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FULL PAPER

The synthesis and molecular structures of the crystalline 1-aza-2-phospha(V)allyllithium compounds $[Li(LL')(OEt_2)_2]$ and $[Li(LL')]_2$ $[LL' = CH(SiMe_3)P(Ph)_2{=}NSiMe_3]$ and the preparation and characterisation of the new phosphinimines $CH(R^1)(R^2)P(Ph)_2{=}NSiMe_3$ $[R^1 = R^2 = SiMe_3;\ R^1 = H,\ R^2 = Si(Me)_2NEt_2]$†

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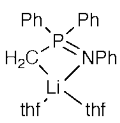
Received 7th July 1999, Accepted 30th July 1999

Reaction of $CH_2(SiMe_3)P(Ph)_2{=}NSiMe_3$ (HLL′) **I** with $LiBu^n$ afforded, after recrystallisation from diethyl ether, $[Li\{CH(SiMe_3)P(Ph)_2{=}NSiMe_3\}(OEt_2)_2]$. Removal of the co-ordinating Et_2O molecules *in vacuo* and subsequent recrystallisation from hexane yielded the solvent-free dimeric lithium complex $[Li\{CH(SiMe_3)P(Ph)_2{=}NSiMe_3\}]_2$. The crystal structures of the crystalline compounds $[Li(LL')(OEt_2)_2]$ 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 ^{31}P-$\{^1H\}$ NMR spectral signals, even at low temperatures. Its reaction with $Me_3SiO_3SCF_3$ afforded the phosphinimine $CH(SiMe_3)_2P(Ph)_2{=}NSiMe_3$ (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 $CH_2\{SiMe_2(NEt_2)\}P(Ph)_2{=}NSiMe_3$ (HLL‴) **III** was synthesized by reaction of $Li[CH_2P(Ph)_2{=}NSiMe_3]$ with $Et_2NSi(Me)_2Cl$ and, similar to the lithiation of **II**, reaction of **III** with $LiBu^n$ 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 $[Li\{CH_2P(Ph)_2{=}NPh\}(thf)_2]$ **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 $CH_3P(Me)_2{=}NSiMe_3$ was treated with $LiBu^n$ the crystalline tetrameric complex $[Li\{CH_2P(Me)_2{=}NSiMe_3\}]_4$ was obtained,[2] believed to contain relatively polar Li–C bonds. Significantly shorter, and thus more ionic, Li–C bonds were found in crystalline $[Li\{CMe_2P(Pr^i)_2{=}NSiMe_3\}]_2$ **2**.[2] Apart from chelating, a 1-aza-2-phospha(V)allyl ligand can also be bridging, as shown by Dehnicke and co-workers[3] in 1997, for the crystalline complexes $[LiCu\{CH(Me)P(Et)_2{=}NSiMe_3\}_2]$ **3**, $[Zn(Cl)\{CH(Me)P(Et)_2{=}NSiMe_3\}]_{12}$ and $[Mg_2I_2\{CH_2P(Me)_2{=}NSiMe_3\}\{OCH(Me)CH_2P(Me)_2{=}NSiMe_3\}(OEt_2)]$ **4**.



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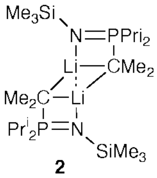

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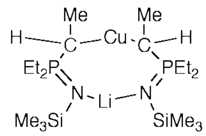

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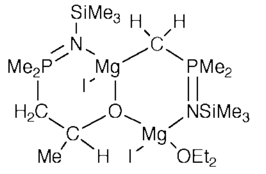

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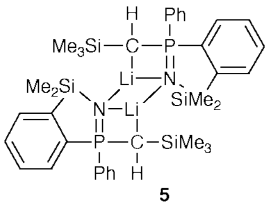

