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FULL PAPER

Synthesis and crystal structures of novel 1-aza-2-silacyclo-but-3-enes

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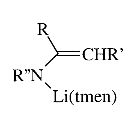
A crystallographic re-investigation of the structure of the 4-aryl(lithio)amino-1-aza-2-silacyclo-but-3-ene derivative, $[Li\{N(Ar)\overline{CC(R)SiR_2N}Ar\}](tmen)$ **F** ($R = SiMe_3$, $Ar = C_6H_3Me_2$-2,6), formed by the treatment of $[Li(SiR_3)(thf)_3]$ with ArNC in the presence of tmen, revealed the presence of two independent molecules within the unit cell. Its protonolysis with cyclopentadiene monomer gave the 1-aza-2-silacyclobutene, $HN(Ar)\overline{CC(R)Si(R)_2N}Ar$ **2b**. Replacing tmen with 1,2-bis(dimethylphosphino)ethane (dmpe), in the reaction of $[Li(SiR_3)(thf)_3]$ with ArNC, gave either $[Li\{N(Ar)\overline{CC(R)Si(R)_2N}Ar\}(thf)_2]$ **4** or the dimer $[Li\{N(Ar)\overline{CC(R)Si(R)_2N}Ar\}(\mu\text{-dmpe})]_2$ **3**, the latter being preferred at low thf concentrations. Each of the compounds **F**, **2b**, **3** and **4** was characterised by multinuclear NMR spectroscopy and (not **4**) X-ray diffraction. The single crystal structures of **2b** and **3** provide the first examples of a neutral $\overline{C{=}CSiN}$ compound and a neutral phosphine-bound alkali metal complex, respectively. The NMR spectra revealed that **3** undergoes speciation in solution.

Introduction

The insertion of an isocyanide R″NC into the Li–C bond of $[Li\{C(H)(R)R'\}]$ ($R = SiMe_3$, $R' = R$ or Ph) has afforded a range of structural types: the lithium 1-azaallyls **A**, the β-diketiminates **B** and **C** and the 1-azabut-1,3-dienyl-3-amide **D**.[1,2] It was suggested that **A** had formed from $Li(CHR_2)$ and R″NC by sequentially (i) a 1 : 1 adduct and its isomerisation into successively (ii) the lithioaldimine **E** and (iii) **A** by a 1,2-Me_3Si shift. A similar sequence involving a further equivalent of R″NC was postulated as the pathway to **B** ($R'' = Ar = 2,6\text{-}Me_2C_6H_3$) or **C** ($R'' = Bu^t$). When the reaction between $[Li\{C(H)(R)Ph\}]$ and 2 ArNC was carried out in the presence of tmen, it was proposed that the insertion of a second equivalent of ArNC into **E** (R″ = Ar) to form the intermediate $[ArNC–Li\{C(=NAr)CH(R)Ph\}(tmen)]$ proceeded faster than the isomerisation **E** ⟶ **A**;[2] a final 1,3-Me_3Si C ⟶ C shift from this intermediate completed the pathway to **D**.[2] A similar role for tmen (or another strong neutral donor) had been noted in the $[Li(CHR_2)]$–PhCN system.[3] The function of tmen may have been to promote an $\eta^3 \longrightarrow \eta^1$ isomerisation of the 1-azaallyl ligand (a 1 : 1 adduct in both the ArNC and PhCN systems), thus enhancing its N- over its C-centred nucleophilicity.

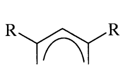
The present study complements our earlier report into the lithium sisyl $[Li(SiR_3)(thf)_3]$ (**1**)[4] system, involving ArNC insertion into the Li–Si bond, as summarised in Scheme 1.[5] It was suggested that the lithium amide **F** had arisen by a pathway closely similar to that proposed for the $[Li(CHR_2)]$–ArNC system, involving successively (i) formation of **G**, (ii) a 1,2-Me_3Si Si ⟶ C shift yielding **H** and (iii) electrocyclic addition **I** of ArNC to **F**. Heating **F** in refluxing benzene yielded the alkyne **J**. The molecular structures of **F** and **J** were determined.[5]

A



R' = R, R" = Ar
R' = Ph, R" = Ar
R' = Ph, R" = Bu^t

B



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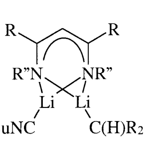

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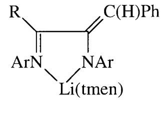

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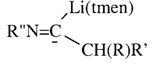

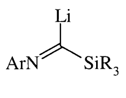

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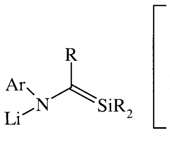

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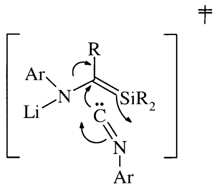
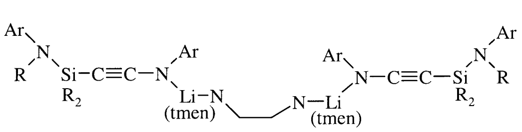


