(1)–2.669(9) Å previously reported for complexes having a lithium–phosphorus interaction.¹⁸ However, the rigidity of the molecule requires these atoms to be close and thus the existence of a significant Li–P bond or interaction is unlikely, as indicated by the previously mentioned MNDO calculations.¹

The C(1)–P–N bond angle in compound **6** of 110.2(1)° is similar to that found in related complexes,^{1,2,3a,5,19} but is significantly wider than the C–P–N angles reported for complexes of Rh, Ir and Pt [94.4(3)–99.1(2)°].^{15,20} The phosphorus atom has a distorted tetrahedral geometry. The slight deviation from this geometry may be due to the rigidity of the ligand [*cf.* the endocyclic C–P–N bond angle in $\text{Pb}[\text{CH}(\text{SiMe}_3)\text{P}(\text{Ph})_2=\text{NSiMe}_3]_2$ is 108.1(2)°].⁵ The Li–C(1)–P bond angle in **6** of 79.6(2)° is similar to the 79.9(2)° in **5**, but the Li–N–P bond angle in the latter [86.2(2)°]⁵ is markedly narrower than in **6** [91.1(2)°], whereas in $[\text{Li}\{\text{CH}_2\text{P}(\text{Me})_2=\text{NSiMe}_3\}]_4$ and **2** they are wider [95.3(4) and 95.8(2)°, respectively],² possibly due to the oligomeric nature of these compounds; the corresponding bond angle in **1** is 93.4(4)°.¹ Finally, it is noted that the lithium atom has a severely distorted tetrahedral geometry, reflected in the very narrow C(1)–Li–N bond angle of 77.4(2)°, which is probably caused by the chelation, *cf.* 80.1(2)° in **5**.⁵



Suitable single crystals of compound **7** were obtained after cooling a hexane solution to -25°C . An ORTEP representation¹⁰ of the molecular structure of **7** is depicted in Fig. 2, endocyclic bond lengths and angles are sketched in 7' and selected bond distances and angles are presented in Table 2. The crystalline molecule **7** is an unsymmetrical dimer, consisting of a fused arrangement of a four- and a six-membered ring. The former, Li(2)–C(20)–P(2)–N(2), is approximately planar (sum of endocyclic angles: 356.5°) whereas for the latter the atoms C(1), P(1), N(1), Li(1) and N(2) are coplanar (sum of endocyclic angles: 539.3°) with Li(2) out of the plane (interplanar angle: 67.65°). Both the three-co-ordinate N(1) and Li(2) are in an approximately planar environment (sum of angles: 359.3° and 357.8°, respectively). The molecule has two chiral atoms, C(1) and C(20), which in principle could give rise to diastereoisomers. Since the molecule is centrosymmetric only the *meso*

Table 2 Selected bond distances (Å) and angles (°) for compound **7**

Li(1)–N(1)	1.898(10)	Li(2) \cdots P(2)	2.591
Li(1)–N(2)	2.000(9)	P(1)–N(1)	1.606(4)
Li(2)–N(2)	2.166(9)	P(2)–N(2)	1.617(3)
Li(1) \cdots Li(2)	2.610(13)	P(1)–C(1)	1.692(4)
Li(2)–C(1)	2.122(9)	P(2)–C(20)	1.714(5)
Li(2)–C(20)	2.190(9)		
Li(1)–N(1)–P(1)	119.2(4)	C(1)–P(1)–N(1)	112.7(2)
Li(1)–N(2)–P(2)	126.9(4)	C(20)–P(2)–N(2)	111.0(2)
N(1)–Li(1)–N(2)	144.2(6)	C(20)–Li(2)–N(2)	78.1(3)

