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# Synthesis and structures of lithium *N*-trimethylsilyl- and -neopentyl-anilides and their $Et_2O$ and tmen adducts; crystal structures of $[(Li\{\mu\text{-}N(Ph)R\}\text{-}\mathit{trans})_2(\mu\text{-tmen})]_\infty$ ($R = SiMe_3$ 1 or $CH_2Bu^t$ 2) and $[Li\{\mu\text{-}N(Ph)CH_2Bu^t\}(OEt_2)]_2$ †

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Treatment of *N*-trimethylsilyl- or -neopentyl-aniline successively with n-butyllithium and tmen in hexane yielded the crystalline polymeric lithium amides $[(Li\{\mu\text{-}N(Ph)R\}\text{-}\mathit{trans})_2(\mu\text{-tmen})]_\infty$ ($R = SiMe_3$ **1** or $CH_2Bu^t$ **2**), which contain the rare bridging, rather than chelating, tmen ligands. Details are also provided of: (i) the preparation of crystalline $[Li\{N(Ph)SiMe_3\}]_4$, hydrocarbon-insoluble $[Li\{N(Ph)CH_2Bu^t\}]_n$, and diethyl ether adducts $[Li\{\mu\text{-}N(Ph)R\text{-}\mathit{trans}\}(OEt_2)]_2$ ($R = SiMe_3$ or $CH_2Bu^t$); (ii) variable temperature multinuclear NMR spectra in toluene-$d_8$ and (iii) three crystal structures.

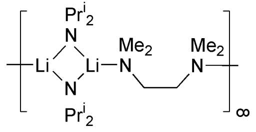
## Introduction

Bulky amides of lithium are important reagents, both in coordination and organic chemistry. As for the former, they are valuable ligand transfer reagents, often giving rise to unusual low coordination number metal amides.[1] Regarding the latter, they are powerful proton abstractors, particularly from acidic hydrocarbons, and are useful in the formation of carbon–carbon bonds;[2] homochiral lithium amides even have a useful role in asymmetric synthesis.[3] The reactivity of lithium amides is related to their degree of aggregation, since the high polarity of the Li–N bond causes them to associate in the absence of a neutral donor.[4] In the presence of *O*- or *N*-centred neutral ligands, dimeric, or more rarely monomeric, molecular complexes usually predominate, at any rate in the crystalline state.[4] Monomers or dimers are generally the most reactive.

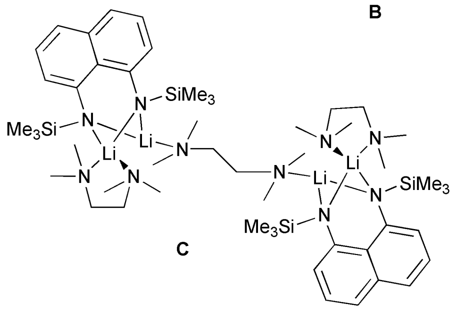
A much favoured neutral ligand is $Me_2NCH_2CH_2NMe_2$ (tmen), which generally functions as a *chelating* bidentate ligand, as in the crystalline $[Li\{\mu\text{-}N(Ph)Me\}(tmen)]_2$,[5] $[Li\{\mu\text{-}N(Ph)C_{10}H_7\text{-}1\}(tmen)]_2$ [a loosely held dimer, by virtue of $(Li\cdots\eta^2\text{-}Ph)_2$ contacts],[5] $[Li\{N(SiMe_3)_2\}(tmen)]_2$,[6] and $[Li\{N(H)C_6H_2Bu^t_3\text{-}2,4,6\}(tmen)]_2$.[7] Whereas the literature is replete with numerous tmen-chelating LiX complexes, those having bidentate bridging tmen ligands are rare.[4] As far as we are aware, there are to date just four such crystalline lithium amides **A**,[8] **B**,[9] **C**[10] and **D**.[11] Other examples of tmen as a bridging ligand in crystalline $(LiX)_n(tmen)_m$ compounds include (i) $[(LiBu^n)(\mu\text{-tmen})]_\infty$, in which only two of the four lithium atoms in each tetranuclear unit are implicated with the tmen ligand;[12] (ii) $[\{Li(OC_6H_4OMe)\}_8(\mu\text{-tmen})]$, having two tetranuclear clusters joined by the tmen bridge;[13] (iii) $[\{Li(tmen)\}_3(\mu\text{-}Cl)_4Li]_2(\mu\text{-tmen})$[14] and (iv) $\{Li(SiMe_3)\}_2(\mu\text{-tmen})$.[15] The case of $LiNPr^i_2$ (LDA) is particularly well studied. The crystalline complex **B** was obtained by crystallising LDA from a tmen–$C_6H_{14}$ mixture.[9] However, when the hexane poorly soluble LDA was treated with tmen (2 mol) the crystalline product had the composition $Li(NPr^i_2)\{N(H)Pr^i_2\}_{1/10}(tmen)_{1/40}$ but X-ray diffraction revealed it to be the helical tmen-free $[Li(\mu\text{-}NPr^i_2)]_\infty$.[16] A toluene-$d_8$ solution of **B** showed ($^{13}C$ NMR spectra) that tmen had been totally dissociated yielding $[Li(\mu\text{-}NPr^i_2)]_2$; and addition of thf or excess of tmen led to $[Li(\mu\text{-}NPr^i_2)(thf)_2]_2$ and $[Li(\mu\text{-}NPr^i_2)(tmen)]_2$ respectively.[9]

$[Ar(Me_3Si)NSi(SiMe_3)_2C{\equiv}CN(Ar)Li(tmen)]_2(\mu\text{-tmen})$

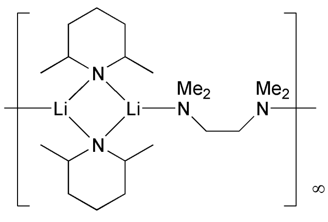
**A** ($Ar = C_6H_3Me_2\text{-}2,6$)



**B**



**C**



**D**

We now present data on the synthesis and structures of the crystalline complexes $[\{Li[N(Ph)R]\}_2(\mu\text{-tmen})]_\infty$ ($R = SiMe_3$ **1** or $CH_2Bu^t$ **2**). Additionally, we provide details on the synthesis and NMR solution spectra of the corresponding tmen-free lithium amides and their diethyl ether adducts, as well as the molecular structure of the crystalline complex $[Li\{\mu\text{-}N(Ph)CH_2Bu^t\}(OEt_2)]_2$.