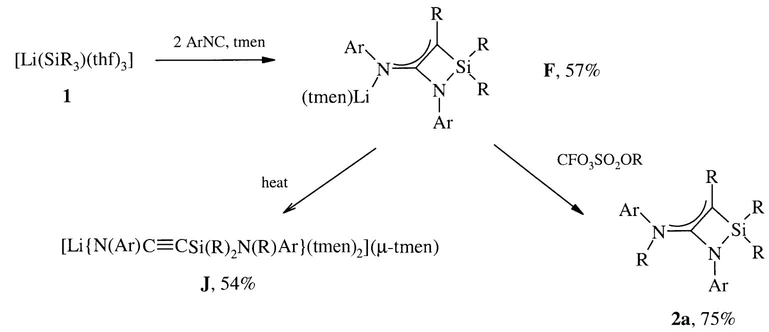
I



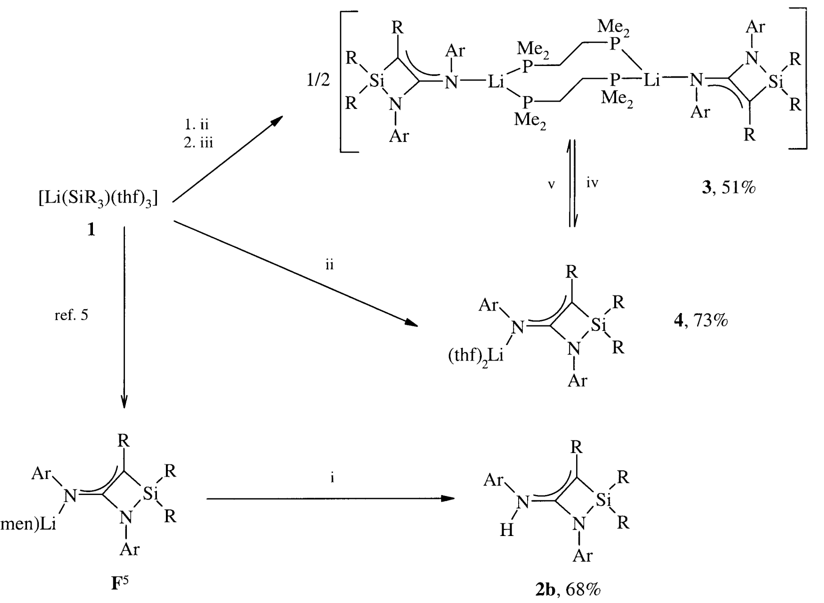
J

Results and discussion

As previously reported, treatment of a pentane solution of $[Li(SiR_3)(thf)_3]$ **1** with the isocyanide ArNC in the presence of tmen at −80 °C yielded **F** as colourless crystals, which were formed independently of stoichiometry (1 or 2 equivalents of ArNC) and of solvent (pentane or Et_2O) (Scheme 1).[5] We now find that by employing a slightly more dilute pentane solution of $[Li(SiR_3)(thf)_3]$ with ArNC in the presence of tmen at −80 °C deep yellow crystals are obtained, which were stable *in vacuo*. The NMR spectroscopic data of the two types of crystals were almost identical, except that the ^{1}H-NMR spectrum revealed substantial broadening of the tmen resonances for the yellow crystals. These observations prompted a crystallographic



Scheme 1 Reactions in the $[\mathrm{Li(SiR_3)(thf)_3}]$–ArNC system (R = $\mathrm{SiMe_3}$, Ar = 2,6-$\mathrm{Me_2C_6H_3}$).[5]



Scheme 2 New reactions in the $[\mathrm{Li(SiR_3)(thf)_3}]$–ArNC system (R = $\mathrm{SiMe_3}$, Ar = 2,6-$\mathrm{Me_2C_6H_3}$). Reactions and reaction conditions: i, $\mathrm{C_5H_6}$, $\mathrm{C_5H_{12}}$, −60 °C, 3 h; ii, dmpe, $\mathrm{C_6H_{14}}$, −80 °C, 16 h; iii, removal of volatiles and extraction with $\mathrm{C_6H_{14}}$; iv, thf; v, dmpe (iv, v, microscale reactions, no yields determined).

investigation of the latter, which revealed it to have structure **F**, but having two independent molecules in the unit cell (see below).

Treatment of **F** with cyclopentadiene monomer yielded (i in Scheme 2) its conjugate acid **2b**.

As part of our continuing interest into the role of a neutral donor in the R′CN and R′NC/lithium silylmethyl or -silyl systems, attention now turned to the soft 1,2-bis(dimethylphosphino)ethane (dmpe) (*cf.*, the hard tmen of Scheme 1). Thus, the lithium sisyl **1** and dmpe in hexane followed by addition of ArNC gave either of two crystalline products, depending on the work-up procedure: the binuclear bis(dmpe)-bridged complex **3** (ii, followed by iii, in Scheme 2), or (ii in Scheme 2) **4**, an analogue of **F**, having $(\mathrm{thf})_2$ in **4** in place of tmen in **F**. If the initial hexane solution was evaporated *in vacuo* and the residue recrystallised from hexane, **3** was obtained; whereas refrigeration of the hexane solution afforded crystalline **4**. We conclude that an equilibrium mixture of **3** and **4** coexisted in solution, eqn. (1). This was further confirmed by converting **3** into **4** by the addition of three equivalents of thf to **3** (iv in Scheme 2),

$$\underset{\mathbf{3}}{[\mathrm{Li}\{\mathrm{N(Ar)}\overline{\mathrm{CN(Ar)Si(R)_2CR}}\}(\mu\text{-dmpe})]_2} + 4\,\mathrm{thf} \rightleftharpoons 2\ \underset{\mathbf{4}}{[\mathrm{Li}\{\mathrm{N(Ar)}\overline{\mathrm{CN(Ar)Si(R)_2CR}}\}(\mathrm{thf})_2]} + 2\,\mathrm{dmpe} \qquad (1)$$

whereas **4** with an excess of dmpe afforded (v in Scheme 2) **3** as a major product. Surprisingly **4** was at best obtained as a minor product when **1** was reacted with ArNC at low temperatures. It is evident from these observations and the compounds **3**, **4** and **F** that the hard lithium ion binds preferentially to a hard (N- or C-centred) rather than the softer P-centred base. The presence of dmpe as a bridging, rather than chelating, ligand in **3** is noteworthy. Indeed, to the best of our knowledge, compound **3** provides the first example of a *neutral* phosphine ligating to lithium.

Crystal structures of the 1-aza-2-silacyclobutenes F, 3 and 2b

The molecular structures of **F**, **3** and **2b** with the atom numbering scheme are shown in Figs. 1–3, while selected bond distances and angles are compared in Table 1.