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We recently reported on applications of *C,N*-centred phosphinimines, such as $CH_2(SiMe_3)P(Ph)_2{=}NSiMe_3$ (HLL′) **I**,[4] as ligand precursors in alkali and Group 14 metal chemistry.[5] Reaction of **I** with $LiBu^n$ was believed to yield Li(LL′) **6** on the basis of its reactions with (i) $KOBu^t$ affording K(LL′),[5] (ii) ½ $PbCl_2$ giving the X-ray characterised $\overline{Pb(LL}')_2$,[5] (iii) $LiBu^n$ yielding the crystalline *ortho*-silylated derivative $[Li\{CH(SiMe_3)\{Ph(1,2\text{-}C_6H_4)P{=}NSiMe_2\}]$ **5**,[5] and (iv) PhCN and then successively $KOBu^t$ and tmen, furnishing $[K\{N(SiMe_3)P(Ph)_2C(H)C(Ph)NSiMe_3\}(tmen)]$.[6]

We now describe the synthesis, characterisation and crystal structures of the crystalline 1-aza-2-phospha(V)allyllithium compounds $[Li(LL')(OEt_2)_2]$ **6** and the solvent-free dimeric analogue $[Li(LL')]_2$ **7** $[LL' = CH(SiMe_3)P(Ph)_2{=}NSiMe_3]$. Furthermore, we report on the synthesis and characterisation of the new phosphinimines $CH(SiMe_3)_2P(Ph)_2{=}NSiMe_3$ (HLL″) **II** and $CH_2\{SiMe_2(NEt_2)\}P(Ph)_2{=}NSiMe_3$ (HLL‴) **III** and their respective lithium complexes Li(LL″) **8** and Li(LL‴) **9**.

Results and discussion

The synthesis of the crystalline complexes $[Li(LL')(OEt_2)_2]$ **6** and $[Li(LL')]_2$ **7** is summarised in Scheme 1. Thus, treatment of **I** with $LiBu^n$ 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 Et_2O was present in solution. Therefore, we suspected that the Et_2O molecules were loosely bound in **6** and this proved to be the case. After exposing $[Li(LL')(OEt_2)_2]$ **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 $LiBu^n$ in hexane.[5,6] As the Et_2O molecules were easily removed from **6**, no elemental analysis of the complex was carried out.

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

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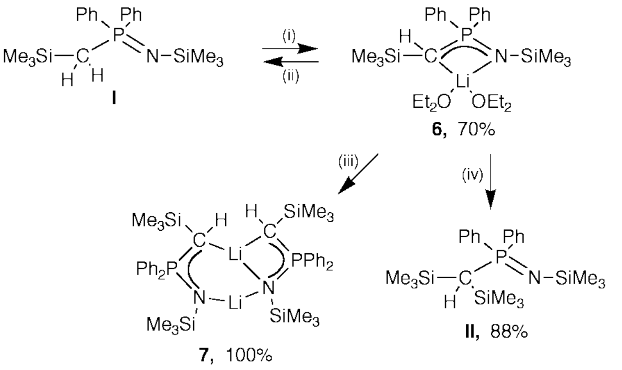
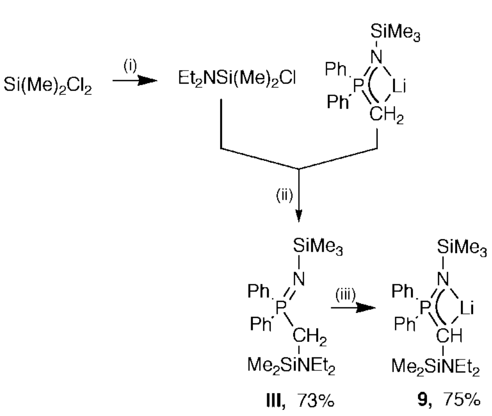