## Results and discussion

The chosen precursors to the target compounds **1** and **2** were

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† In memoriam Ron Snaith, a valued friend and scientist.

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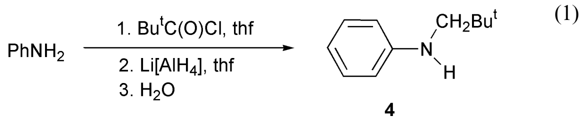
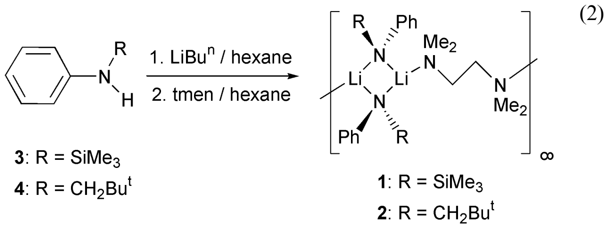
the secondary amines HN(Ph)R (R = $SiMe_3$ **3** or $CH_2Bu^t$ **4**). The amine **3** was prepared from aniline and successively $LiBu^n$ and $ClSiMe_3$, as described by Schumann *et al.*[17] Compound **4** was likewise obtained from aniline, as shown in eqn. (1). It had



(1)

previously been isolated either by $Na[BH_4]$ reduction of $Bu^tCH{=}NPh$,[18a] or by treatment of $HN(Ph)CH_2SPh$ successively with $LiBu^t$ and water.[18b] The crystalline, tmen-bridged binuclear lithium amide polymers **1** and **2** were obtained as shown in eqn. (2).



(2)

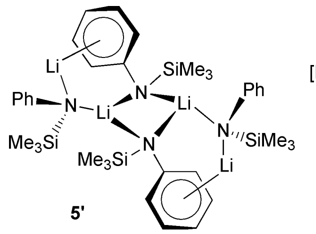
**3**: R = $SiMe_3$
**4**: R = $CH_2Bu^t$

**1**: R = $SiMe_3$
**2**: R = $CH_2Bu^t$

The crystalline, neutral, ligand-free $[Li\{N(Ph)SiMe_3\}]_4$ **5** had previously been made from the amine **3** and $LiBu^n$ in pentane.[16] The molecular structure, determined by single crystal X-ray diffraction, revealed its unusual tetranuclear arrangement, shown schematically in **5′**.[19] The ether-free amide $[Li\{N(Ph)CH_2Bu^t\}]_n$ **6** was insoluble even in hot toluene or xylene and is presumed to be a polymer. Treatment of **5** with diethyl ether afforded crystals of $[Li\{\mu\text{-}N(Ph)SiMe_3\}(OEt_2)]_2$ **7**[19] (see also ref. 20). The crystalline neopentyl analogue **8** has now been prepared by a procedure similar to that of eqn. (2) except that diethyl ether was used in place of tmen–$C_6H_{14}$, and, like **1** and **2**, has been crystallographically characterised, see below.

Li{N(Ph)R}

**5**: R = $SiMe_3$
**6**: R = $CH_2Bu^t$



**5'**

$[Li\{\mu\text{-}N(Ph)R\}(OEt_2)]_2$

**7**: R = $SiMe_3$
**8**: R = $CH_2Bu^t$

Suitable single crystals of compounds **1** and **2** were obtained from hot hexane (**1**) or a toluene–hexane (**2**) mixture. Their structures are broadly similar, each comprising an infinite chain along the *a* axis direction, linked *via* inversion centres which are the centroids of the bridging tmen ligands and the centres of the $Li_2N_2$ rings. A dinuclear unit of each is shown in Figs. 1 (**1**) and 2 (**2**) and some comparative geometric data are assembled in Table 1. The central N(1)LiN(1′)Li′ ring is essentially planar. The endocyclic angles are wider at the lithium (**1** ⩾ **2**) than at the nitrogen (**2** ⩾ **1**) atoms. The two Li–N bond lengths in each unit are unequal and the mean values are slightly longer in **1** (2.059 Å) than in **2** (2.038 Å), whereas the exocyclic Li–N bonds are longer in **2** [2.121(4) Å] than in **1** [2.065(10) Å]. There is a *trans* arrangement of the substituents at the endocyclic nitrogen atoms and the N–C(Ph-*ipso*) bonds are significantly longer in **1** [1.422(6) Å] than in **2** [1.386(3) Å]. The aromatic C–C bond lengths are very slightly shorter (by an av. 0.01 Å) in **1** than in **2**. The (*ipso*-Ph)C–N–Li (or Li′) bond angles are rather similar and close to tetrahedral in **2** [109.2 ± 2.7°], whereas in **1** they differ widely [103.6 ± 13.5°]. The lithium atoms are in a distorted trigonal and nearly planar environment, the sum of the angles at the Li atoms being 356.6° in **1** and 358.2 in **2**.

**Table 1** Selected bond lengths (Å) and angles (°) for compounds **1** and **2**

| | **1** | **2** |
|---|---|---|
| Li···Li′ | 2.391(10) | 2.471(4) |
| Li–N(1) | 2.030(10) | 1.999(4) |
| Li–N(1′) | 2.088(10) | 2.077(4) |
| Li–N(2) | 2.065(10) | 2.121(4) |
| N(1)–C(1) | 1.422(6) | 1.386(3) |
| N(1)–C(7) | — | 1.471(3) |
| N(1)–Li–N(1′) | 109.0(4) | 105.38(17) |
| Li–N(1)–Li′ | 71.0(4) | 74.62(17) |
| N(1)–Li–N(2) | 125.2(5) | 128.5(2) |
| N(2)–Li–N(1′) | 122.4(5) | 124.29(19) |
| C(1)–N(1)–Li | 117.1(4) | 107.56(17) |
| C(1)–N(1)–Li′ | 90.1(4) | 112.93(18) |