As discussed above a sample of **F** was isolated which in colour and stability appeared to differ from that originally[5] described, although the NMR spectra were very similar. The X-ray crystal structure was solved in the space group $P2_1/c$ with two molecules in the asymmetric unit. In the previously determined structure,[5] the neutral tmen substituent on **F** is disordered resulting in the generation of a centre of inversion between the two molecules. In the new crystal structure the tmen substituent is no longer disordered and the "extra" inversion centre is no longer present. The result is, that there are two molecules in the asymmetric unit and the unit cell volume is double that of the original structure. The space group and overall crystal packing of the original structure have however been retained. While conversion to the original cell is possible, it

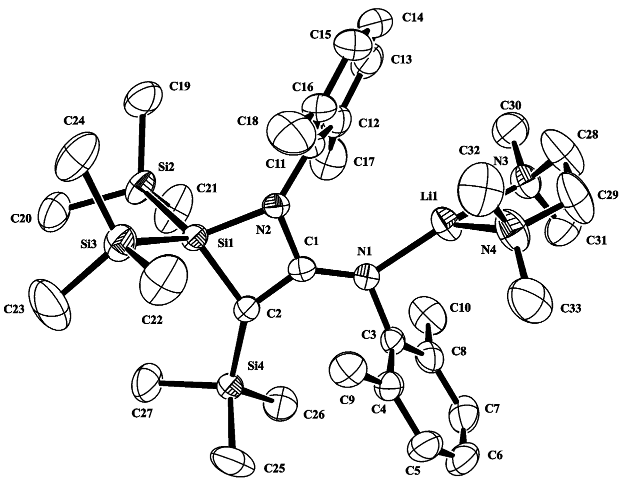


Fig. 1 Molecular structure of **F**.

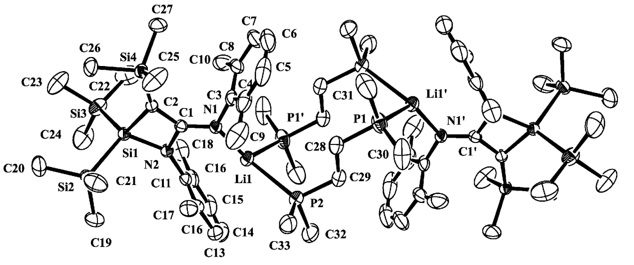


Fig. 2 Molecular structure of **3**.

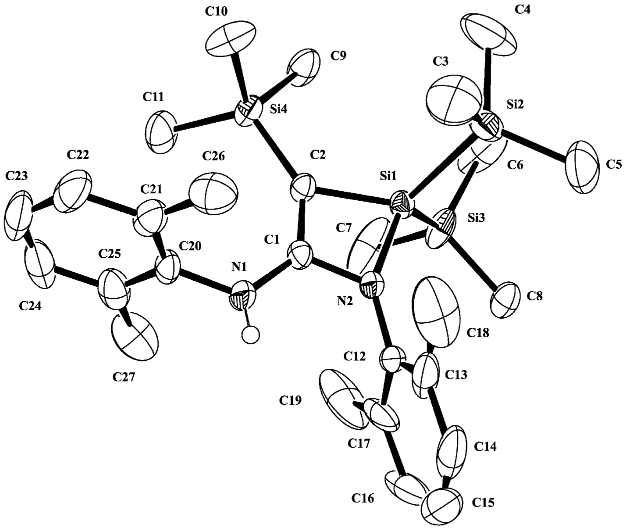
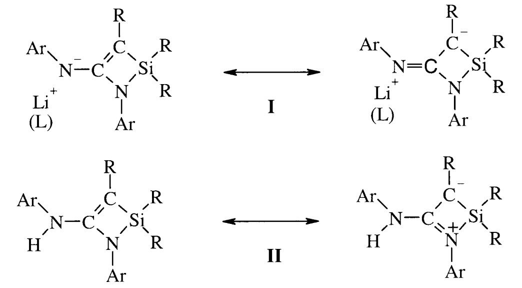


Fig. 3 Molecular structure of **2b**.

was found that the quality of the solution decreased significantly. Such a solution is also undesirable as it would lead to a loss of information by artificially requiring disorder on the tmen substituents.

All three compounds are rare examples of four-membered $\overline{\mathrm{CCSiN}}$ heterocycles and comprise to the best of our knowledge the first structurally characterised derivatives of a 1-aza-2-silacyclobutene. Each crystal structure reveals that the atoms of the four-membered ring and the exocyclic nitrogen atom N1 are essentially coplanar and that each of the ring atoms N2, C1, and C2 is in an almost planar environment. Of the endocyclic bond angles, only C2–C1–N2 is obtuse [*ca.* 105.5° for **F** and **3**, 108.8(2)° for **2b**], and of the remainder only that of Si1 [*ca.* 77°] deviates significantly from 90°. The latter is largely imposed by the geometry of the four-membered ring, being similar to those found in other SiNCC heterocycles, such as $\overline{\mathrm{Si(Bu^t_2)N(SiBu^t_2Ph)C\{H(OEt)\}C}}\mathrm{H_2}$ [79.5(1)°][6] or $\overline{\mathrm{Si(Ph)_2N(SiMe_2Ph)C(H)(Ph)C}}\mathrm{(H)Pr^i}$ [76.2(1)°].[7] Apart from the Si2–Si1–Si3 angle, the other angles at Si1 deviate significantly from the tetrahedral value. The short N2–C1 (1.335 Å) and long C1–C2 (1.419 Å) distances in the ionic amides **F** and **3** indicate that there is a considerable π-delocalisation in the N$\cdot\!\!\cdot$C$\cdot\!\!\cdot$C moiety, as shown in **I** in valence bond terms. In the covalent protic compound **2b**, the endocyclic CC distance of 1.372(3) Å is at the upper limit for a silacyclobutene C=C bond, which lie in the range of 1.34–1.37 Å;[8,9] *cf.*[8] 1.338(4) Å in 2,4,6,-$\mathrm{Pr^i_3C_6H_2}\overline{\mathrm{Si(Me)C(H){=}C(Ph)C}}\mathrm{(SiMe_2OSiMe_3)Ad}$ (Ad = adamantyl). The N–C exocyclic [1.357(2) Å] and endocyclic [1.399(3) Å] bond lengths are significantly longer and shorter, respectively, than in **F** or **3**; the endocyclic N–C bond in **2b** is also much shorter than in $\overline{\mathrm{Si(Bu^t_2)N(SiBu^t_2Ph)C(H)(OEt)C}}\mathrm{H_2}$ [1.473(4) Å][6] and $\overline{\mathrm{Si(Ph)_2N(SiMe_2Ph)C(H)(Ph)C}}\mathrm{(H)Pr^i}$ [1.513(4) Å].[7] In valence bond terms, some degree of endocyclic conjugation, as illustrated in the canonical structures **II**, is therefore indicated. The different electronic environments at C1 and C2 are also evident from their $^{13}\mathrm{C}\{^1\mathrm{H}\}$ chemical shifts in $\mathrm{C_6D_6}$: δ = 152.7 and 81.5, respectively. The exocyclic C–N–C bond angle at the ring nitrogen atom N1 is considerably wider [124.2(2)°] in **2b** than in either of the two lithium amides [118.9(1)° for **F**, 117.9(1)° for **3**], indicating that there is considerable steric strain in the latter between the molecules of the neutral donor ligand and the aryl substituent at N1. Both the endo- and exocyclic bonds to Si(1) in the three compounds **2**, **3** and **F** are unexceptional; *cf.* Si–N and Si–C bond lengths in $\overline{\mathrm{Si(Bu^t_2)N(SiBu^t_2Ph)C(H)(OEt)C}}\mathrm{H_2}$ [1.750(3) and 1.879(4) Å, respectively][6] and $\overline{\mathrm{Si(Ph)_2N(SiMe_2Ph)C(H)(Ph)C}}\mathrm{(H)Pr^i}$ [1.737(3) and 1.883(4) Å, respectively][7] and average Si–Si in $[\mathrm{Li(SiR_3)(thf)_3}]$ of 2.331(4) Å.[4]



