

Unusual alkali metal α - or β -phenyl(trimethylsilyl)amides†‡

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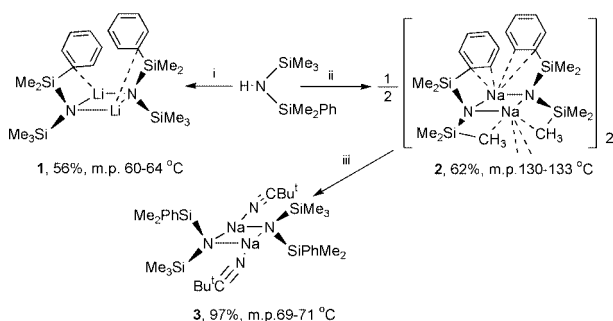
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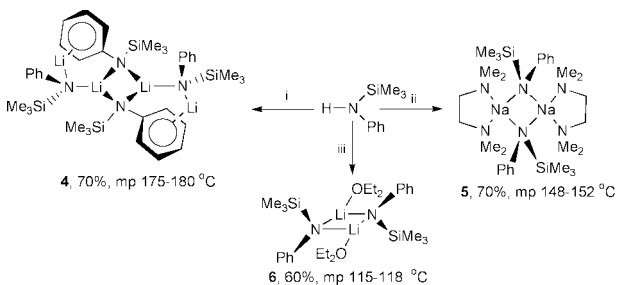
The synthesis (1–3 and 5) and structures (1–5) of the crystalline, hydrocarbon-soluble metal amides $[M\{\mu\text{-N}(\text{SiMe}_3)(\text{SiMe}_2\text{Ph})\}(\text{NCBu}^t)_n]_2$ [$n = 0$ and $M = \text{Li}$ (1 *cis*), $M = \text{Na}$ 2 (*trans*) having intermolecular $\text{Na}\cdots\text{C}$ contacts, or $n = 1$ and $M = \text{Na}$ (*cis*) 3], $[\text{Li}\{\mu\text{-N}(\text{SiMe}_3)\text{Ph}\}\text{-cis}]_2[\mu\text{-}\{\text{N}(\text{SiMe}_3)\text{Ph}\}\text{Li}\text{-cis}]_2$ 4 and *trans*- $[\text{Na}\{\mu\text{-N}(\text{SiMe}_3)\text{Ph}\}\text{-tmen}]_2$ 5 are reported.

Bulky crystalline metal amides display a diversity of structures.¹ In the absence of a neutral coligand, they are polymers, e.g. $[\text{Na}\{\mu\text{-N}(\text{SiMe}_3)_2\}]_\infty$, trimers, e.g. $[\text{M}\{\mu\text{-N}(\text{SiMe}_3)_2\}]_3$ ($M = \text{Li}$ or Na),² or, for $[\text{M}\{\mu\text{-NC}(\text{Me})_2(\text{CH}_2)_3\text{CMe}_2\}]_4$,³ tetramers. Crystalline bis(trimethylsilyl)amides of the heavier alkali metals are dimers.² Addition of tmen to a bulky Li or Na amide results in its fragmentation into a crystalline mono- or binuclear compound, such as $[\text{Li}\{\text{N}(\text{SiMe}_3)_2\}(\text{tmen})]$,⁴ *trans*- $[\text{Li}\{\mu\text{-N}(\text{Me})\text{Ph}\}(\text{tmen})]_2$,⁵ or *trans*- $[\text{Na}\{\mu\text{-N}(\text{Pr}^i)\text{C}_6\text{H}_{11}\text{-c}\}(\text{tmen})]_2$.⁶

We now report on the synthesis (1–5) (Schemes 1 and 2) and structures (1, 2 and 4) of the crystalline Li and Na trimethylsilylamides having an additional α - or β -phenyl *N*-centered



Scheme 1 Synthesis of the crystalline Li and Na amides 1–3 (yields are for crystals, from C_6H_6). Reagents and conditions: i, LiBu^t in C_6H_{14} , C_5H_{12} , -70 to 20 °C; ii, NaCH_2Ph , C_6H_{14} , -78 to 35 °C; iii, $2\text{Bu}^t\text{CN}$, C_5H_{12} , -78 to 20 °C.



