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# Trisilylmethane as a Structural Backbone in Multifunctional Lithium Amides: Syntheses and Structures of $HC\{(CH_3)_2SiN(Li)$-*t*-$Bu\}_3$ and Its Solvate $HC\{(CH_3)_2SiN(Li)$-*t*-$Bu\}_3 \cdot 2THF$[†]

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The trisilylmethane derivatives $HC\{(CH_3)_2SiH\}_3$ (**1**) and $C_6H_5C\{(CH_3)_2SiH\}_3$ (**2**) have been synthesized. Bromination and subsequent aminolysis with *t*-$BuNH_2$ yielded $HC\{(CH_3)_2SiNH$-*t*-$Bu\}_3$ (**5**) and $C_6H_5C\{(CH_3)_2SiNH$-*t*-$Bu\}$-$\{[(CH_3)_2Si]_2N$-*t*-$Bu\}$ (**8**), respectively. **5** was lithiated with 3 molar equiv of *n*-BuLi both in pentane and in THF yielding the trilithium triamide $HC\{(CH_3)_2SiN(Li)$-*t*-$Bu\}_3$ (**9**) and its bis-THF solvate $HC\{(CH_3)_2SiN(Li)$-*t*-$Bu\}_3 \cdot 2THF$ (**11**) which have been structurally characterized by single crystal X-ray structure analyses. **9**: monoclinic, $P2_1/c$, $a = 17.379(6)$ Å, $b = 8.483(3)$ Å, $c = 18.801(3)$ Å, $\beta = 91.39°$, $V = 1053.2$ Å$^3$, $Z = 4$, $R = 0.053$; **11**: monoclinic, $P2_1/n$, $a = 11.783(4)$ Å, $b = 19.026(6)$ Å, $c = 16.761(5)$ Å, $\beta = 104.34(8)°$, $V = 1063.5$ Å$^3$, $Z = 4$, $R = 0.058$. **9** has an adamantane-type cage structure incorporating a puckered $(LiN)_3$ ring while **11** contains two THF-solvated Li atoms bridging, respectively, two amido-*N* atoms while the third, nonsolvated Li has close bonding contacts to all three N-centers, thus generating a unique structural arrangement for a $(LiN)_3$ unit. $^1H$- and $^7Li$-NMR spectroscopic studies of the generation of **9** indicate a certain degree of cooperativity in the metalation process with the preferential formation of the trimetalated species even after addition of subequivalent amounts of *n*-BuLi. Variable temperature $^1H$- and $^7Li$-NMR studies of **11** in solution indicate rapid chemical exchange within the system, which displays an effective 3-fold symmetry. This process could not be frozen out at 180 K.

## Introduction

There has been considerable interest in the structural chemistry of lithiated monofunctional amines due to their abundant use as mild deprotonating agents in organic synthesis as well as precursors in the preparation of transition metal amido complexes.[1] Their isolation as crystalline solids has established the chemical nature of many solvated and unsolvated lithium amides. This has offered some insight into the structural origins of their chemical reactivity and, from a more practical point of view, a greater freedom in the choice of the reaction conditions (such as for instance the reaction medium) for the subsequent conversions. While attempts to elucidate their structures in solution have only recently been made,[2] the amount of data concerning their solid-state structures which is now available has enabled a relatively systematic analysis of the observed structural patterns.[3–9] It appears that in many cases the structures of these species, mostly higher aggregates, may be rationalized in terms of a simple electrostatic model and seem to be determined by the steric requirements of the organic moieties attached to the nitrogen centers.[10] On the other hand, the imposition of geometrical constraints by the structural backbone present in multifunctional amines should lead to Li–N arrays distinct from those observed to date and displaying a somewhat different reactivity.

Our recent work has focussed on lithiated triamines of the type $[H_3CC\{CH_2N(Li)R\}_3]_2$ (R = alkyl, silyl) in which the amido groups are attached to a neopentane framework.[11] Single-crystal X-ray structure analyses of $[H_3CC\{CH_2N(Li)CH(CH_3)_2\}_3]_2$ and $[H_3CC\{CH_2N(Li)Si(CH_3)_3\}_3]_2$ along with NMR spectroscopic and cryoscopic studies have established the dimeric aggregation of these and a number of related compounds both in solution and in the solid. The relatively low flexibility of the backbone structure appears to imply an almost identical geometry of the central $(LiN)_6$ unit for the whole series of these compounds. As another consequence of this situation they were found to be ideal tripodal ligand systems for some early first-row transition metals but somewhat less useful for the preparation of complexes containing second- and third-row metals.[12]

To overcome these limitations we set out to replace the neopentane-derived triamines by their presumably more flexible trisilylmethane-derived analogues. In view of the previous results

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[†] We dedicate this paper to Professor Lord Lewis on the occasion of his 65th birthday.