The coordination sphere around each lithium atom in **F** and **3** deviates significantly from a trigonal planar arrangement (Σ°Li 350.7° for **F**, 345.5° for **3**); there is a comparatively short contact between the lithium and the *ipso*-carbon atom of the aryl substituent bound to N1 (2.63 Å for **F**, 2.87 Å for **3**).

As **3** is to the best of our knowledge the first example of a structurally characterised complex encompassing phosphine coordination *via* a *neutral* ligand to lithium it seems appropriate to comment on this in more detail. In all previously reported cases $\mathrm{PR_3}$ coordination to lithium was achieved *via* an anionic ligand of types (**i**)–(**x**), shown in Fig. 4.[10] By binding of the anionic centre(s) to the lithium atom it is in close proximity to intramolecular P atom(s). Many of these compounds adopt oligomeric structures, in which the lithium atom is bound in a chelating fashion to the anionic centre and the phosphine, while a neutral donor solvent such as thf or ether completes the coordination sphere around the lithium atom. The resulting solid-state structures for ligand **i**, **ii**, **iii** and **v**, for example, consist of ligand (L): Li: neutral donor solvent (D) stoichiometries of 2 : 3 : 2(dme), 1 : 1 : 0 (no donor solvent), 1 : 2 : 1(thf) or 1 : 2 : 2(thf), and 1 : 1 : 1($\mathrm{OEt_2}$), respectively. For the ligand **x** (Fig. 4), fused tricyclic structures are formed, in which the alkoxide ligands are P- and O-chelating with respect to one lithium centre and are O-bridging to the second.[10o] These

Table 1 Selected structural parameters of compounds **F**, **3** and **2b**

Bond distances and angles /Å and °	**F**[a]	**2b**	**3**
N1–Li	1.968(3)	—	1.939(3)
Li–N3 (P1)	2.130(4)	—	2.648(3)
Li–N4 (P2)	2.166(4)	—	2.651(3)
N1–C1	1.330(2)	1.357(3)	1.336(2)
N2–C1	1.433(2)	1.399(3)	1.432(2)
C1–C2	1.419(2)	1.372(3)	1.419(2)
Li · · · C3	2.63	—	2.87
C2–Si1	1.841(2)	1.853(2)	1.842(2)
N1–Si1	1.787(2)	1.794(2)	1.792(2)
Si1–Si(2,3) av.	2.359(1)	2.348(1)	2.361(1)
Si2–Si1–Si3	108.81(3)	111.76(4)	111.61(2)
C2–Si1–N2	77.40(7)	76.31(9)	77.25(7)
C1–N1–C3 (C20)	118.9(1)	124.2(2)	117.9(1)
C1–N1–Li1	134.7(2)	—	124.5(2)
C3–N1–Li1	105.1(2)	—	116.5(2)
C2–C1–N2	105.4(1)	108.8(2)	105.5(1)
N1–C1–N2	118.5(1)	118.0(2)	117.9(1)
N1–C1–C2	136.2(2)	133.1(2)	136.7(2)
N3–Li–N4 (P1–Li–P2)	85.4(1)	—	96.6(1)
Σ°N1	358.6	—	358.9
Σ°N2	356.2	358.9	358.2
Σ°C1	360.1	359.9	360.1
Σ°C2	358.3	359.9	359.5
Σ°Li	350.7	—	345.5
Deviation from plane	C1(A), N2 0.008(1)	N1, N2 0.006(1)	N2 0.016(1)

[a] The given values are averages of the two independent molecules.

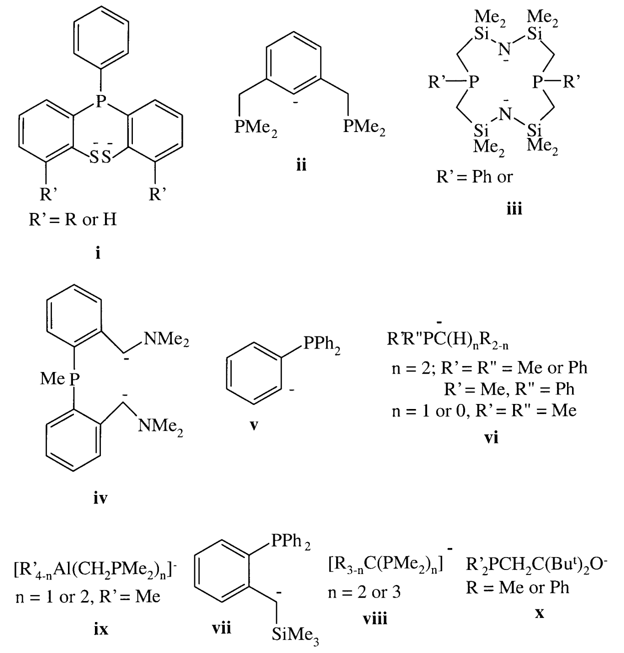
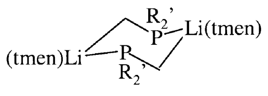


Fig. 4 Anionic ligands **i–x** containing neutral P(III) binding sites.