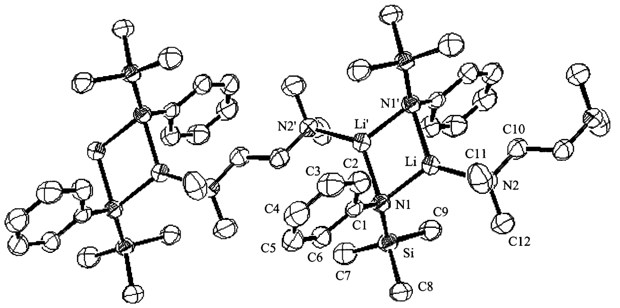


**Fig. 1** Molecular structure and atom labelling for compound **1**.

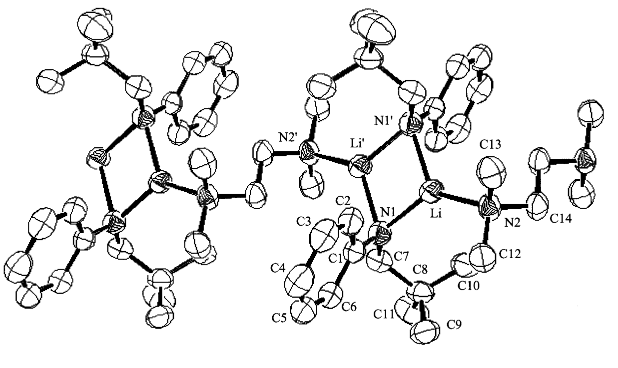


**Fig. 2** Molecular structure and atom labelling for compound **2**.

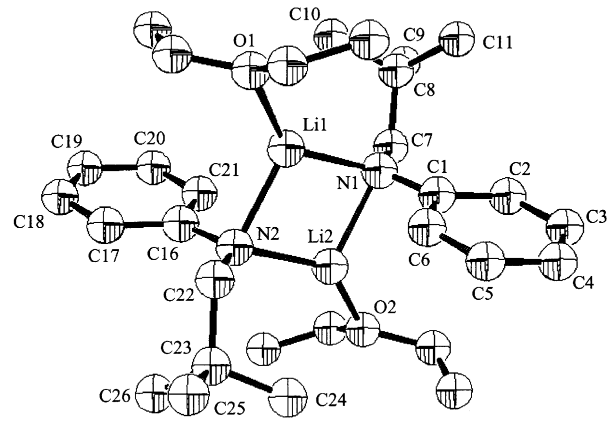


**Fig. 3** Molecular structure and atom labelling for compound **8**.

The structure of the crystalline dinuclear complex *trans*-$[Li\{\mu\text{-}N(Ph)CH_2Bu^t\}(OEt_2)]_2$ **8** is illustrated in Fig. 3. Selected geometric data are in Table 2. There are no surprises, as may be judged by comparing some core data for **8** with those for $[Li\{\mu\text{-}N(SiMe_3)_2\}(OEt_2)]_2$[21] and $[Li(\mu\text{-}NPh_2)(OEt_2)]_2$,[22]

**Table 2** Selected geometric parameters (lengths in Å, angles in °) for compound **8**, [Li{μ-N(SiMe$_3$)$_2$}(OEt$_2$)]$_2$ and [Li{μ-N(Ph)$_2$}(OEt$_2$)]$_2$

| | [Li{μ-N(Ph)CH$_2$Bu$^t$}(OEt$_2$)]$_2$ **8** | [Li{μ-N(SiMe$_3$)$_2$}(OEt$_2$)]$_2$[21] | [Li{μ-N(Ph)$_2$}(OEt$_2$)]$_2$[22] |
|---|---|---|---|
| Li···Li′ | 2.505 | 2.492 | 2.501 |
| Li–N | 2.038[a] | 2.055(5) | 2.02[a] |
| Li–O | 1.965[a] | 1.943(6) | 1.882[a] |
| N–C(Ph) | 1.373[a] | — | 1.406[a] |
| N–C(Np) | 1.462[a] | — | — |
| N–Li–N′ | 104.2[a] | 104.9(3) | 103.45[a] |
| Li–N–Li′ | 75.8[a] | 75.1(2) | 76.31[a] |
| O–Li–N | 116.3, 135.5 | 127.5(1) | 129.13, 128.42 and 120.37, 134.47 |

Np = Neopentyl. [a] Mean value.

**Table 3** Variable temperature selected $^1$H NMR spectroscopic chemical shifts (δ) at 300.1 MHz for compounds **1**, **2** and tmen in toluene-d$_8$

| | δ (tmen) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | NCH$_3$ | | | CH$_2$N | | | δ (R)[a] | |
| *T*/K | **1** | **2** | [b] | **1** | **2** | [b] | Si(CH$_3$)$_3$ (**1**) | C(CH$_3$)$_3$ (**2**) |
| 193 | 1.81, 1.77 | — | 2.04 | 1.52, 1.36 | — | 2.28 | 0.53, 0.38 | — |
| 223 | — | 1.66 | 2.05 | — | 1.66 | 2.28 | — | 0.78, 1.21 |
| 253 | 1.64 | 1.73 | 2.07 | 1.49 | 1.66 | 2.30 | 0.39 | 0.78, 1.17 |
| 293 | 1.66 | 1.77 | 2.09 | 1.53 | 1.73 | 2.30 | 0.30 | 0.78, 1.09 |
| 323 | 1.71, 1.68 | — | — | 1.63, 1.59 | — | — | 0.25 | — |
| 373 | 1.80 | 1.91 | — | 1.77 | 1.95 | — | 0.19 | 0.85 |

[a] Refers to [Li{μ-N(Ph)R}]$_2$(μ-tmen)] (R = SiMe$_3$ or CH$_2$Bu$^t$). [b] Values for tmen.

indicated in Table 2. Several other examples of related crystalline dimeric lithium amide diethyl etherates are known.[23]

While the NMR spectra of the diethyl ether complexes [Li{μ-N(Ph)R}(OEt$_2$)$_2$] (R = SiMe$_3$ **7** or CH$_2$Bu$^t$ **8**) in C$_6$D$_5$CD$_3$ or C$_6$D$_6$ at ambient temperature are unexceptional (for assignments, see Experimental section), those of the crystalline amides [Li{μ-N(Ph)R}]$_2$(μ-tmen) (R = SiMe$_3$ **1** or CH$_2$Bu$^t$ **2**) and [Li{N(Ph)SiMe$_3$}]$_4$ **5** require further comment. It had previously been noted briefly that the $^7$Li NMR spectrum of **5** in toluene-d$_8$ at 163 K was consistent with the tetranuclear structure **5′** of the crystalline **5** being preserved, whereas at higher temperatures fluxional processes became operative;[19] these data and conclusions are now presented in greater detail.