Scheme 1 Preparation of the crystalline 1-aza-2-phospha(v)allyllithium compounds $[Li(LL')(OEt_2)_2]$ **6** and $[Li(LL')]_2$ **7** and the phosphinimine $CH(SiMe_3)_2P(Ph)_2{=}NSiMe_3$ **II**. *Reagents and conditions*: (i) $LiBu^n$ in hexane, Et_2O, −40 °C, 1 h; (ii) MeOH in hexane, 0 °C, 0.5 h; (iii) 40 °C/10^{-3} Torr, 3 h; (iv) $Me_3SiO_3SCF_3$ 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 Me_3SiCl was added to a solution of compound **7** in pentane no reaction occurred. Since the analogue $Li[CH_2P(Me)_2{=}NSiMe_3]$ was reported to react readily with Me_3SiCl to afford $CH_2(SiMe_3)P(Me)_2{=}NSiMe_3$,[7] the $SiMe_3$ group on the C atom in **7** evidently provides additional protection of the Li atom. However, a reaction did take place when $Me_3SiO_3SCF_3$ was used, instead of Me_3SiCl. In this way the phosphinimine $CH(SiMe_3)_2P(Ph)_2{=}NSiMe_3$ (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 $CH(SiMe_3)_2P(Ph)_2$, a product of the reaction between $LiCH(SiMe_3)_2$ 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 $^{31}P\text{-}\{^1H\}$ 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 $CH_2\{SiMe_2(NEt_2)\}P(Ph)_2{=}NSiMe_3$ (HLL‴) **III** was obtained from $Et_2NSi(Me)_2Cl$ and $Li[CH_2P(Ph)_2{=}NSiMe_3]$ in Et_2O at low temperature (Scheme 2). The chlorosilane was prepared similarly to the reported procedure for the *in situ* synthesis of $Me_2NSi(Me)_2Cl$,[8] and $Li[CH_2P(Ph)_2{=}NSiMe_3]$ from the phosphinimine $CH_3P(Ph)_2{=}NSiMe_3$[9] and $LiBu^n$ at low temperature. Compound **III**, satisfactorily analysed by multinuclear NMR spectroscopy and elemental analysis, was readily lithiated with $LiBu^n$ in hexane at −20 °C to yield Li(LL‴) **9**. The $^7Li\text{-}\{^1H\}$ 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 NEt_2 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 NEt_2 group.



Scheme 2 Preparation of the phosphinimine HLL‴ **III** and its lithium complex Li(LL‴) **9**. *Reagents and conditions*: (i) $LiNEt_2$, Et_2O, −50 °C, 3 h; (ii) hexane, Et_2O, −78 °C, 16 h; (iii) $LiBu^n$ in hexane, −20 °C, 3 h.

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)

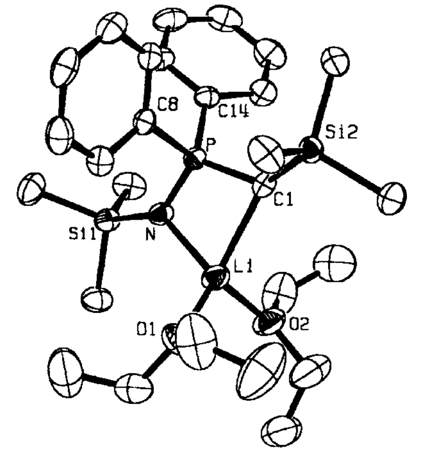
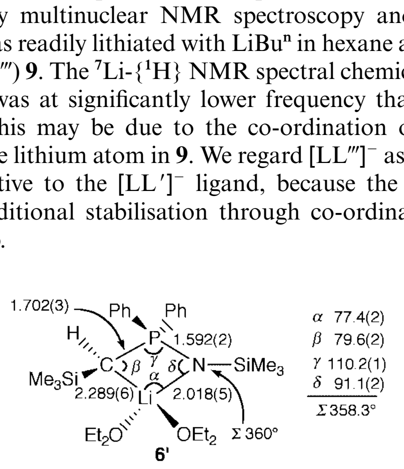


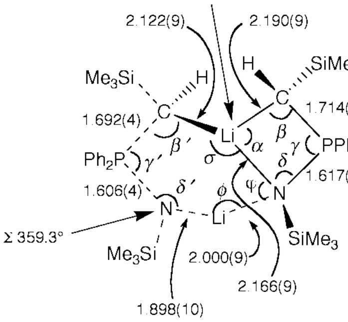
Fig. 1 The molecular structure of crystalline complex **6**.