Scheme 2 Synthesis of the crystalline Li and Na amides 4–6 (yields are for crystals, from PhMe , C_5H_{12} for 5 and Et_2O for 6). Reagents and conditions: i, LiBu^t , C_6H_{14} , 0 to 20 °C (cf. ref. 8); ii, $\text{NaN}(\text{SiMe}_3)_2$, Et_2O , 0 to 20 °C; then tmen to the precipitate in C_5H_{12} - PhMe ; iii, LiBu^t , Et_2O , 0 to 20 °C.

† Electronic supplementary information (ESI) available: spectroscopic and analytical data, details of crystallography, and comparative data for 1–4, 7 and 8. See <http://www.rsc.org/suppdata/cc/b0/b003169k/>

‡ No reprints available.

substituent: *cis*- $[\text{Li}\{\mu\text{-N}(\text{SiMe}_3)(\text{SiMe}_2\text{Ph})\}]_2$ 1, *trans*- $[\text{Na}\{\mu\text{-N}(\text{SiMe}_3)(\text{SiMe}_2\text{Ph})\}]_2$ 2, *trans*- $[\text{Na}\{\mu\text{-N}(\text{SiMe}_3)(\text{SiMe}_2\text{Ph})\}(\text{NCBu}^t)]_2$ 3, $[\text{Li}\{\mu\text{-N}(\text{SiMe}_3)\text{Ph}\}\text{-cis}]_2[\mu\text{-}\{\text{N}(\text{SiMe}_3)\text{Ph}\}\text{Li}\text{-cis}]_2$ 4 and $[\text{Na}\{\mu\text{-N}(\text{SiMe}_3)\text{Ph}\}(\text{tmen})]_2$ 5.

Treatment of {phenyl(dimethyl)silyl}(trimethylsilyl)amine⁷ with *n*-butyllithium or benzylna in pentane or hexane at low temperature yielded 1 or 2, respectively. Addition of 2-cyano-2-methylpropane to 2 in pentane, irrespective of stoichiometry, afforded the 1 : 1 adduct 3. Each of 1–3 furnished X-ray quality crystals from hexane for 1 and 3 or benzene for 2.

Similar low temperature reactions between *N*-trimethylsilylaniline⁸ and *n*-butyllithium in hexane or bis(trimethylsilyl)amidosodium in diethyl ether yielded 4, or a white precipitate of the presumed sodium analogue which with tmen in pentane–toluene gave 5. X-Ray quality crystals of 4 (from toluene) or 5 (from pentane) were obtained upon recrystallisation. Compound 4 had previously been made similarly⁸ and used to make corresponding amides of Zn, Cd and Hg.⁹ A material related to 4, and believed to have been $[\text{Li}\{\text{N}(\text{SiMe}_3)\text{Ph}\}]_2\text{OEt}_2$, was used *in situ* for the synthesis of $[\text{M}'\{\text{N}(\text{SiMe}_3)\text{Ph}\}_3\text{Cl}]$ ($\text{M}' = \text{Zr}$ or Hf); it was obtained from aniline and successively LiBu^t , Me_3SiCl , LiBu^t and Et_2O .¹⁰ In our hands, this procedure afforded *trans*- $[\text{Li}\{\mu\text{-N}(\text{SiMe}_3)\text{Ph}\}(\text{OEt}_2)]_2$ 6.

The new colourless (1–4 and 6) or pale pink (5), air-sensitive, benzene-soluble, compounds 1–3, 5 and 6 gave satisfactory analyses and ambient temperature benzene solution multinuclear NMR spectra. Such data for 4 were similar to those in the literature,¹⁰ but ²⁹Si and ⁷Li spectral details are new (ESI†). The X-ray structures of each of 1–5 have been elucidated; those for 3 and 5 will be reported in the full paper. §

Numerous neutral donor-free lithium amide crystals structures are known; those for 1 and 4 display new features.

As for 1 (Fig. 1), only a single previous example of a dinuclear complex, albeit of opposite stereochemistry, *trans*- $[\text{Li}\{\mu\text{-N}(\text{SiMe}_3)\text{C}_6\text{H}_3\text{Pr}^i\text{-2,6}\}]_2$ 7 was known.¹¹ Each Li atom in 1 and 7 has a close (< 2.45 Å) contact to its *ipso*-carbon, which is γ - in 1 but β - in 7; in the latter there are two further more distant [$2.76(2)$ Å] contacts to the γ - and δ - (CHMe_2) carbon atoms.¹¹ The LiNLiN core in 1, unlike in 7, deviates from a planar rhombus, the Li–N bonds ranging from 1.980(3) to 2.019(3) Å, the four atoms alternating above and below the plane by *ca.* 0.033 Å. The amide 1 has a two-fold symmetry axis; 7 is centrosymmetric.