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(2) Studies of lithium amides in solution include: (a) Reed, D.; Barr, D.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Dalton Trans.* **1986**, 557. (b) Kallman, N.; Collum, D. B. *J. Am. Chem. Soc.* **1987**, *109*, 7466. (c) Jackman, L. M.; Scarmoutzos, L. M. *J. Am. Chem. Soc.* **1987**, *109*, 5348. (d) Galiano-Roth, A. S.; Michaelides, E. M.; Collum, D. M. *J. Am. Chem. Soc.* **1988**, *110*, 2658.

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(10) Theoretical studies include: (a) Kaufmann, E.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 1856. (b) Gregory, K.; Bremer, M.; Bauer, W.; Schleyer, P. v. R.; Lorenzen, N. P.; Kopf, J.; Weiss, E. *Organometallics* **1990**, *9*, 1485. (c) Romesberg, F. E.; Collum, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 2112.

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referred to above, the lithiation of the amine precursors and the structures of the lithium amides obtained were of prime interest. Here we report the synthesis of trisilylmethane-derived amines and the study of the trilithium triamide $HC\{(CH_3)_2SiN(Li)\text{-}t\text{-}Bu\}_3$ (**9**) as well as its THF solvate both in solution and in the solid.

## Experimental Section

All manipulations were performed under an inert gas atmosphere of dried argon in standard (Schlenk) glassware which was flamed with a Bunsen burner prior to use. Solvents were dried according to standard procedures and saturated with Ar. The deuterated solvents used for the NMR spectroscopic measurements were dried over 4-Å molecular sieves.

The $^1H$-, $^{13}C$, $^{29}Si$- and $^7Li$-NMR spectra were recorded on a Bruker AC 200 spectrometer (at 200.13, 50.32, 39.76, and 77.78 MHz, respectively) with tetramethylsilane and $LiI/H_2O$ (1 M, external) as references. Infrared spectra were recorded on Perkin Elmer 1420 and Bruker IFS 25 FT IR-spectrometers. Elemental analyses were carried out in the microanalytical laboratory of the chemistry dept. at Würzburg. $\alpha,\alpha,\alpha$-Tribromotoluene was prepared according to a literature procedure.[13] All other chemicals used as starting materials were obtained commercially and, with the exception of $t\text{-}BuNH_2$, which was dried over $CaH_2$, used without further purification.

**Preparation of Compounds.** **$HC\{(CH_3)_2SiH\}_3$ (1).** To a stirred, refluxing mixture of dimethylchlorosilane (50.0 g = 0.528 mol), magnesium turnings (13.9 g = 0.570 mol) in 170 mL of THF was added a solution of bromoform (44.5 g = 0.176 mol) in 200 mL of THF over a period of 3 h. The external heating was removed at the beginning of the addition and the dropping rate adjusted so as to maintain gentle reflux during the process. The reaction mixture was subsequently stirred under reflux for another 4 h, cooled to room temperature, filtered, and poured onto 200 g of crushed ice. To this mixture solid $NaHCO_3$ was added until the evolution of $CO_2$ subsided. The separation of the phases was enhanced by the addition of 100 mL of hexanes. After the separation, the organic phase was washed with $H_2O$ and dried over anhydrous $Na_2SO_4$. Evaporation of the solvent yielded a yellow oil, which was subjected to vacuum distillation. The fraction distilling between 75 and 80 °C at 25 Torr was collected. Yield: 10.3 g (31%). Anal. Calcd for $C_7H_{22}Si_3$: C, 44.13; H, 11.64. Found: C, 44.21, H, 11.46. $^1H$-NMR ($C_6D_6$, 295 K): $\delta = -0.88$ (q, $\mathit{H}CSi_3$, $^3J_{HH(Si)} = 2.4$ Hz), 0.05 (d, $(C\mathit{H}_3)_2SiH$, $^3J_{HH(Si)} = 3.7$ Hz), 3.96 (d of sept, $(CH_3)_2Si\mathit{H}(CH)$, $^3J_{HH(CH)} = 1.3$ Hz). $\{^1H\}^{13}C$-NMR ($C_6D_6$, 295 K): $\delta = -3.05$ ($H\mathit{C}\{SiH(CH_3)_2\}$), $-1.65$ ($SiH(\mathit{C}H_3)_2$). $^{29}Si$-NMR ($C_6D_6$, 295 K): $\delta = -15.2$ (m, $^1J_{SiH} = 184.6$). IR (film): 2952 (s), 2898 (m), 2102 (s), 1410 (m), 1250 (s), 1070 (msh), 1040 (s), 1022 (s), 1005 (ssh), 895 (vs), 827 (vs), 783 (vs), 745 (s) 690 (m), 630 (w) $cm^{-1}$.