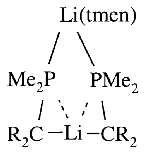
dimeric 1 : 1 complexes have three-coordinate lithium atoms. Ligand **iv** is exceptional, in that it forms a 1 : 1 dimer in which the carbanionic centres are bridged intermolecularly to P atoms by Li atoms, owing to the stabilising influence of an internal N-centred donor.[10g] As in **3**, a classical double bridging structural motif resulting in the formation of a ring system has been observed for the anionic phosphinomethanides (**vi**). Thus, in the presence of a strong neutral donor such as tmen, intermolecular phosphine complexation is available *via* dimerisation. For example, the ligands $\bar{C}H_2PR'R''$ (**vi**) bridge successive lithium centres through the *ipso* carbon and P^{III} atoms in a head-to-tail arrangement as part of six atom heterocycles, with tmen chelating each of the Li atoms. For R′ = R″ = Me[10j] or Ph[10i] and $n = 2$, chair conformations **K** are assumed, while for R′ = Me, R″ = Ph and $n = 2$,[10j] the six membered ring has a boat conformation.[10j] Alkyl substitution at the *ipso* carbon ($n = 1$) invokes a twist in the six membered ring so that each Li atom not only links the two phosphinomethanides through Li–C and Li–P interactions, but each Li atom also bridges one of the central P–C bonds.[10r] Further alkyl substitution ($n = 0$; R′ = R″ = Me) establishes a head-to-head arrangement **L** for the phosphinomethanides in the six membered ring, with almost equal lengths between each lithium atom and each of the phosphorus atoms;[10c] tmen is excluded from the coordination sphere of the carbon bound lithium atom because of the steric bulk of the $SiMe_3$ (= R) substituents. An example of the role of the ligand in **viii** is shown in the structure of **M**.[10a,b] Derivatives of **vii** in the presence of an equivalent of tmen, lead to monomeric structures in which the chelating ligand provides close contacts to the lithium atom; the tmen completing the distorted tetrahedral geometry at the lithium atom.[10j] Of all the ligands of Fig. 4 (phosphinomethyl)aluminates **ix**[10e,f] in **N** shows the closest similarity to **3**. Unlike the other ligands of Fig. 4, in which coordination is complicated by Li · · · C, Li · · · S or Li · · · N interactions, in **N** the negatively charged aluminate centres do not compete with the phosphorus atom for the electrophilic lithium atom; the location of the anionic charge in a more remote position with respect to the phosphorus donor atom resembles a simple tertiary phosphine. Complex **N** differs from **3** in the respect that the two phosphorus atoms chelate the lithium atom, whereas in **3** they are bridging.

The P1–Li–P2 angle of 96.6(1)° in **3** is narrower than the angles in the four-coordinate, six-membered ring species, **L** [106.1(3)°][10c] and **N** [105.7(3)°],[10f] and differs substantially from that in the four-membered ring formed from phosphorus chelation in **M** [65.3(1)°].[10b] The P–Li bond distances [mean = 2.650(3) Å] are close to those reported for **N** [2.606(5) Å],[10f] which can be considered as standard distances for complexes formed under the exclusive formation of P^{III}–Li bonds. The P^{III}–Li distances for the anionic ligands of Fig. 4 range from 2.40(1) Å for $[\{Li_2(L)(dme)\}_2]$ (L = **i**, R′ = R)[10p] to the 2.81(3) Å mean distance for **L**;[10c] these are well within the sum of their van der Waals radii (3.65 Å).[11]

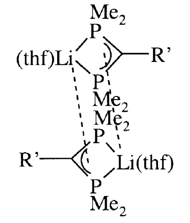
Approximately axial and equatorial positions are occupied by the methyl substituents in the ten-membered ring of **3**, with similar mean $P–CH_3$ and $P–CH_2$ bond distances. This



R' = Me or Ph **K**

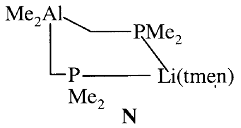


L



R' = R or PMe$_3$

M



N

double-boat conformation is rare and has previously been observed only for biphosphines bound to Group 11 metals.[12] The shortening of P–CH$_2$ with respect to P–CH$_3$ bonds as observed in **K** and **N**, has been ascribed as arising in part from the stabilising influence of phosphorus by polarisation,[13] or alternatively, its ylide character due to each P atom being four-coordinate.[10f,j] We conclude that dmpe behaves as a neutral donor in **3** by virtue of stabilising P^{III}–Li bonds. This may be attributed to the polarisation of the lithium as a result of delocalisation of electron density away from N1 in accordance with resonance structures **I**, although packing forces may also contribute to the formation of these inherently weak bonds. Differences in P^{III}–Li bond lengths have previously been ascribed to the crystalline environment, as for a lithium complex derived from the ligand **ii**.[10e]

The paucity of information on dative P ··· Li bonding, as in **3**, has previously been attributed to the weakness of such interactions.[10k] Some relevant observations are: (i) experimental enthalpies for solvation of alkyllithium compounds by sulfides and phosphines are low compared with those by ethers or amines,[14] (ii) the increased polarisability of a P compared to a N atom renders a stabilisation of Li by P insignificant[15] and, (iii) *ab initio* calculations on 2-aminophenyllithium and 2-phosphinophenyllithium indicate that P–Li bonding interaction is negligible for the monomeric compounds, whereas, intramolecular P ··· Li interaction in dimeric organolithium compounds has a significant stabilising influence.[10k] The structure of **3** now demonstrates that P ··· Li dative bonds can have a stabilising influence on lithium species in the solid state, in cases where a neutral O- or N-centred donor or an intramolecular anionic centre is not available.