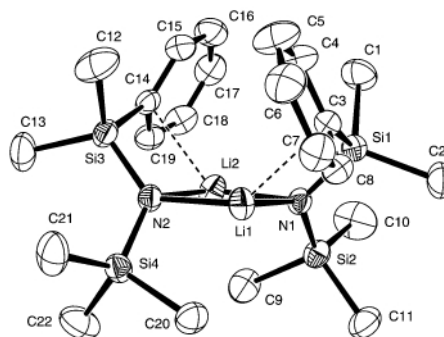


Fig. 1 Molecular structure (ORTEP) of 1 with atom labelling, H omitted for clarity.

The tetranuclear, crystalline lithium amide **4** (Fig. 2) has an unprecedented structure. Unlike its only prior tetranuclear neutral donor-free complex, the planar octacyclic $[\text{Li}\{\mu\text{-NC}(\text{Me})_2(\text{CH}_2)_3\text{CMe}_2\}]_4$,¹² the centrosymmetric **4** has two distinct and different lithium atom environments. The four lithium atoms are arranged in a stair-like fashion, the central two, Li(1) and Li(2), are separated by 2.601(9) Å, while the two terminal, Li...Li(1 or 2) distances are longer at 3.121(9) Å, the Li–Li(1 or 2)–Li angles being 118(1)°. The atoms Li(1) and Li(2) are each bound to three nitrogen atoms at distances of 2.057(9) to 2.183(9) Å. Each of the terminal lithium atoms is bound slightly more tightly to a terminal nitrogen atom [Li(3 or 4)–N(3 or 4) 2.004(9) or 1.983(10) Å] and also has close η^6 -contacts to the phenyl ring attached to a bridging nitrogen atom [av. Li(3 or 4)...M(1 or 2) 2.17(2) Å], the N–Li–M angle being 128.8(5) or 134.1(5)° at Li(3) or Li(4), respectively [M(1) and M(2) are the centroids of the phenyl rings attached to N(1) and N(2), respectively]. The Li(1)–N(1)–M(1) and Li(2)–N(2)–M(2) angles are 95.1 and 97.2°, respectively, compared with Li(1)–N(1)–C(1) and Li(2)–N(2)–C(10) angles of 95.6 and 98.0°, respectively; hence the Ph rings are essentially flat. The central (LiN)₂ ring is puckered, the torsion angle between the Li(1)N(1)Li(2) and Li(1)N(2)Li(2) planes being 14.6(4)°. The substituents at N(1) and N(2) are arranged in a *cis* fashion, while the two terminal $\{\text{N}(\text{SiMe}_3)\text{Ph}\}\text{Li}(3 \text{ or } 4)$ fragments attached to Li(1 or 2) also have the *cis*-orientation.

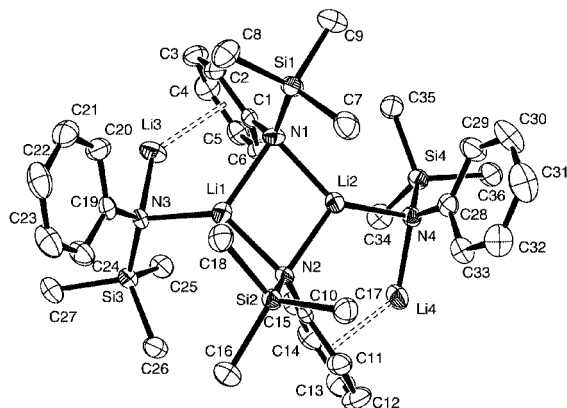


Fig. 2 Molecular structure (ORTEP) of **4** with atom labelling, H omitted for clarity.

The crystalline sodium amide **2** (Fig. 3) is a polymer made up of linked dinuclear units; each is attached to its neighbour by close intermolecular Na...C contacts. Neutral donor-free dinuclear Na amides are, we believe, unprecedented. Like its isoleptic complex **1**, each monomer unit of **2** has a two-fold rotation axis along Na(1)Na(2), but differs from **1** in having a *trans*-arrangement of the substituents at the N atoms and in having different environments for each of the alkali metal