6′

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 representation[10] of the molecular structure of **6** is shown in Fig. 1, endocyclic bond lengths and angles are sketched in **6′** and selected bond distances and angles are presented 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 Et_2O 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 $[Li\{CH_2P(Me)_2{=}NSiMe_3\}]_4$ (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 $[Li_2C\{P(Ph)_2{=}NSiMe_3\}_2]$, average 2.38(1) Å,[11] a complex bearing a dianionic 1-aza-2-phospha(v)allyl ligand with an additional $Ph_2P{=}NSiMe_3$ 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] $\overline{\text{Pb[CH(SiMe}_3\text{)P(Ph)}_2\text{=N}}\text{SiMe}_3]_2$ [1.568(4) Å],[6] or $Li[(NSiMe_3)_2PPh_2](thf)_2$, 1.579(4),[14] but slightly shorter than in $[\overline{\text{Rh\{CH}_2\text{P(Ph)}_2\text{=N}}\text{C}_6\text{H}_4\text{Me-4\}(COD)]}$, 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 $[NP(CH_2SiMe_3)_2]_3$[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 · · · 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 $\overline{\text{Pb[CH(SiMe}_3\text{)P(Ph)}_2\text{=N}}\text{SiMe}_3]_2$ 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 $[Li\{CH_2P(Me)_2{=}NSiMe_3\}]_4$ 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]



7′

α	78.1(3)	β′	112.1(3)
β	82.2(3)	γ′	112.7(2)
γ	111.0(2)	δ′	119.2(4)
δ	85.2(3)	ϕ	144.2(6)
Σ 356.5°		φ	77.5(4)
		σ	115.9(4)

Suitable single crystals of compound **7** were obtained after cooling a hexane solution to −25 °C. An ORTEP representation[10] 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* diastereoisomer is present. One of the $SiMe_3$ groups is situated above the plane of the four-membered ring and the other below. The $SiMe_3$ 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) · · · Li(2) distance of 2.610(13) Å in **7** an Li · · · Li interaction is possible, as suggested by Snaith and co-workers[21] for $[Li\{N{=}CPh_2\}(py)]_4$, with a mean Li · · · 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 · · · 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

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

Li(1)–N(1)	1.898(10)	Li(2) · · · 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) · · · 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)

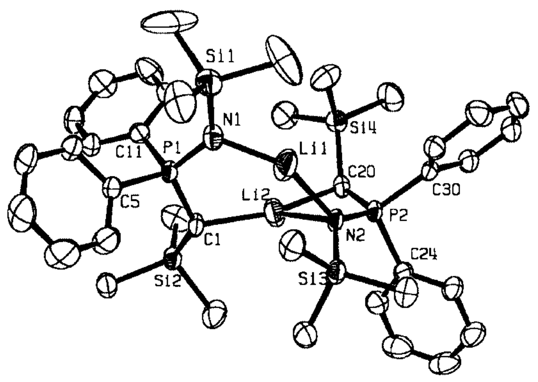


Fig. 2 The molecular structure of crystalline complex **7**.