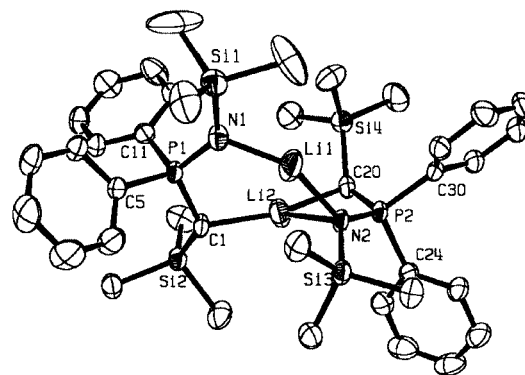


Fig. 2 The molecular structure of crystalline complex **7**.

diastereoisomer is present. One of the SiMe₃ groups is situated above the plane of the four-membered ring and the other below. The SiMe₃ groups on N(1) and C(1), however, are only slightly out of the C(1)–P(1)–N(1)–Li(1)–N(2) plane and are thus in equatorial positions. The fact that one of the [LL'][–] ligands is bridging and the other is chelating (and bridging) has not previously, to our knowledge, been observed. However, a related ligand can bridge two metal atoms; *i.e.* in **3** the nitrogen atoms are bonded to the lithium atom and the carbon atoms to the copper atom.^{3a} Without the Li(2)–N(2) bonding interaction, **7** would have a similar structure, albeit that **3** is hetero- while **7** is homo-bimetallic. On the basis of the Li(1) \cdots Li(2) distance of 2.610(13) Å in **7** an Li \cdots Li interaction is possible, as suggested by Snaith and co-workers²¹ for $[\text{Li}\{\text{N}=\text{CPh}_2\}(\text{py})]_4$, with a mean Li \cdots Li distance of 2.663 Å. However, geometric considerations alone require that Li(2) is in the vicinity of Li(1), a consequence of the four-membered ring. Relatively short Li \cdots Li contacts have been observed previously in related lithium oligomers.^{2,3a} The three Li–N bond distances in **7** vary in length. The longest is Li(2)–N(2), 2.166(9) Å. The Li(1)–N(1) bond of 1.898(10) Å in **7** is shorter than that in **6** [2.018(5) Å], but is similar to the average Li–N bond distance in **2** [1.928(6) Å]² and the mixed metal complex **3** [1.942(4) Å].^{3a} In compounds having two-co-ordinate lithium and four-co-ordinate nitrogen, Li–N bond lengths range from 1.97 to 2.00 Å.²² Thus, the Li(1)–N(2) bond, 2.000(9) Å, is unexceptional. The Li–C bond distances in **7** [2.122(9) and 2.190(9) Å] are slightly shorter than that in **6** [2.289(6) Å]. This is probably because Li(2) in **7** is three-co-ordinate, whereas in **6** Li is four-co-ordinate. Moreover, since the Li(2)–N(2) bond in **7** is relatively long, the Li atom requires additional stabilisation, which appears to be provided by the short bonds to C(1) and C(20).

Complex **7** demonstrates the rigidity of the [LL'][–] ligand, using the following criteria: (i) the P–N bond lengths in the bridging and the chelating ligand are approximately identical [1.606(4) and 1.617(3) Å, respectively], as are (ii) the P–C bond distances [1.692(4) and 1.714(5) Å], and (iii) the endocyclic C–P–N bond angles differ only slightly [112.7(2) at P(1) and 111.0(2)° at P(2)]. This is further indicated by noting that the P–N [1.592(2) Å] and P–C [1.702(3) Å] bond distances and the endocyclic C–P–N bond angle [110.18(13)°] in **6** are approximately similar to those in **7**. However, in the lead compound

Pb(LL'), the P–N bond [1.569(4) Å] is shorter, and the P–C bond [1.756(5) Å] is longer than in either **6** or **7**.⁵ The Li...P contact in **7** (2.591 Å) is essentially identical to that in **6** [2.593(5) Å], but this is an artefact caused by the rigidity of the ligand, requiring the Li atom to be close to the P atom.