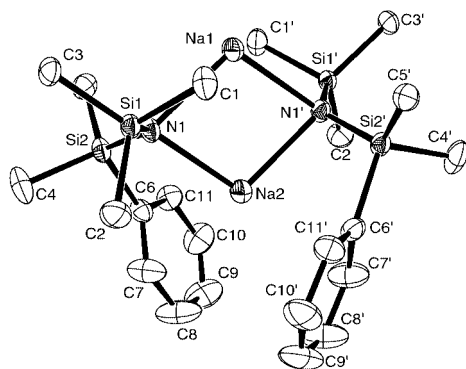


Fig. 3 Molecular structure (ORTEP) of **2** with atom labelling, H omitted for clarity.

atoms. Each sodium atom has four additional Na...C close contacts: for Na(2) from the *ipso*-[2.686(1) Å] and one of the adjacent *ortho*-[2.884(2) Å] carbon atoms of the aromatic rings and for Na(1) from the C(1) carbon atoms of the *trans*-SiMe₃ groups [2.948(2) Å] and from the C(3) carbon atoms of an inversion centered related molecule [3.060(2) Å]. The Si–N–Si' angle is slightly wider in **2** [av. 126.3(1)°] than in **1** [av. 123.9(5)°], but narrower than in its Bu^tCN complex **3** [129.9(1)°].¹³ As for $[\text{Li}\{\mu\text{-N}(\text{SiMe}_3)_2\}(\text{NCBu}^t)]_2$,¹⁴ **3** may be regarded as a model MR'(NCR) intermediate for reaction of RCN with an organometallic compound MR'.

The crystalline, dinuclear *trans*-sodium amide **5** is broadly similar to others, such as *trans*-[Na{ μ -N(Prⁱ)C₆H₁₁-c}-(tmen)]₂.⁶ Comparative data on **1–4**, **7** and **8** are listed (ESI[†]).

The tetranuclear lithium amide **4** at 163 K in toluene-*d*₈ showed two ⁷Li environments of equal intensity at δ 0.89 and –4.6, corresponding to the central and terminal lithium atoms in the crystal, whereas at higher temperatures various exchange processes (2D ⁷Li EXSY) were observed.

The present results serve to highlight (*cf.* also ref. 1) the diversity of structural motifs available to alkali metal amides; the role of complexes **1–5** as reagents is being explored.

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Notes and references

§ Crystallographic data for each of **1**, **2** and **4** were collected at 173(2) K on an Enraf-Nonius Kappa CCD (**1** and **2**) or CAD4 (**4**) diffractometer (ESI[†]).

1: C₂₂H₄₀Li₂N₂Si₄, *M* = 458.8, monoclinic, space group *P*2₁/*n* (no. 14), *a* = 14.2980(3), *b* = 13.6936(3), *c* = 15.2530(3) Å, β = 98.635(1)°, *U* = 2952.6(1) Å³, *Z* = 4, *D*_c = 1.03 g cm^{–3}, $\mu(\text{Mo-K}\alpha)$ = 0.21 mm^{–1}. Final residual was *R*₁ = 0.041 for the 5613 reflections with *I* > 2 σ (*I*) and *wR*₂ = 0.113 for all the 6948 reflections. **2**: C₂₂H₄₀N₂Na₂Si₄, *M* = 491.0, monoclinic, space group *C*2/*c* (no. 15), *a* = 16.6414(6), *b* = 14.6700(5), *c* = 11.6899(4) Å, β = 93.187(2)°, *U* = 2849.4(1) Å³, *Z* = 4, *D*_c = 1.14 g cm^{–3}, $\mu(\text{Mo-K}\alpha)$ = 0.25 mm^{–1}. Final residual was *R*₁ = 0.038 for the 2958 reflections with *I* > 2 σ (*I*) and *wR*₂ = 0.103 for all the 3364 reflections. **4**: C₃₆H₅₆Li₄N₄Si₄, *M* = 684.97, triclinic, space group *P* $\bar{1}$ (no. 2), *a* = 10.103(4), *b* = 10.873(5), *c* = 20.223(7) Å, α = 99.82(3), β = 91.76(3), γ = 113.16(3)°, *U* = 2001(1) Å³, *Z* = 2, *D*_c = 1.14 g cm^{–3}, $\mu(\text{Mo-K}\alpha)$ = 0.18 mm^{–1}. Final residual was *R*₁ = 0.073 for the 4136 reflections with *I* > 2 σ (*I*) and *wR*₂ = 0.194 for all the 7003 reflections. CCDC 182/1657. See <http://www.rsc.org/suppdata/cc/b0/b003169k/> for crystallographic files in .cif format.

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