$\overline{\mathrm{Pb(LL'}})_2$ 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 dialkyllithiate $[\equiv\mathrm{C{-}Li{-}C}\equiv]^-$, whereas that of Li(1) is akin to a bis(imino)lithium species $[\equiv\mathrm{N{-}Li{-}N}\equiv]^+$. In support, we draw attention to the crystalline compound [Li(tmen)$_2$][Li{C(SiMe$_3$)$_2$SiMe$_2$CH$_2$}$_2$] **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 ^{7}Li-{^{1}H} and ^{31}P-{^{1}H} NMR spectra of **7** in benzene-d_6, and the ^{1}H NMR spectrum likewise provided no evidence of the [LL′]$^-$ ligands exhibiting different coordination modes. Therefore, low temperature NMR spectral studies in toluene-d_8 were carried out. Owing to broadening of the signals in the ^{1}H NMR spectrum, no definite conclusions are drawn. In the ^{7}Li-{^{1}H} and ^{31}P-{^{1}H} 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 CH$_2$(SiMe$_3$)P(Ph)$_2$=NSiMe$_3$ **I**,[6] CH$_3$P(Ph)$_2$=NSiMe$_3$[9] and Et$_2$NSi(Me)$_2$Cl[8] were prepared according to published procedures. The NMR spectra were recorded in C_6D_6 or $C_6D_5CD_3$ at 298 K on a Bruker DPX 300 spectrometer (^{1}H, 300.1; ^{7}Li, 81.1; ^{13}C, 75.4; ^{31}P, 84.4 MHz) and the solvent resonances were used as the internal references for ^{1}H and ^{13}C spectra. The compounds LiCl (1 mol dm^{-3} aqueous solution) and H$_3$PO$_4$ (85% aqueous solution) were the external references for ^{7}Li and ^{31}P NMR spectra, respectively. Chemical shifts (δ) are reported in ppm. All NMR spectra other than ^{1}H 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(SiMe$_3$)P(Ph)$_2$=NSiMe$_3$}(OEt$_2$)$_2$] 6. The compound LiBu^n (6.2 cm^3 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 Et$_2$O (25 cm^3) 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%). ^{1}H NMR (C_6D_6): δ 0.06 (s, 9 H, CSiMe$_3$), 0.10 (s, 9 H, NSiMe$_3$), 1.48 [d, 1 H, CH, $^2J(^1\mathrm{H}\text{-}^{31}\mathrm{P}) = 14.7$ Hz], 1.06 (t, 6 H, Et$_2$O), 3.18 (q, 4 H, Et$_2$O), 7.04–7.19 (m, 6 H, Ph) and 7.81–7.88 (m, 4 H, Ph). ^{13}C NMR (C_6D_6): δ 3.84 (s, CSiMe$_3$), 4.10 (s, NSiMe$_3$), 13.88 [d, CH, $^2J(^{13}\mathrm{C}\text{-}^{31}\mathrm{P}) = 86.7$], 15.29 (s, Et$_2$O), 65.99 (s, Et$_2$O), 119.40 (s, *m*-C in Ph), 130.00 (s, *p*-C in Ph), 131.93 [d, *o*-C in Ph, $^2J(^{13}\mathrm{C}\text{-}^{31}\mathrm{P}) = 10.3$ Hz], *ipso*-C in Ph not observed. ^{31}P NMR (C_6D_6): δ 60.00 (s). ^{7}Li NMR (C_6D_6): δ 2.57 (s).