NMR-spectroscopy and solution behaviour

While the large difference in the ^{13}C-NMR spectral chemical shift values (δ) of the two ring carbons of **F** (CR: 48.6; CN$_2$: 168.4), **2a** (CR: 51.5; CN$_2$: 168.4), **3** (CR: not resolved; CN$_2$: 167.0) and **2b**(CR: 81.5; CN$_2$: 157.2) suggests that the solid state structures were retained in C_6D_6 solution at ambient temperature, it was evident from multinuclear NMR spectral studies that **3** speciated in solution. At 333 K, the ^{31}P{^{1}H}NMR spectrum of a C_7D_8 solution of **3**, consisted of a broad signal at δ −48.3 ($\Delta w_{1/2}$ = 1000 Hz) which shifted to slightly lower frequency to δ −49.2 at 248 K, while narrowing considerably ($\Delta w_{1/2}$ = 115 Hz). As the temperature was lowered further, the signal shifted further to δ −48.3, and was accompanied by the appearance of another peak at 198 K (δ −53.2, $\Delta w_{1/2}$ = 350 Hz). At 183 K both peaks had narrowed ($\Delta w_{1/2}$ = 45 and 280 Hz, respectively), and a further shift had occurred for the former to δ −47.9. The relative ratios of these peaks (8 : 1) varied only marginally in the temperature range 198 to 183 K. This temperature-dependent chemical shift and linewidth behaviour for the higher frequency resonance is consistent with chemical exchange behaviour and the interaction of phosphorus with a quadrupolar nucleus, in this case lithium-7. For an $I = 1/2$ nucleus coupled to a quadrupolar nucleus such as ^{7}Li, lineshapes have been found to be dependent on the inverse lifetime ($1/\tau$) of the quadrupolar nucleus.[16] Consequently, for the condition of rapid quadrupolar relaxation (low T, $J \ll 1/\tau$), consistent with increased solvent viscosity, the ^{31}P signal of **3** sharpened as the spin system became effectively decoupled because the transitions of the ^{31}P nucleus were no longer associated with any particular spin state of the quadrupolar nucleus. The observed line broadening at higher temperatures is attributed to slower quadrupolar relaxation. The fact that $^1J(^{31}P–^{6/7}Li)$ was not resolved indicates either that the exchange contribution to the linewidth was dominant or that an unsymmetrical field gradient was present. Efficient quadrupolar relaxation, arising from non-zero electric field gradients caused by distortions from symmetry can yield linewidths which are too broad to resolve.

The coincidence of the chemical shift of **3** with that of free dmpe (δ −49.4),[17] is consistent with the marginal coordination shifts arising from the formation of P^{III}–Li bonds {*cf.* (δ = −14.3 for CH$_2$(SiMe$_3$)C$_6$H$_4$PPh$_2$-*o* *vs.* δ = −14.7 for [Li{CH(SiMe$_3$)C$_6$H$_4$PPh$_2$-*o*}(tmen)] (**vii**, Fig. 4)}.[10j] The assignment of the minor peak at δ −53.2 is uncertain, in part because of the small temperature range over which it was observed (198–183 K). The following observations are, however, noteworthy: (*i*) there was no simple coalescence pattern, as the peak arose directly from the baseline, (*ii*) the value of this chemical shift was unchanged in this temperature range and, (*iii*) the linewidth narrowed significantly upon cooling from 198 to 183 K, while temperatures above 198 K rendered this peak undetectable. These observations are consistent with there being an equilibrium involving the formation of a stable low temperature species. An alternative interpretation is that the dissolution of **3** in C_7D_8 may be accompanied by dissociation into multiple species with the resonance at δ −53.2 appearing only at lower temperatures (faster quadrupolar relaxation of lithium). Previously, it had been shown that δ[^{31}P{^{1}H}] arising from the stable copper–phosphine complex ($I = 3/2$ for ^{65}Cu) [Cu(dppe)$_2$]$^+$ broadened beyond detection as a result of the slower quadrupolar relaxation of ^{65}Cu upon increasing the temperature.[18]

The ^{7}Li and ^{1}H NMR spectra of **3** in C_7D_8 were also consistent with temperature-dependent equilibria and rapid exchange processes at higher temperatures. At 333 K, the ^{7}Li spectra of **3** consisted of two broad partially overlapped multiplets centred at δ 1.1 and δ −1.5 in a ratio of *ca.* 2 : 1, with linewidths of *ca.* 330 Hz. As the temperature was lowered, these multiplets shifted to higher frequency and broadened, while the relative ratio of the multiplets became approximately equal. Consequently, at 183 K the spectrum consisted of overlapping multiplets centred at δ 1.4 and δ −1.2 in a ratio of *ca.* 1 : 1. At temperatures below 248 K, the former multiplet was partially resolved into three broad peaks. The slow exchange limit was not achieved. At 248 K the ^{1}H-NMR spectra consisted of numerous resonances for the trimethylsilyl groups arising from multiple species in slow exchange. Consistent with the low temperature equilibrium observed in the ^{31}P-NMR spectral regime, was the appearance of additional peaks in the aromatic region in the temperature range 198–183 K. The dmpe ligand gave rise to signals in intermediate exchange at low temperatures with two different environments being observed for the methyl substituents and a broad signal for the CH$_2$ protons. For bidentate phosphines with (CH$_2$)$_2$ backbones the CH$_2$ protons constitute the AA′ part of an $A_2XX'A'_2$ spin system as a result of unequal ^{1}H–^{31}P spin–spin coupling to the two P atoms and give rise to a quasi-triplet in which the separation of the outer two peaks corresponds approximately to [$^2J(^1H–^{31}P)$ + $^3J(^1H–^{31}P)$].[19] While this pattern has been observed for the dmpe ligand,