The Li(2)–N(2)–P(2) bond angle in compound **7** [85.2(3)°] is slightly narrower than that in **6** [91.1(2)°]. The Li(1)–N(1)–P(1) [119.2(4)°] and Li(1)–N(2)–P(2) [126.9(4)°] bond angles are evidently wider than in **6**, since Li(1) is not chelated by either of the ligands. These angles are also wider than the average endocyclic Li–N–P bond angle in **3** [112.3(2)°], possibly because of the proximity of the atoms Li(1) and Li(2) in **7**, whereas in **3** the Li atom is not in the vicinity of the Cu atom.^{3a} Considering the chelating ligand, the C(20)–Li(2)–N(2) bond angle of 78.1(3)° is virtually the same as in its counterpart in **6**, 77.4(2)°, despite the differences in the environments of the two lithium atoms in the two molecules. The N(1)–Li(1)–N(2) bond angle of 144.2(6)° in **7** is markedly narrower than the N–Li–N' bond angle in **3** [169.9(3)°], possibly attributable to the proximity of the atoms Li(1) and Li(2).

In terms of bonding, we suggest that the Li(2) environment resembles that of a dialkylolithiate [≡C–Li–C≡], whereas that of Li(1) is akin to a bis(imino)lithium species [≡N–Li–N≡]⁺. In support, we draw attention to the crystalline compound [Li(tmen)₂][Li{C(SiMe₃)₂SiMe₂CH₂}]₂ **10**, having Li–C bond distances of 2.156(4) Å, identical to the average of Li(2)–C(1) and Li(2)–C(26) in **7**, while the average Li(1)–N bond distance of 1.95 Å is not too remote from the Li–N distance of 2.09 Å in **10**.²³

Since the crystalline molecule **7** is unsymmetrical, it might have been expected that this would be reflected in the NMR spectra, provided the dimeric nature of the complex is retained in solution. At room temperature only one signal was observed in both the ⁷Li–{¹H} and ³¹P–{¹H} NMR spectra of **7** in benzene-*d*₆, and the ¹H NMR spectrum likewise provided no evidence of the [LL'][−] ligands exhibiting different co-ordination modes. Therefore, low temperature NMR spectral studies in toluene-*d*₈ were carried out. Owing to broadening of the signals in the ¹H NMR spectrum, no definite conclusions are drawn. In the ⁷Li–{¹H} and ³¹P–{¹H} NMR spectra, however, no splitting of the signals was observed. Thus, we conclude either that **7** is monomeric or symmetrical in solution, or that intramolecular bond cleavage and formation processes, if existing, are too fast to be observed on the NMR timescale.

Experimental

All reactions were performed under an argon atmosphere using standard Schlenk techniques. Diethyl ether was dried using sodium–benzophenone and hexane with Na/K alloy. The phosphinimines CH₂(SiMe₃)P(Ph)₂=NSiMe₃ **I**,⁶ CH₃P(Ph)₂=NSiMe₃⁹ and Et₂NSi(Me)₂Cl⁸ were prepared according to published procedures. The NMR spectra were recorded in C₆D₆ or C₆D₅CD₃ at 298 K on a Bruker DPX 300 spectrometer (¹H, 300.1; ⁷Li, 81.1; ¹³C, 75.4; ³¹P, 84.4 MHz) and the solvent resonances were used as the internal references for ¹H and ¹³C spectra. The compounds LiCl (1 mol dm^{−3} aqueous solution) and H₃PO₄ (85% aqueous solution) were the external references for ⁷Li and ³¹P NMR spectra, respectively. Chemical shifts (δ) are reported in ppm. All NMR spectra other than ¹H were proton-decoupled. Elemental analyses were carried out by Medac Ltd, Brunel University. Melting points were determined under an argon atmosphere in sealed capillaries on an electrothermal apparatus and are uncorrected.