The bonding in crystalline compound **5** (*cf.* **5′**) may be described as comprising a central LiNLiN core with each of these Li atoms acting as a Lewis acid site for binding by a terminal lithium amide, as indicated by the Li–N bond lengths in **5″**.

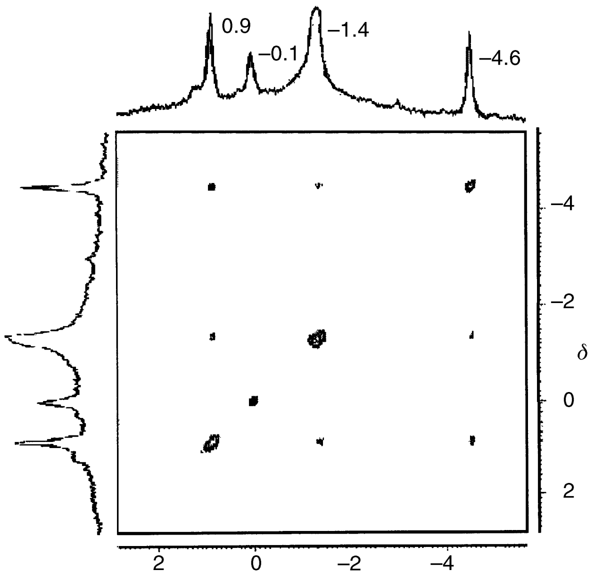
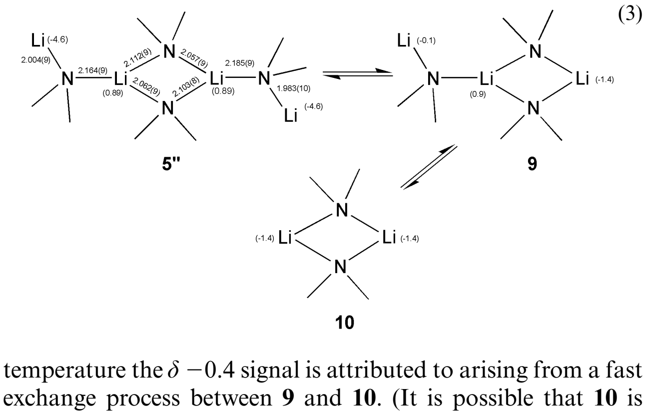


**Fig. 4** 2-D $^7$Li EXSY spectrum of compound **5** at 183 K.



**5″** **9** **10** (3)

The case of the neutral donor-free lithium amide **5** is first considered. Unlike its neopentyl analogue [Li{N(Ph)CH$_2$Bu$^t$}]$_n$ **6**, it was soluble in aromatic hydrocarbons. The $^7$Li-{H} NMR spectroscopic data are particularly informative. At 163 K two signals of equal intensity at δ 0.9 and −4.6 were observed. The relatively low frequency of the latter is consistent with it being assigned to the terminal lithium nuclei of structure **5′** experiencing the ring current of the adjacent phenyl rings. The δ 0.89 signal is attributed to the core lithium atoms (these assignments are shown in parentheses in **5″**). At 183 K the spectrum showed four signals at δ 0.9, −0.1, −1.4 and −4.6. The 2-D $^7$Li EXSY spectrum at this temperature (Fig. 4) demonstrates that the signals at δ 0.9 and −4.6 exchanged more rapidly with one another than either did with the intense signal at δ −1.4; hence an intramolecular exchange of the ligands is the fastest. At 298 K there was just one signal at δ −0.4, which presumably is the time-averaged value. These data are interpreted in terms of the equilibrium (3), involving not only **5′** but also **9** and **10**. The latter two are suggested to arise by successive thermal dissociation of each of the terminal lithium amides from **5′** (the $^7$Li assignments are shown in parentheses for each of **9** and **10**), each monomer rapidly dimerising to afford **10**. At ambient temperature the δ −0.4 signal is attributed to arising from a fast exchange process between **9** and **10**. (It is possible that **10** is a cyclooligomer rather than the cyclodimer shown.) The $^1$H

NMR spectrum of **5** at 183 K in toluene-$d_8$ is consistent with the data of eqn. (3), but at 298 K the spectrum simplified into only one set of signals (see Experimental section). It is possible that if the $^7$Li NMR spectra were to be recorded at higher dilution the intensities of the signals attributed to **9** and **10** might increase.

The $^1$H NMR spectra of each of compounds **1** and **2** in toluene-$d_8$ were shown to be temperature-dependent, as summarised in Table 3; for the tmen and $E(CH_3)_3$ (E = Si or C) chemical shifts comparative data for free tmen are also listed.

From $^7$Li-{H} NMR spectroscopic data and reference to those for compound **5** in eqn. (3), there is no evidence of dissociation of **1** into tmen and **5**. Thus, at 193 K, two $^7$Li signals were observed at $\delta$ 1.06 and −0.11 in a 2 : 1 relative intensity ratio, respectively. At 233 and 323 K these gave way to single signals at $\delta$ 0.85 and −0.97, respectively, indicative of the presence of fast exchange processes.

The absence of free tmen at various temperatures in solutions of compound **1** or **2** in toluene-$d_8$ is borne out by noting the relative values of the $^1$H chemical shifts for the $CH_2$ and the $CH_3$ protons, which invariably were found at higher frequency for the latter, whereas for free tmen this order is reversed (see Table 3). For example, for $[Li\{N(SiMe_3)_2\}(tmen)]$, the tmen protons are $\delta(CH_2)$ 1.63 and $\delta(CH_3)$ 1.81, with $\delta(^7Li)$ 0.41;[24a] while for [Li{N(Ph)Me}(tmen)], $\delta(CH_2)$ 1.72 and $\delta(CH_3)$ 1.80, with $\delta(^7Li)$ −1.60.[24b]

At 193 K the $^1$H NMR spectrum of compound **1** (see Table 3) showed (i) two $SiMe_3$ signals in relative intensity 2 : 1, (ii) broad and not fully resolved Ph signals and (iii) two sets (rel. intensity 1 : 1) of tmen signals. Upon warming this solution the tmen appeared as singlets and the $SiMe_3$ and Ph signals, although broad at 298 K, became sharp at 323 K.