$J(^1H–^{31}P)$ coupling was not observed in **3** and this may account for the width of the signal at δ 2.32. Similarly, while the methyl carbons exhibit $^{13}C–^{31}P$ spin–spin coupling in the $^{13}C\{^1H\}$ NMR spectra of the free dmpe, they were expected to appear as quasi-triplets for **3** as a result of second order $^{13}C–^{31}P(CH_2)_2–^{31}P$ spin systems; but in practice only a broad singlet was observed. This may have been due to the rapid relaxation of the ^{31}P nucleus (by ^7Li) and hence the ^{13}C spin transitions were not associated with any particular spin state of the ^{31}P nucleus and thus the ^{13}C signal was effectively decoupled. A similar broad singlet was observed for the CH_2 carbon atoms. Calculations for the spectral appearance of the A part of an AXX′ system (A = ^{13}C, X, X′ = ^{31}P) for different values of J(XX′) revealed that a *quasi* triplet is to be observed in the ^{13}C spectrum of bisphosphine complexes in all cases where $|J_{(AX)}–J_{(AX')}|^2 < 8J_{(XX')}\Delta w_{1/2}$.[20]

Experimental

All manipulations were carried out under argon, using standard Schlenk techniques. Solvents were distilled from drying agents and degassed. The NMR spectra were recorded in C_6D_6 at ambient probe temperature or in $C_6D_5CD_3$ at various temperatures using Bruker DRX 400 (^{1}H, 400.32; ^{31}P, 161.98; ^{7}Li, 155.51 MHz), DPX 300 (^{1}H, 300.1; ^{7}Li 116.6; ^{13}C 75.5 MHz) or Bruker AC200 (^{1}H, 200.13; ^{13}C, 50.32); ^{1}H and ^{13}C-NMR spectra were referenced internally to residual solvent resonances (data in δ). The ^{7}Li, ^{31}P and ^{29}Si spectra were referenced externally to LiCl, H_3PO_4 or $SiMe_4$, respectively. Unless otherwise stated, all NMR spectra other than ^{1}H were proton-decoupled. Electron impact mass spectra were from solid samples using a Kratos MS 80 RF instrument. Melting points were taken in sealed capillaries and are uncorrected. Elemental analyses were determined by Medac Ltd., Brunel University, Uxbridge, UK or Institute for Soil, Climate and Water, Pretoria, SA. The following abbreviations are used throughout the experimental section: vd = virtual doublet, vt = virtual triplet, bs = broad singlet, m = multiplet.

Preparations

HN(Ar)$\overline{\text{CC(R)Si(R)}_2\text{N}}$Ar 2b. A solution of freshly cracked cyclopentadiene monomer (0.05 cm^3, 0.63 mmol) was slowly added to a solution of **F** (0.4 g, 0.63 mmol) in pentane (20 cm^3) at −60 °C. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. The solvent was removed *in vacuo* and the residue extracted with pentane (30 cm^3). Filtration of the extract and concentration of the filtrate gave upon cooling to −25 °C colourless crystals of **2b** (0.32 g, 68%) (Found: C, 62.5; H, 9.03; N, 5.20. $C_{27}H_{46}N_2Si_4$ requires C, 63.4; H, 9.07; N, 5.48%), mp 190 °C (decomp.). Mass spectrum [*m*/*z* (%)]: 511 (12 $[M]^+$), 510 (25 $[M - H]^+$), 496 (12 $[M - Me]^+$), 495 (25 $[M - H - Me]^+$), 437 (100 $[M - SiMe_3]^+$); ^{1}H NMR (C_6D_6): δ −0.08 (s, 9 H, CSiMe$_3$), 0.29 (s, 18 H, SiSiMe$_3$), 2.38 and 2.39 (s, 12 H, Me), 4.41 (s, 1 H, NH), 6.84–7.00 (s, 6 H, Ph); ^{29}Si-NMR (C_6D_6): δ −18.5 (s, *Si*R$_2$), −17.7 (s, Si*Si*Me$_3$), 19.2 (s, C*Si*Me$_3$); ^{13}C NMR (C_6D_6): δ 0.0 (s, SiSi*Me*$_3$), 2.5 (s, CSi*Me*$_3$), 19.1 and 19.9 (s, Me), 81.5 (s, CR), 125.9, 127.3, 128.3, 128.7 (s, *m*- & *p*-Ph), 136.6 [s, *ipso*-C(Me)], 137.9 (s, *ipso*-C), 139.4 [s, *ipso*-C(Me)], 157.2 (s, CN); IR (in Nujol): ν(N–H) 3356 (m).

[Li{N(Ar)$\overline{\text{CC(R)Si(R)}_2\text{N}}$Ar}(dmpe)]$_2$ 3. The ligand dmpe (0.24 g, 1.60 mmol) was added *via* syringe to a solution of [Li(SiR$_3$)(thf)$_3$] (0.75 g, 1.60 mmol) in hexane (35 cm^3) at room temperature. The reaction mixture was stirred for 10 min and then cooled to −80 °C, prior to the addition of 2,6-$Me_2C_6H_3NC$ (0.42 g, 3.20 mmol). This temperature was maintained for 1 h, followed by gradual warming of the reaction mixture to room temperature, with stirring, over 16 h. Removal of volatiles *in vacuo* and extraction of the residue with hexane (35 cm^3), filtration of the extract and concentration of the filtrate gave, upon cooling, colourless crystals of **3** (1.09 g, 51%) (Found: C, 59.3; H, 8.87; N, 4.63. $C_{66}H_{122}Li_2N_4P_4Si_8$ requires C, 59.4; H, 9.22; N, 4.20%), mp 74–82 °C (decomp.). ^{1}H NMR ($C_6D_5CD_3$) 300 K: δ 0.16 (s), 0.13 (s), 0.14 (s), 0.20 (s), 0.24 (s), 0.29 (s), 0.39 (s, CSiMe$_3$, SiSiMe$_3$), 0.75, 1.18 (bs, P–Me), 2.34 (s, P–CH$_2$–), 2.35, 2.36 (s, Me(LiNAr)), 2.43 (s, Me(NAr)), 6.77 (vt, J = 7.4), 6.78 (s), 6.80 (m), 6.87 (s), 6.88 (s), 6.89 (s), 6.90 (s), 6.92 (s), 6.97 (vt, J = 1.0), 7.01 (m), 7.09 (m) (Ph); ^{13}C NMR (C_6D_6): δ 0.2, 0.5 (s, SiSi*Me*$_3$), 1.7, 3.7 (s, CSi*Me*$_3$), 12.6 (bs, P–Me), 27.2 (bs), 20.0, 20.5, 20.6, 20.8 (s, Me), not resolved (s, *C*SiMe$_3$), 121.1, 122.0, 124.3, 126.0, (s, *m*-Ph), 130.7, 133.7, 135.1, 139.1 (s, *ipso*-C), 167.0 (s, CN$_2$); ^{31}P NMR ($C_6D_5CD_3$) 183 K: δ −47.96 (bs), −53.24 (bs); ^{7}Li NMR ($C_6D_5CD_3$) 183 K: δ 1.4 (m), −1.2 (m).