Preparations

[Li{CH(SiMe₃)P(Ph)₂=NSiMe₃}(OEt)₂] **6**. The compound LiBuⁿ (6.2 cm³ of a 1.6 mol dm^{−3} solution in hexanes, 9.92 × 10^{−3} mol) was added to a solution of **I** (3.55 g, 9.87 × 10^{−3} mol)

in Et₂O (25 cm³) at *ca.* −40 °C. The mixture was allowed to warm to room temperature and stirred for 1 h. The resulting clear yellow solution was concentrated *in vacuo* and stored at −30 °C, yielding the slightly yellow crystalline compound **6** (3.02 g, 70%). ¹H NMR (C₆D₆): δ 0.06 (s, 9 H, CSiMe₃), 0.10 (s, 9 H, NSiMe₃), 1.48 [d, 1 H, CH, ²J(¹H–³¹P) = 14.7 Hz], 1.06 (t, 6 H, Et₂O), 3.18 (q, 4 H, Et₂O), 7.04–7.19 (m, 6 H, Ph) and 7.81–7.88 (m, 4 H, Ph). ¹³C NMR (C₆D₆): δ 3.84 (s, CSiMe₃), 4.10 (s, NSiMe₃), 13.88 [d, CH, ²J(¹³C–³¹P) = 86.7], 15.29 (s, Et₂O), 65.99 (s, Et₂O), 119.40 (s, *m*-C in Ph), 130.00 (s, *p*-C in Ph), 131.93 [d, *o*-C in Ph, ²J(¹³C–³¹P) = 10.3 Hz], *ipso*-C in Ph not observed. ³¹P NMR (C₆D₆): δ 60.00 (s). ⁷Li NMR (C₆D₆): δ 2.57 (s).

[Li{CH(SiMe₃)P(Ph)₂=NSiMe₃}]₂ **7**. Solid compound **6** (1.94 g, 3.78 × 10^{−3} mol) was dried *in vacuo* at *ca.* 40 °C for 3 h, yielding off-white **7** (1.38 g, 100%). Recrystallisation from hexane at −25 °C yielded colourless crystals (Found: C, 62.3; H, 8.02; N, 3.95. C₁₉H₂₉LiNPSi₂ requires C, 62.4; H, 8.00; N, 3.83%), mp 135–138 °C. Mass spectrum [*m/z* (%): 359 (32, [M_{1/2} – Li + 1]⁺), 344 (100, [M_{1/2} – Me – Li + 1]⁺), 272 (26, [M_{1/2} – Li – CHSiMe₃]⁺), 135 (29, [M_{1/2} – Li – (SiMe₃)₂ – Ph]⁺) and 73 (22, [SiMe₃]⁺). ¹H NMR (C₆D₅CD₃): δ 0.00 (s, 9 H, CSiMe₃), 0.05 (s, 9 H, NSiMe₃), 1.68 [d, 1 H, CH, ²J(¹H–³¹P) = 10.5 Hz], 7.11–7.17 (m, 6 H, Ph) and 7.74–7.81 (m, 4 H, Ph). ¹³C NMR (C₆D₅CD₃): δ 3.64 [d, CSiMe₃, ³J(¹³C–³¹P) = 3.54], 4.12 [d, NSiMe₃, ³J(¹³C–³¹P) = 4.44], 14.34 [d, CH, ¹J(¹³C–³¹P) = 84.9], 128.07 [d, *m*-C in Ph, ³J(¹³C–³¹P) = 11.0], 130.20 [d, *p*-C in Ph, ⁴J(¹³C–³¹P) = 2.26], 131.97 [d, *o*-C in Ph, ²J(¹³C–³¹P) = 10.3] and 139.61 [d, *ipso*-C in Ph, ¹J(¹³C–³¹P) = 86.8 Hz]. ³¹P NMR (C₆D₅CD₃): δ 33.03 (s). ⁷Li NMR (C₆D₅CD₃): δ 1.85 (s).