Observations on the behaviour of crystalline $[Li\{N(Ph)CH_2Bu^t\}]_2(\mu\text{-tmen})$ **2** in toluene-$d_8$ solutions were rather different in detail. Thus, the $^7$Li NMR spectra revealed only single signals at both 223 ($\delta$ 1.02) and 373 K (0.90). The $^1$H NMR spectrum at 293 K of a dilute solution of **2** showed broad signals centred at $\delta$ 0.78 and 1.09 for the Bu$^t$ protons (which coalesced in a concentrated solution); this situation remained unchanged down to 223 K, but appeared as a sharp singlet at 373 K.

## Experimental

### General procedures

All manipulations were performed under argon using standard Schlenk techniques. Toluene and diethyl ether were dried using sodium. Pentane and hexane were dried using sodium–potassium alloy; thf was first dried over $CaH_2$ then sodium. tmen (Aldrich) was distilled from $CaH_2$ prior to use. The NMR spectra were recorded on a Bruker DPX 300 ($^1$H, $^{13}$C and $^7$Li) or AMX 500 ($^{29}$Si, 2-D $^7$Li EXSY as well as low temperature $^1$H and $^{13}$C) instruments and referenced externally ($^{29}$Si, using $SiMe_4$) or internally to the residual solvent resonances (chemical shift data in $\delta$). Unless otherwise stated, all NMR spectra were measured at 298 K in $C_6D_6$ and other than $^1$H were proton-decoupled. Electron impact mass spectra were taken from solid samples using a Kratos MS 80 RF instrument. Melting points were taken in sealed capillaries and are uncorrected. Elemental analyses (empirical formulae shown) were determined by Medac Ltd., Brunel University.

### Preparations

**HN(Ph)R (R = SiMe$_3$ 3 or CH$_2$Bu$^t$ 4).** The amine **3** was prepared from aniline, as described in the literature.[17] The known amine **4**[18] was obtained as follows. A solution of trimethylacetyl chloride (26.4 g, 219 mmol) in thf (100 cm$^3$) was added dropwise at room temperature to a solution of aniline (20.0 g, 215 mmol) and triethylamine (21.8 g, 216 mmol) in thf (400 cm$^3$). The resulting thick white suspension was stirred for *ca.* 3 h then filtered. The filtrate was concentrated *in vacuo*, and the residue crystallised from diethyl ether, to give colourless needles of *N*-pivaloylaniline (34.2 g, 90%) (Found: C, 74.6; H, 8.56; N, 7.91. $C_{11}H_{15}NO$ requires C, 74.5; H, 8.53; N, 7.90%), mp 129–130 °C. $^1$H NMR ($CDCl_3$): $\delta$ 7.58 (d, 2 H, $^3J_{HH}$ = 8.7, *m*-H), 7.53 (br s, 1 H, NH), 7.34 (t, 2 H, $^3J_{HH}$ = 8.7, *o*-H), 7.13 (t, 1 H, $^3J_{HH}$ = 7.5 Hz, *p*-H) and 1.35 (s, 9 H, $CH_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ 177.1 (CO), 138.4, 129.2, 120.5 and 119.4 (Ph), 39.3 ($CCH_3$) and 27.9 ($CH_3$). EI-MS (*m*/*z*, %): 177 {78, [*M*]$^+$} and 57 {100, [Bu$^t$]$^+$}.

A solution of *N*-pivaloylaniline (34.1 g, 192 mmol) in thf (200 cm$^3$) was added dropwise to a cooled (0 °C) suspension of $Li[AlH_4]$ (14.0 g, 368 mmol) in thf (300 cm$^3$). After 2 d at *ca.* 25 °C and 12 h at reflux the grey suspension was carefully hydrolysed at 0 °C by a mixture of water and thf. After filtration, concentration of the filtrate and distillation of the residue under reduced pressure, compound **4** was obtained as a colourless oil (27.9 g, 89%) (Found: C, 81.0; H, 10.65; N, 8.49. $C_{11}H_{17}N$ requires C, 80.9; H, 10.49; N, 8.58%), bp 85–87 °C/5 Torr. $^1$H NMR ($CDCl_3$): $\delta$ 6.75–7.34 (m, 5 H, Ph), 3.03 (s, 2 H, $NCH_2$), 3.75 (br s, 1 H, NH) and 1.14 (s, 9 H, $CH_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ 149.5, 129.7, 117.3 and 113.1 (Ph), 56.2 ($NCH_2$), 32.3 ($CCH_3$) and 28.1 ($CH_3$). EI-MS (*m*/*z*, %): 163 {60, [*M*]$^+$} and 106 {100, [*M* − Bu$^t$]$^+$}.