[Li{N(Ar)$\overline{\text{CC(R)Si(R)}_2\text{N}}$Ar}(thf)$_2$] 4. The ligand dmpe (0.45 g, 3.02 mmol) was added *via* syringe to a solution of [Li(SiR$_3$)(thf)$_3$] (1.42 g, 3.02 mmol) in hexane (70 cm^3) at room temperature. The reaction mixture was stirred for 10 min and then cooled to −80 °C, prior to the addition of 2,6-$Me_2C_6H_3NC$ (0.79 g, 6.04 mmol). This temperature was maintained for 1 h, followed by gradual warming of the reaction mixture to room temperature, with stirring, over 16 h. Keeping the mixture at −20 °C overnight produced a small amount of precipitate, which was separated by filtration. Cooling the filtrate to −20 °C over a *ca.* 24 h period gave yellow crystals of **4** (0.38 g). The liquor was decanted and concentrated slightly, thereby affording another crop of **4** (overall yield: 1.46 g, 73%). ^{1}H NMR (C_6D_6): δ 0.26 (s, 9 H, CSiMe$_3$), 0.56 (s, 18 H, SiSiMe$_3$), 1.17 (m, 8 H, CH$_2$), 2.62, 2.69 (s, 12 H, Me), 3.00 (m, 8 H, OCH$_2$), 6.80 (vt, 1 H, J = 6.6, Ph), 6.96 (vd, 2H, J = 7.5, Ph) (both N–Ar rings), 7.04 (vt, 1 H, J = 6.78, Ph), 7.25 (vd, J = 6.3, 2 H, Ph) (both LiNAr units); ^{13}C NMR (C_6D_6): δ 0.6 (s, SiSi*Me*$_3$), 3.8 (s, CSi*Me*$_3$), 20.3 and 20.6 (s, Me), 51.5 (s, *C*SiMe$_3$), 25.2 (s, CH$_2$), 68.0 (s, OCH$_2$), 124.0, 126.0 (s, *m*-Ph), 133.8, 138.6, 144.0, 151.0 (s, *ipso*-C), 168.4 (s, CN$_2$).

Crystal data and refinement details

All crystals were enclosed in paraffin oil and frozen in a stream of cold nitrogen gas at −100 °C.

Data for **2b** were collected on an Enraf-Nonius CAD4 diffractometer using monochromatic Mo-Kα radiation (λ 0.71073 Å). Cell dimensions were calculated from the setting angles for 25 reflections with $7 < \theta < 10°$. Intensities were measured by an $\omega/2\theta$ scan. There was no crystal decay as measured by two standard reflections. Positions of non-hydrogen atoms were derived by direct methods using *SHELXS-86*[21] and refined on F^2 with anisotropic thermal parameters for non-hydrogen atoms and H atoms in riding mode, by full-matrix least-squares using *SHELXL-93*.[22]

Intensity data for **F** and **3** were collected on a Bruker SMART 1K CCD area detector diffractometer with graphite monochromated Mo Kα radiation. The collection method involved ω-scans of width 0.3°. Data reduction was carried out using the program *SAINT+*[23] and absorption corrections were made using the program *SADABS*.[24] The crystal structures were solved by direct methods using *SHELXTL*.[25] Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculation based on F^2 using *SHELXTL*. Hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms. Diagrams and publication material were generated using *SHELXTL* and *ORTEP3*.[26] Further details are summarised in Table 2.

CCDC reference numbers 181494–181496.

See http://www.rsc.org/suppdata/dt/b2/b202629p/ for crystallographic data in CIF or other electronic format.

Table 2 Crystal data and refinement for complexes **F**, **3** and **2b**

Compound	**F**	**2b**	**3**
Formula	$C_{33}H_{61}LiN_4Si_4$	$C_{27}H_{46}N_2Si_4$	$C_{66}H_{122}Li_2N_4P_4Si_8$
M	633.16	511.02	1334.16
T/K	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a/Å	17.600(3)	9.179(2)	10.1824(16)
b/Å	18.995(4)	20.683(7)	12.756(2)
c/Å	24.897(4)	16.784(7)	18.168(3)
α/°	—	—	100.496(3)
β/°	105.285(4)	98.05(3)	100.679(3)
γ/°	—	—	111.366(3)
V/Å	8029(3)	3148(2)	2077.5(6)
Z	8	4	1
Density calculated/Mg m^{-3}	1.048	1.078	1.066
μ(Mo-Kα)	0.173	0.206	0.243
F(000)	2768	1112	724
Theta range	1.2 to 28.3	2 to 28	1.2 to 28.3
Index ranges	$-23 \leqslant h \leqslant 22$	$0 \leqslant h \leqslant 12$	$-13 \leqslant h \leqslant 12$
	$-25 \leqslant k \leqslant 24$	$0 \leqslant k \leqslant 27$	$-14 \leqslant k \leqslant 16$
	$-33 \leqslant l \leqslant 21$	$-22 \leqslant l \leqslant 21$	$-23 \leqslant l \leqslant 24$
Reflections collected	55808	8019	14560
Independent reflections	19843	7577	10016
Data/restraints/parameters	19843/0/791	7577/0/315	10016/0/396
Goodness-of-fit	1.052	1.023	1.018
$R1[I > 2\sigma(I)]$	0.045	0.055	0.044
$wR2$ (all data)	0.135	0.140	0.132
Largest diff. peak, hole/eÅ^{-3}	0.60 and −0.34	0.40 and −0.43	0.37 and −0.31

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