CH(SiMe₃)₂P(Ph)₂=NSiMe₃ **II**. Compound **7** (0.56 g, 1.53 × 10^{−3} mol) was dissolved in hexane (20 cm³) and cooled to −78 °C. Trimethylsilyl triflate (trifluoromethanesulfonate) (0.3 cm³, 1.65 × 10^{−3} mol) was added dropwise, the reaction mixture was allowed to warm to room temperature and subsequently stirred for 0.5 h. The mixture was filtered and the volatiles from the filtrate were removed *in vacuo*. This yielded compound **II** as a nearly colourless oil (0.58 g, 88%). ¹H NMR (C₆D₆): δ 0.06 (s, 18 H, CSiMe₃), 0.52 (s, 9 H, NSiMe₃), 1.19 [d, 1 H, CH, ²J(¹H–³¹P) = 12.4 Hz], 7.01–7.08 (m, 6 H, Ph) and 7.61–7.68 (m, 4 H, Ph). ³¹P NMR (C₆D₆): δ 0.97 (s).

CH₂(SiMe₃(NEt₂))P(Ph)₂=NSiMe₃ **III**. The compound LiBuⁿ (28.0 cm³ of a 1.6 mol dm^{−3} solution in hexanes, 44.8 × 10^{−3} mol) was added to a stirred solution of CH₃P(Ph)₂=NSiMe₃ (12.7 g, 44.0 × 10^{−3} mol) in Et₂O (100 cm³) at −50 °C. The solution was stirred at room temperature for 3 h and recooled to −78 °C. The compound Et₂NSi(Me)₂Cl (7.50 g, 45.0 × 10^{−3} mol) was added dropwise and the reaction mixture stirred for 16 h at room temperature. The precipitate was filtered off and volatiles were removed from the filtrate *in vacuo* to yield a viscous oil. Distillation under reduced pressure yielded the pale yellow, oily compound **III** (13.5 g, 73%) (Found: C, 62.9; H, 8.73; N, 6.42. C₂₂H₃₇N₂PSi₂ requires C, 63.4; H, 8.95; N, 6.72%), bp 150 °C/0.025 Torr. ¹H NMR (CDCl₃): δ −0.08 (s, 6 H, SiMe₂), −0.04 (s, 9 H, SiMe₃), 0.94 (t, 6 H, NCH₂CH₃), 1.69 [d, 2 H, PCH₂, ²J(¹H–³¹P) = 15.4 Hz], 2.82 (q, 4 H, NCH₂), 7.37–7.41 (m, 6 H, Ph) and 7.65–7.71 (m, 4 H, Ph). ¹³C NMR (CDCl₃): δ 0.31 [d, SiMe₂, ³J(¹³C–³¹P) = 2.5], 2.63 [d, SiMe₃, ³J(¹³C–³¹P) = 2.6], 15.76 (s, NCH₂CH₃), 20.34 [d, PCH₂, ¹J(¹³C–³¹P) = 69.5], 39.50 (s, NCH₂), 127.89 [d, *m*-C in Ph, ³J(¹³C–³¹P) = 11.6], 130.09 [d, *p*-C in Ph, ⁴J(¹³C–³¹P) = 2.4], 130.83 [d, *o*-C in Ph, ²J(¹³C–³¹P) = 10.2] and 138.51 [d, *ipso*-C in Ph, ¹J(¹³C–³¹P) = 94.8 Hz]. ³¹P NMR (CDCl₃): δ −0.83 (s).

Li[CH(SiMe₂(NEt₂))P(Ph)₂=NSiMe₃] **9**. The compound LiBuⁿ (1.60 cm³ of a 1.6 mol dm^{−3} solution in hexanes,

Table 3 Crystal data and refinement for complexes **6** and **7**

	6	7
Formula	C ₂₇ H ₄₉ LiNO ₂ PSi ₂	C ₃₈ H ₅₈ Li ₂ N ₂ P ₂ Si ₄
<i>M</i>	513.8	731.0
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> $\bar{1}$ (no. 2)
<i>a</i> /Å	9.332(2)	10.988(2)
<i>b</i> /Å	10.682(4)	11.478(2)
<i>c</i> /Å	17.870(5)	18.753(3)
<i>a</i> °	89.36(3)	100.75(1)
<i>β</i> °	79.07(3)	94.93(1)
<i>γ</i> °	65.26(3)	108.83(1)
<i>U</i> /Å ³	1583.9(9)	2171.96(6)
<i>Z</i>	2	2
<i>μ</i> (Mo-Kα)/mm ⁻¹	0.18	0.24
<i>T</i> /K	173(2)	173(2)
Total reflections	5545	7615
Independent reflections	5545	7615
Reflections with <i>I</i> > 2σ(<i>I</i>)	4413	4860
<i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)]	0.054	0.064
<i>wR</i> 2 (all data)	0.145	0.176