[Li{CH(SiMe$_3$)P(Ph)$_2$=NSiMe$_3$}]$_2$ 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. $C_{19}H_{29}LiNPSi_2$ requires C, 62.4; H, 8.00; N, 3.83%), mp 135–138 °C. Mass spectrum [*m*/*z* (%)]: 359 (32, $[M_{½} - \mathrm{Li} + 1]^+$), 344 (100, $[M_{½} - \mathrm{Me} - \mathrm{Li} + 1]^+$), 272 (26, $[M_{½} - \mathrm{Li} - \mathrm{CHSiMe_3}]^+$), 135 (29, $[M_{½} - \mathrm{Li} - (\mathrm{SiMe_3})_2 - \mathrm{Ph}]^+$) and 73 (22, [SiMe$_3$]$^+$). ^{1}H NMR ($C_6D_5CD_3$): δ 0.00 (s, 9 H, CSiMe$_3$), 0.05 (s, 9 H, NSiMe$_3$), 1.68 [d, 1 H, CH, $^2J(^1\mathrm{H}\text{-}^{31}\mathrm{P}) = 10.5$ Hz], 7.11–7.17 (m, 6 H, Ph) and 7.74–7.81 (m, 4 H, Ph). ^{13}C NMR ($C_6D_5CD_3$): δ 3.64 [d, CSiMe$_3$, $^3J(^{13}\mathrm{C}\text{-}^{31}\mathrm{P}) = 3.54$], 4.12 [d, NSiMe$_3$, $^3J(^{13}\mathrm{C}\text{-}^{31}\mathrm{P}) = 4.44$], 14.34 [d, CH, $^1J(^{13}\mathrm{C}\text{-}^{31}\mathrm{P}) = 84.9$], 128.07 [d, *m*-C in Ph, $^3J(^{13}\mathrm{C}\text{-}^{31}\mathrm{P}) = 11.0$], 130.20 [d, *p*-C in Ph, $^4J(^{13}\mathrm{C}\text{-}^{31}\mathrm{P}) = 2.26$], 131.97 [d, *o*-C in Ph, $^2J(^{13}\mathrm{C}\text{-}^{31}\mathrm{P}) = 10.3$] and 139.61 [d, *ipso*-C in Ph, $^1J(^{13}\mathrm{C}\text{-}^{31}\mathrm{P}) = 86.8$ Hz]. ^{31}P NMR ($C_6D_5CD_3$): δ 33.03 (s). ^{7}Li NMR ($C_6D_5CD_3$): δ 1.85 (s).

CH(SiMe$_3$)$_2$P(Ph)$_2$=NSiMe$_3$ II. Compound **7** (0.56 g, 1.53 × 10^{-3} mol) was dissolved in hexane (20 cm^3) and cooled to −78 °C. Trimethylsilyl triflate (trifluoromethanesulfonate) (0.3 cm^3, 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%). ^{1}H NMR (C_6D_6): δ 0.06 (s, 18 H, CSiMe$_3$), 0.52 (s, 9 H, NSiMe$_3$), 1.19 [d, 1 H, CH, $^2J(^1\mathrm{H}\text{-}^{31}\mathrm{P}) = 12.4$ Hz], 7.01–7.08 (m, 6 H, Ph) and 7.61–7.68 (m, 4 H, Ph). ^{31}P NMR (C_6D_6): δ 0.97 (s).

CH$_2${SiMe$_2$(NEt$_2$)}P(Ph)$_2$=NSiMe$_3$ III. The compound LiBu^n (28.0 cm^3 of a 1.6 mol dm^{-3} solution in hexanes, 44.8 × 10^{-3} mol) was added to a stirred solution of CH$_3$P(Ph)$_2$=NSiMe$_3$ (12.7 g, 44.0 × 10^{-3} mol) in Et$_2$O (100 cm^3) at −50 °C. The solution was stirred at room temperature for 3 h and recooled to −78 °C. The compound Et$_2$NSi(Me)$_2$Cl (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. $C_{22}H_{37}N_2PSi_2$ requires C, 63.4; H, 8.95; N, 6.72%), bp 150 °C/0.025 Torr. ^{1}H NMR (CDCl$_3$): δ −0.08 (s, 6 H, SiMe$_2$), −0.04 (s, 9 H, SiMe$_3$), 0.94 (t, 6 H, NCH$_2$C*H*$_3$), 1.69 [d, 2 H, PCH$_2$, $^2J(^1\mathrm{H}\text{-}^{31}\mathrm{P}) = 15.4$ Hz], 2.82 (q, 4 H, NCH$_2$), 7.37–7.41 (m, 6 H, Ph) and 7.65–7.71 (m, 4 H, Ph). ^{13}C NMR (CDCl$_3$): δ 0.31 [d, SiMe$_2$, $^3J(^{13}\mathrm{C}\text{-}^{31}\mathrm{P}) = 2.5$], 2.63 [d, SiMe$_3$, $^3J(^{13}\mathrm{C}\text{-}^{31}\mathrm{P}) = 2.6$], 15.76 (s, NCH$_2$*C*H$_3$), 20.34 [d, PCH$_2$, $^1J(^{13}\mathrm{C}\text{-}^{31}\mathrm{P}) = 69.5$], 39.50 (s, NCH$_2$), 127.89 [d, *m*-C in Ph, $^3J(^{13}\mathrm{C}\text{-}^{31}\mathrm{P}) = 11.6$], 130.09 [d, *p*-C in Ph, $^4J(^{13}\mathrm{C}\text{-}^{31}\mathrm{P}) = 2.4$], 130.83 [d, *o*-C in Ph, $^2J(^{13}\mathrm{C}\text{-}^{31}\mathrm{P}) = 10.2$] and 138.51 [d, *ipso*-C in Ph, $^1J(^{13}\mathrm{C}\text{-}^{31}\mathrm{P}) = 94.8$ Hz]. ^{31}P NMR (CDCl$_3$): δ −0.83 (s).