**[Li{N(Ph)SiMe$_3$}]$_4$ 5.** n-Butyllithium (12 cm$^3$ of a 1.6 mol dm$^{-3}$ solution in hexane, 19.2 mmol) was added dropwise during *ca.* 15 min to a cooled (0 °C) solution of trimethylsilylaminobenzene (3.00 g, 18.2 mmol) in hexane (50 cm$^3$). After *ca.* 30 min at 0 °C and then *ca.* 2 h at *ca.* 25 °C the mixture was filtered, the white precipitate washed with hexane and dried *in vacuo* yielding compound **5** (3.15 g, 98%) as a white powder. Crystallisation from hot toluene gave colourless crystals of **5** (2.20 g, 70%) (Found: C, 62.6; H, 8.05; N, 8.33. $C_9H_{14}LiNSi$ requires C, 63.1; H, 8.24; N, 8.18%), mp 175–177 °C. It was sparingly soluble in toluene at low temperature. $^1$H NMR: $\delta$ 7.13 (t, 2 H, $^3J_{HH}$ = 7, *m*-H), 6.70 (t, 1 H, $^3J_{HH}$ = 7, *p*-H), 6.56 (d, 2 H, $^3J_{HH}$ = 7 Hz, *o*-H) and 0.09 (s, 9 H, $SiMe_3$). $^{13}$C NMR: $\delta$ 116.4, 123.4, 130.2, 159.2 (*ipso*-C) and 2.2 ($SiMe_3$). $^{29}$Si NMR (benzene-$d_6$): $\delta$ −8.1. $^7$Li NMR: $\delta$ −0.4. EI-MS (*m*/*z*, %) 349 {25, $[(PhNSiMe_3)_2Li_3]^+$}, 342 {20, $[(PhNSiMe_3)_2Li_2]^+$}, 327 {10, $[(PhNSiMe_3)_2Li_2 - Me]^+$}, 178 {100, $[(PhNSiMe_3)Li_2]^+$}, 165 {45, $[PhNHSiMe_3]^+$} and 150 {95, $[PhNHSiMe_2]^+$}.

**[{Li[N(Ph)SiMe$_3$]}$_2$(μ-tmen)]$_\infty$ 1.** To a suspension of the lithium amide **5** (0.88 g, 5.13 mmol [based on monomer]) in hexane (50 cm$^3$) tmen (0.75 g, 6.45 mmol) was added. The mixture was heated to reflux, whereupon the solid dissolved. Concentration of the solution *in vacuo* yielded white crystals of compound **1** (1.08 g, 90%) (Found: C, 60.9; H, 9.22; N, 12.01. $C_{12}H_{22}LiN_2Si$ requires C, 62.8; H, 9.67; N, 12.21%), mp 105–106 °C. $^1$H NMR (toluene-$d_8$): $\delta$ 7.18–6.62 (m, 10 H, Ph), 1.66 (s, 12 H, $NCH_3$), 1.53 (s, 4 H, $CH_2N$) and 0.30 (s, 18 H, $SiMe_3$). $^{13}$C NMR (toluene-$d_8$): $\delta$ 160.7 (*ipso*-C), 129.7 (*m*-C), 121.5 (*o*-C), 113.0 (*p*-C), 56.0 ($CH_2N$), 44.7 ($NCH_3$) and 2.6 ($SiMe_3$). $^7$Li NMR (toluene-$d_8$): $\delta$ 1.0. $^{29}$Si NMR (toluene-$d_8$): $\delta$ −6.85. EI-MS (*m*/*z*, %): (L = N(Ph)SiMe$_3$) 349 (50, $[L_2Li_3]^+$), 342 (35, $[L_2Li_2]^+$), 327 (25, $[L_2Li_2 - Me]^+$), 222 (10, $[L_2 - PhN]^+$), 178 (100, $[LLi_2]^+$), 165 (65, $[L]^+$), 150 (95, $[L - Me]^+$) and 73 (35, $[SiMe_3]^+$).

**[Li{N(Ph)SiMe$_3$}(OEt$_2$)]$_2$ 7.** n-Butyllithium (18.0 cm$^3$ of a 1.6 mol dm$^{-3}$ solution in hexane, 28.8 mmol) was added dropwise during *ca.* 15 min to a cooled (0 °C) solution of trimethylsilylaminobenzene (4.64 g, 28.1 mmol) in diethyl ether (100 cm$^3$). The resulting colourless solution was set aside for *ca.* 20 min at 0 °C, then 2 h at *ca.* 25 °C and concentrated *in vacuo* yielding colourless crystals of compound **7** (4.21 g, 60%) (Found: C, 63.6; H, 9.85; N, 6.30. $C_{13}H_{24}LiNOSi$ requires

**Table 4** Crystal data and refinement for compounds **1**, **2** and **8**

| | **1** | **2** | **8** |
|---|---|---|---|
| Formula | $C_{24}H_{44}Li_2N_4Si_2$ | $C_{14}H_{24}LiN_2$ | $C_{30}H_{52}Li_2N_2O_2$ |
| *M* | 434.34 | 227.29 | 486.62 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | *P*2$_1$/*c* (no. 14) | *P*2$_1$/*c* (no. 14) | *P*2$_1$/*n* (no. 14) |
| *a*/Å | 9.259(1) | 8.0808(6) | 9.9810(2) |
| *b*/Å | 18.225(2) | 19.835(2) | 16.1914(4) |
| *c*/Å | 9.3338(7) | 9.4817(6) | 19.2524(4) |
| $\beta$/° | 118.617(6) | 106.504(5) | 95.796(1) |
| *U*/Å$^3$ | 1382.6(2) | 1457.2(2) | 3095.4(1) |
| *Z* | 2 | 4 | 4 |
| $\mu$(Mo-K$\alpha$)/mm$^{-1}$ | 0.15 | 0.06 | 0.06 |
| *T*/K | 173(2) | 173(2) | 173(2) |
| Total reflections | 11797 | 6759 | 25409 |
| Independent reflections, $R_{int}$ | 1900, 0.113 | 2536, 0.042 | 7257, 0.050 |
| Reflections with $I > 2\sigma(I)$ | 1469 | 2005 | 5366 |
| *R*1 [$I > 2\sigma(I)$] | 0.082 | 0.070 | 0.061 |
| *wR*2 (all data) | 0.200 | 0.195 | 0.180 |

C, 63.4; H, 9.86; N, 5.71%), mp 115–116 °C. $^1$H NMR: $\delta$ 7.23 (t, 2 H, $^3J_{HH} = 7$, 2 H, *m*-H), 6.89 (d, 2 H, $^3J_{HH} = 7$, *o*-H), 6.70 (t, 1 H, $^3J_{HH} = 7$, *p*-H), 3.07 (q, 4 H, $^3J_{HH} = 7.2$, OC*H*$_2$CH$_3$), 0.78 (t, 6 H, $^3J_{HH} = 7.2$ Hz, OCH$_2$C*H*$_3$) and 0.40 (s, 9 H, SiMe$_3$). $^{13}$C NMR: $\delta$ 159.4 (*ipso*-C), 129.7 (*m*-C), 123.0 (*o*-C), 115.3 (*p*-C), 64.9 (O*C*H$_2$CH$_3$), 2.8 (SiMe$_3$) and 14.4 (OCH$_2$*C*H$_3$). $^{29}$Si NMR: $\delta$ −8.8. $^7$Li NMR: $\delta$ 1.0. EI-MS (*m*/*z*, %), 349 {55, [(PhNSiMe$_3$)$_2$Li$_3$]$^+$}, 342 {50, [(PhNSiMe$_3$)$_2$Li$_2$]$^+$}, 327 {20, [(PhNSiMe$_3$)$_2$Li$_2$ − Me]$^+$}, 252 [10], 178 {100, [(PhNSiMe$_3$)Li$_2$]$^+$}, 165 {60, [PhNSiMe$_3$]$^+$}, 150 {80, [PhNSiMe$_2$]$^+$}, 134 [20], 123 [25], 73 {35, [SiMe$_3$]$^+$} and 58 [65].