2.56×10^{-3} mol) was added to a stirred solution of **III** (1.05 g, 2.52×10^{-3} mol) in hexane (30 cm³) at -20°C . The solution was stirred at room temperature for 3 h, then concentrated *in vacuo* and stored at room temperature, yielding the colourless crystalline compound **9** (0.80 g, 75%) (Found: C, 62.7; H, 8.64; N, 6.65. C₂₂H₃₆LiN₂PSi₂ requires C, 62.5; H, 8.59; N, 6.63%), mp 179–182 °C. Mass spectrum [*m/z* (%): 416 (9, [*M* – Li + 1]⁺), 344 (62, [*M* – NEt₂ – Li + 1]⁺), 272 (100, [Ph₂PN-SiMe₃]⁺), 200 (73, [Ph₂PNH]⁺) and 185 (53, [Ph₂P]⁺). ¹H NMR (C₆D₆): δ –0.13 (s, 9 H, SiMe₃), 0.17 (s, 6 H, SiMe₂), 0.97 (t, 6 H, NCH₂CH₃), 2.88 (q, 4 H, NCH₂), 7.15–7.23 (m, 6 H, Ph), 7.95 (m, 4 H, Ph), CH not observed. ¹³C NMR (C₆D₆): δ 3.62 (s, SiMe₂), 3.87 [d, SiMe₃, ³*J*(¹³C–³¹P) = 4.8], 11.59 [d, CH, ¹*J*(¹³C–³¹P) = 83.4], 13.43 (s, NCH₂CH₃), 38.32 (s, NCH₂), 127.87 [d, *m*-C in Ph, ³*J*(¹³C–³¹P) = 11.0], 130.13 [d, *p*-C in Ph, ⁴*J*(¹³C–³¹P) = 2.7], 132.52 [d, *o*-C in Ph, ²*J*(¹³C–³¹P) = 10.1] and 140.34 [d, *ipso*-C in Ph, ¹*J*(¹³C–³¹P) = 88.0 Hz]. ³¹P NMR (C₆D₆): δ 32.56 (s). ⁷Li NMR (C₆D₆): δ –0.76 (s).

Crystallography

Crystallographic details are given in Table 3. Data were collected on an Enraf-Nonius CAD4 diffractometer in the θ – 2θ mode with monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS 86)²⁴ and refined by full-matrix least squares on all *F*² (SHELXL 93).²⁵ For compound **7** the H atoms on C(1) and C(20) were freely refined. Other H atoms were included in riding mode.

CCDC reference number 186/1601.

See <http://www.rsc.org/suppdata/dt/1999/3413/> for crystallographic files in .cif format.

References

- 1 F. López-Ortiz, E. Peláez-Arango, B. Tejerina, E. Pérez-Carreño and S. García-Granda, *J. Am. Chem. Soc.*, 1995, **117**, 9972.