Li[CH{SiMe$_2$(NEt$_2$)}P(Ph)$_2$=NSiMe$_3$] 9. The compound LiBu^n (1.60 cm^3 of a 1.6 mol dm^{-3} solution in hexanes,

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

	6	**7**
Formula	$C_{27}H_{49}LiNO_2PSi_2$	$C_{38}H_{58}Li_2N_2P_2Si_4$
M	513.8	731.0
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	9.332(2)	10.988(2)
b/Å	10.682(4)	11.478(2)
c/Å	17.870(5)	18.753(3)
α/°	89.36(3)	100.75(1)
β/°	79.07(3)	94.93(1)
γ/°	65.26(3)	108.83(1)
U/Å^3	1583.9(9)	2171.96(6)
Z	2	2
μ(Mo-Kα)/mm^{-1}	0.18	0.24
T/K	173(2)	173(2)
Total reflections	5545	7615
Independent reflections	5545	7615
Reflections with $I > 2\sigma(I)$	4413	4860
$R1$ [$I > 2\sigma(I)$]	0.054	0.064
$wR2$ (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 cm^3) 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. $C_{22}H_{36}LiN_2PSi_2$ 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 − NEt_2 − Li + 1]$^+$), 272 (100, [$Ph_2PNSiMe_3$]$^+$), 200 (73, [Ph_2PNH]$^+$) and 185 (53, [Ph_2P]$^+$). ^{1}H NMR (C_6D_6): δ −0.13 (s, 9 H, $SiMe_3$), 0.17 (s, 6 H, $SiMe_2$), 0.97 (t, 6 H, NCH_2CH_3), 2.88 (q, 4 H, NCH_2), 7.15–7.23 (m, 6 H, Ph), 7.95 (m, 4 H, Ph), CH not observed. ^{13}C NMR (C_6D_6): δ 3.62 (s, $SiMe_2$), 3.87 [d, $SiMe_3$, $^3J(^{13}C\text{-}^{31}P) = 4.8$], 11.59 [d, CH, $^1J(^{13}C\text{-}^{31}P) = 83.4$], 13.43 (s, NCH_2CH_3), 38.32 (s, NCH_2), 127.87 [d, *m*-C in Ph, $^3J(^{13}C\text{-}^{31}P) = 11.0$], 130.13 [d, *p*-C in Ph, $^4J(^{13}C\text{-}^{31}P) = 2.7$], 132.52 [d, *o*-C in Ph, $^2J(^{13}C\text{-}^{31}P) = 10.1$] and 140.34 [d, *ipso*-C in Ph, $^1J(^{13}C\text{-}^{31}P) = 88.0$ Hz]. ^{31}P NMR (C_6D_6): δ 32.56 (s). ^{7}Li NMR (C_6D_6): 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.

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Paper 9/05464B