**[Li{N(Ph)CH$_2$Bu$^t$}]$_n$ 6.** n-Butyllithium (4.0 cm$^3$ of a 1.6 mol dm$^{-3}$ solution in hexane, 6.4 mmol) was added dropwise during *ca.* 15 min to a cooled (0 °C) solution of neopentylaminobenzene (1.0 g, 6.12 mmol) in pentane (10 cm$^3$). The resulting beige suspension was stirred for *ca.* 20 min at *ca.* 25 °C, then filtered. The precipitate was washed with pentane and dried *in vacuo* yielding compound **6** as a white solid (1.03 g, 99%) (Found: C, 76.4; H, 9.52; N, 8.45. $C_{11}H_{16}LiN$ requires C, 78.1; H, 9.53; N, 8.28%), mp > 250 °C.

**[{Li[N(Ph)CH$_2$Bu$^t$]}$_2$(μ-tmen)]$_\infty$ 2.** To a suspension of lithium amide **6** (3.94 g, 23.3 mmol [based on monomer]) in a mixture of hexane (70 cm$^3$) and toluene (30 cm$^3$) was added tmen (0.75 g, 6.45 mmol). The mixture was heated to reflux, whereupon the solid dissolved. Cooling the solution to *ca.* 25 °C yielded pale pink crystals of compound **2** (4.12 g, 78%) (Found: C, 73.0; H, 10.58; N, 12.40. $C_{14}H_{24}LiN_2$ requires C, 74.0; H, 10.64; N, 12.32%), mp 109 °C (decomp.). $^1$H NMR (toluene-d$_8$): $\delta$ 7.14–6.40 (m, 10 H, Ph), 2.90 (br s, 4 H, Bu$^t$C*H*$_2$), 1.77 (s, 12 H, NCH$_3$), 1.73 (s, 4 H, C*H*$_2$NMe), 1.09 and 0.78 (br s, 18 H, CCH$_3$). $^{13}$C NMR (toluene-d$_8$): $\delta$ 161.7 (*ipso*-C), 130.2 (*m*-C), 121.5 (*o*-C), 112.5 (*p*-C), 62.9 (*C*H$_2$Bu$^t$), 56.3 (*C*H$_2$NMe), 45.1 (NCH$_3$), 33.2 (*C*CH$_3$) and 29.1 (C*C*H$_3$). $^7$Li NMR (toluene-d$_8$): $\delta$ 1.1. MS: only signals corresponding to the parent amine (*m*/*z* = 163) were observed.

**[Li{N(Ph)CH$_2$Bu$^t$}(OEt$_2$)]$_2$ 8.** n-Butyllithium (17.0 cm$^3$ of a 1.6 mol dm$^{-3}$ solution in hexane, 27.2 mmol) was added dropwise during *ca.* 15 min to a cooled (0 °C) solution of neopentylaminobenzene (4.25 g, 26.0 mmol) in diethyl ether (100 cm$^3$). The resulting yellow solution was stirred for *ca.* 1 h at *ca.* 25 °C, then concentrated *in vacuo* to *ca.* 40 cm$^3$. Cooling at 0 °C afforded colourless crystals of compound **8** (5.60 g, 89%) (Found: C, 73.3; H, 11.02; N, 5.89. $C_{15}H_{26}LiNO$ requires C, 74.0; H, 10.77; N, 5.76%), mp *ca.* 240 °C (decomp.). $^1$H NMR: $\delta$ 7.25 (t, $^3J_{HH} = 7$, 4 H, *m*-H), 6.70 (t, $^3J_{HH} = 7$, 4 H, *o*-H), 6.47 (t, $^3J_{HH} = 7$, 2 H, *p*-H), 3.32 (s, 4 H, NCH$_2$), 3.05 (q, $^3J_{HH} = 7$, 8 H, OC*H*$_2$CH$_3$), 1.12 (s, 18 H, CCH$_3$) and 0.75 (t, $^3J_{HH} = 7$ Hz, 12 H, CH$_2$C*H*$_3$). $^{13}$C NMR: $\delta$ 162.2 (*ipso*-C), 130.4 (*m*-C), 112.7 (*o*-C), 110.4 (*p*-C), 65.3 (*C*H$_2$CH$_3$) 59.8 (NCH$_2$), 35.8 (*C*CH$_3$), 29.2 (C*C*H$_3$) and 14.2 (CH$_2$*C*H$_3$). $^7$Li NMR: $\delta$ 1.1. MS: only signals corresponding to the parent amine (*m*/*z* = 163) were observed.

### Crystal data and refinement details for compounds 1, 2 and 8

Diffraction data were collected on an Enraf-Nonius Kappa-CCD diffractometer using monochromated Mo-K$\alpha$ radiation, $\lambda$ 0.71073 Å. Crystals were directly mounted on the diffractometer under a stream of cold nitrogen gas. Those of compound **1** were extremely thin plates; the diffraction data were limited and weak. The structures were refined on all $F^2$ using SHELXL 97.[25] Further details are in Table 4.

CCDC reference numbers 154172–154174.

See http://www.rsc.org/suppdata/dt/b0/b009724l/ for crystallographic data in CIF or other electronic format.

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## References

1 M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Srivastava, *Metal and Metalloid Amides*, Horwood-Wiley, Chichester, 1980; R. Kempe, *Angew. Chem., Int. Ed.*, 2000, **39**, 469.