- 2 A. Müller, B. Neumüller and K. Dehnicke, *Chem. Ber.*, 1996, **129**, 253.
- 3 (a) A. Müller, B. Neumüller and K. Dehnicke, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2350; (b) A. Müller, M. Krieger, B. Neumüller, K. Dehnicke and J. Magull, *Z. Anorg. Allg. Chem.*, 1997, **623**, 1081.
- 4 J. C. Wilburn and R. H. Neilson, *Inorg. Chem.*, 1979, **18**, 347.
- 5 P. B. Hitchcock, M. F. Lappert and Z.-X. Wang, *Chem. Commun.*, 1997, 1113.
- 6 P. B. Hitchcock, M. F. Lappert and Z.-X. Wang, *J. Chem. Soc., Dalton Trans.*, 1997, 1953.
- 7 H. Schmidbaur and G. Jonas, *Chem. Ber.*, 1967, **100**, 1120.
- 8 C. H. Yoder, D. R. Griffith and C. D. Schaeffer, Jr., *J. Inorg. Nucl. Chem.*, 1970, **32**, 3689; S. S. Washburne and W. R. Peterson, *J. Organomet. Chem.*, 1970, **21**, 59.
- 9 K. Itoh, M. Okamura and Y. Ishii, *J. Organomet. Chem.*, 1974, **65**, 327.
- 10 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
- 11 C. M. Ong and D. W. Stephan, *J. Am. Chem. Soc.*, 1999, **121**, 2939; A. Kasani, R. P. Kamalesh Babu, R. McDonald and R. G. Cavell, *Angew. Chem., Int. Ed.*, 1999, **38**, 1483.
- 12 H. R. Allcock, *Chem. Rev.*, 1972, **72**, 315.
- 13 J. Emsley and D. Hall, *The Chemistry of Phosphorus*, Harper & Row, London, 1976.
- 14 A. Recknagel, A. Steiner, M. Noltemeyer, S. Brooker, D. Stalke and F. T. Edelmann, *J. Organomet. Chem.*, 1991, **414**, 327; A. Steiner and D. Stalke, *Inorg. Chem.*, 1993, **32**, 1977.
- 15 P. Imhoff, S. C. A. Nefkens, C. J. Elsevier, K. Goubitz and C. H. Stam, *Organometallics*, 1991, **10**, 1421.
- 16 H. R. Allcock, W. D. Coggio, M. Parvez and M. L. Turner, *Organometallics*, 1991, **10**, 677.
- 17 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
- 18 R. A. Jones, A. L. Stuart and T. C. Wright, *J. Am. Chem. Soc.*, 1983, **105**, 7459; H. H. Karsch, K. Zellner and G. Müller, *Organometallics*, 1991, **10**, 2884; E. Hey-Hawkins and E. Sattler, *J. Chem. Soc., Chem. Commun.*, 1992, 775; A. Pape, M. Lutz and G. Müller, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2281.
- 19 A. Müller, B. Neumüller, K. Dehnicke, J. Magull and D. Fenske, *Z. Anorg. Allg. Chem.*, 1997, **623**, 1306.
- 20 P. Imhoff and C. J. Elsevier, *J. Organomet. Chem.*, 1989, **361**, C61; P. Imhoff, J. H. Gülpen, K. Vrieze, W. J. J. Smeets, A. L. Spek and C. J. Elsevier, *Inorg. Chim. Acta*, 1995, **235**, 77; P. Imhoff, R. van Asselt, J. M. Ernsting, K. Vrieze, C. J. Elsevier, W. J. J. Smeets, A. L. Spek and A. P. M. Kentgens, *Organometallics*, 1993, **12**, 1523; M. W. Avis, K. Vrieze, H. Kooijman, N. Veldman, A. L. Spek and C. J. Elsevier, *Inorg. Chem.*, 1995, **34**, 4092; M. W. Avis, K. Vrieze, J. M. Ernsting, C. J. Elsevier, N. Veldman, A. L. Spek, K. V. Katti and C. L. Barnes, *Organometallics*, 1996, **15**, 2376.
- 21 D. Barr, W. Clegg, R. E. Mulvey and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1984, 79.
- 22 R. D. Rogers, J. L. Atwood and R. Grüning, *J. Organomet. Chem.*, 1978, **157**, 229; D. Barr, W. Clegg, R. E. Mulvey and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1984, 285.
- 23 C. Eaborn, Z.-R. Lu, P. B. Hitchcock and J. D. Smith, *Organometallics*, 1996, **15**, 1651.
- 24 G. M. Sheldrick, SHELXS 86, a package for the solution of crystal structures, University of Göttingen, 1986.
- 25 G. M. Sheldrick, SHELXL 93, a package for crystal structure refinement, University of Göttingen, 1993.