2 B. J. Wakefield, *Best Synthetic Methods: Organolithium Methods*, Academic Press, London, 1988; L. Brandsma and H. Verkuijsse, *Preparative Polar Organometallic Chemistry 1*, Springer, Berlin, 1987; D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 1989, **27**, 1624; G. Boche, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 277; A. M. Sapse and P. v. R. Schleyer (Editors), *Lithium Chemistry*, Wiley, New York, 1994; V. Snieckus, *Chem. Rev.*, 1990, **90**, 879.

3 P. J. Cox and N. S. Simpkins, *Tetrahedron: Asymmetry*, 1991, **2**, 1; P. Beak, A. Basu, D. J. Gallagher, Y. S. Park and S. Thayumanavan, *Acc. Chem. Res.*, 1996, **29**, 552; D. Hoppe and T. Hense, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2282.

4 (*a*) W. N. Setzer and P. v. R. Schleyer, *Adv. Organomet. Chem.*, 1985, **24**, 353; (*b*) K. Gregory, P. v. R. Schleyer and R. Snaith, *Adv. Inorg. Chem.*, 1991, **37**, 47; (*c*) R. E. Mulvey, *Chem. Soc. Rev.*, 1991, **20**, 167; (*d*) U. Olsher, R. M. Izatt, J. S. Bradshaw and N. K. Dalley, *Chem. Rev.*, 1991, **91**, 137; (*e*) D. B. Collum, *Acc. Chem. Res.*, 1993, **26**, 227; (*f*) T. Koizumi, K. Morihashi and O. Kikuchi, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 305.

5 D. Barr, W. Clegg, R. E. Mulvey, R. Snaith and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1987, 716.

6 J. L. Atwood, M. F. Lappert, W.-P. Leung and H. Zhang, unpublished results cited in ref. 4(*c*).

7 T. Fjeldberg, A. J. Thorne, P. B. Hitchcock and M. F. Lappert, *J. Chem. Soc.*, *Chem. Commun.*, 1984, 822.

8 P. B. Hitchcock, M. F. Lappert and M. Layh, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 501.

9 M. P. Bernstein, F. E. Romesberg, D. J. Fuller, A. T. Harrison, D. B. Collum, Q.-Y. Liu and P. G. Williard, *J. Am. Chem. Soc.*, 1992, **114**, 5100.

10 C. H. Galka, D. J. M. Trösch, I. Rüdenauer, L. H. Gade, I. Scowen and M. McPartlin, *Inorg. Chem.*, 2000, **39**, 4615.

11 W. Clegg, L. Horsburgh, S. A. Couper and R. E. Mulvey, *Acta Crystallogr.*, *Sect. C*, 1999, **55**, 867.

12 M. A. Nichols and P. G. Williard, *J. Am. Chem. Soc.*, 1993, **115**, 1568.

13 S. Harder, J. Boersma, L. Brandsma and J. A. Kanters, *J. Organomet. Chem.*, 1988, **339**, 7.

14 D. Hoffmann, A. Dorigo, P. v. R. Schleyer, H. Reif, D. Stalke, G. M. Sheldrick, E. Weiss and M. Geissler, *Inorg. Chem.*, 1995, **34**, 262; C. L. Raston, B. W. Skelton, C. R. Whitaker and A. H. White, *Aust. J. Chem.*, 1988, **41**, 1925.

15 B. Teclé, W. H. Ilsey and J. P. Oliver, *Organometallics*, 1982, **1**, 875.

16 N. D. R. Barnett, R. E. Mulvey, W. Clegg and P. A. O'Neil, *J. Am. Chem. Soc.*, 1991, **113**, 8187.

17 H. Schumann, J. Winterfeld, E. C. E. Rosenthal, H. Hemling and L. Esser, *Z. Anorg. Allg. Chem.*, 1995, **621**, 122.

18 (*a*) J. Larsen and K. A. Joergensen, *J. Chem. Soc.*, *Perkin Trans. 2*, 1992, **8**, 1213; (*b*) J. J. Eisch, J. F. McNulty and X. Shi, *J. Org. Chem.*, 1994, **59**, 7.

19 F. Antolini, P. B. Hitchcock, M. F. Lappert and P. Merle, *Chem. Commun.*, 2000, 1301.

20 J. R. Galsworthy, M. L. H. Green, N. Maxted and M. Müller, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 387.

21 L. M. Engelhardt, A. S. May, C. L. Raston and A. H. White, *J. Chem. Soc.*, *Dalton Trans.*, 1983, 1671; M. F. Lappert, M. J. Slade, A. Singh, J. L. Atwood, R. G. Rogers and R. Shakir, *J. Am. Chem. Soc.*, 1983, **105**, 302.

22 R. P. Davies, R. Snaith, P. R. Raithby and J. E. Davies, unpublished results (cited in the Cambridge database).

23 B. Çetinkaya, P. B. Hitchcock, M. F. Lappert, M. C. Misra and J. A. Thorne, *J. Chem. Soc.*, *Chem. Commun.*, 1984, 148; D. Barr, W. Clegg, R. E. Mulvey and R. Snaith, *J. Chem. Soc.*, *Chem. Commun.*, 1984, 285; D. R. Armstrong, R. E. Mulvey, G. T. Walker, D. Barr, R. Snaith, W. Clegg and D. Reed, *J. Chem. Soc.*, *Dalton Trans.*, 1988, 617; L. M. Jackman, L. M. Scarmoutzos, B. D. Smith and P. G. Williard, *J. Am. Chem. Soc.*, 1988, **110**, 6058; W. N. Setzer, P. v. R. Schleyer, W. Mahdi and H. Dietrich, *Tetrahedron*, 1988, **44**, 3339; A. Mommertz, G. Geiseler, K. Harms and K. Dehnicke, *Z. Naturforsch.*, *Teil B*, 1998, **53**, 977.

24 (*a*) B. S. Jolly, D.Phil. Thesis, University of Sussex, 1987; (*b*) D. Barr, Ph.D. Thesis, Strathclyde University, 1988.

25 G. M. Sheldrick, SHELXL 97, Program for Crystal Structures Refinement, University of Göttingen, 1997.