**$C_6H_5C\{(CH_3)_2SiH\}_3$ (2).** A solution of $\alpha,\alpha,\alpha$-tribromotoluene (23 g = 0.07 mol in 300 mL THF) was added to a boiling mixture of magnesium turnings (5.5 g = 0.23 mol) and dimethylchlorosilane (20 g = 0.21 mol) in 200 mL of THF over a period of 4 h. The system was heated externally during the addition of the tribromotoluene to maintain reflux and was subsequently stirred at the same temperature for another 2 h. After filtration, the reaction mixture was poured onto crushed ice; hexane (50 mL) was added. The organic phase was separated, washed with $H_2O$, and dried over $Na_2SO_4$. The solvent was then removed in vacuo and the yellow oily residue subjected to vacuum distillation. The fraction distilling between 99 and 104 °C at 1 Torr contained the pure trisilane. Yield: 7.9 g (43%). Anal. Calcd for $C_{13}H_{26}Si_3$: C, 58.57; H, 9.83. Found: C, 58.56; H, 10.06. $^1H$-NMR ($CDCl_3$, 295 K): $\delta = 0.32$ (d, $SiH(C\mathit{H})_3$, $^3J_{HH(Si)} = 3.7$ Hz), 4.49 (sept, $Si\mathit{H}(CH_3)_2$), 7.11–7.47 (m, $C_6\mathit{H}_5$). $\{^1H\}^{13}C$-NMR ($CDCl_3$, 295 K): $\delta = -2.7$ ($SiH(\mathit{C}H_3)_2$), 14.6 ($Ph\text{–}\mathit{C}Si_3$), 123.8, 128.2, 130.2, 142.1 (*p*-, *o*-, *m*-, ipso-C of $\mathit{C}_6H_5$). $^{29}Si$-NMR ($CDCl_3$, 295 K): $\delta = -12.7$ (m, $^1J_{SiH} = 187.7$ Hz). IR ($CCl_4$): 3065 (w), 3041 (w), 3020 (w), 2940 (m), 2888 (w), 2121 (s), 1590 (w) 1582 (w), 1564 (w), 1488 (m), 1470 (w), 1432 (w), 1259 (s), 1550 (s) 1160 (m) $cm^{-1}$.

**$HC\{(CH_3)_2SiBr\}_3$ (3).** Bromine (25.7 g = 160.6 mmol) was added dropwise to a stirred solution of **1** (10.2 g = 53.54 mmol in 80 mL of benzene) which was externally cooled to 5 °C. Until ca. 90% of the required amount of bromine had been added, the reaction mixture was discolored immediately after the addition of every drop of $Br_2$. After the addition was complete the reaction mixture was stirred at room temperature for 15 h. The solvent and any unreacted bromine were removed in vacuo and the residue distilled. The product which distilled at 101 °C (0.1 Torr) solidified in the condenser and had to be transferred to the receiving flask by gentle heating with a heat gun. Yield: 13.9 g (61%). Anal. Calcd for $C_7H_{19}Br_3Si_3$: C, 19.68; H, 4.48. Found: C, 19.64; H, 4.60. $^1H$-NMR ($C_6D_6$, 295 K): $\delta = 0.25$ (s, $\mathit{H}C\{SiBr(CH_3)_2\}_3$), 0.67 (s, $HC\{SiBr(C\mathit{H}_3)_2\}_3$). $\{^1H\}^{13}C$-NMR ($C_6D_6$, 295 K): $\delta = 7.4$ ($SiBr(\mathit{C}H_3)_2$), 15.0 ($H\mathit{C}\{SiBr(CH_3)_2\}$). $^{29}Si$-NMR ($C_6D_6$, 295 K): $\delta = 22.0$ (d of sept, $^2J_{SiH(methyl)} = 6.9$ Hz, $^2J_{SiH(methine)} = 10.8$ Hz). IR ($CCl_4$): 2948 (m), 2887 (w), 1396 (m), 1253 (s) $cm^{-1}$.

**$C_6H_5C\{(CH_3)_2SiBr\}_3$ (4).** Reaction conditions were analogous to those of **3**. Workup: After removal of the solvent the residue was recrystallized from pentane yielding 63% of the pure product as colorless crystals. Anal. Calcd for $C_{13}H_{23}Br_3Si_3$: C, 31.02; H, 4.61. Found C, 31.20; H, 4.74. $^1H$-NMR ($C_6D_6$, 295 K): $\delta = 0.69$ (s, $SiBr(C\mathit{H}_3)_2$), 7.16–7.39 (m, $C_6\mathit{H}_5$). $\{^1H\}^{13}C$-NMR ($C_6D_6$, 295 K): $\delta = 9.2$ ($SiBr(\mathit{C}H_3)_2$), 37.2 ($Ph\text{–}\mathit{C}Si_3$), 126.0, 128.3, 131.5, 136.4 (*p*-, *o*-, *m*-, ipso-C in $\mathit{C}_6H_5$).

**$HC\{(CH_3)_2SiNH\text{-}t\text{-}Bu\}_3$ (5).** A solution of **3** (5.67 g = 13.27 mmol) in 30 mL of diethyl ether was added dropwise to a solution of *tert*-butylamine (14.62 g in 80 mL of diethyl ether) which was cooled to 0 °C with an ice bath. After warming up to room temperature, the reaction mixture was stirred for another 2.5 h. The solvent and excess *tert*-butylamine were removed in vacuo, the residue was extracted with 100 mL of diethyl ether, and the extract was concentrated until a white crystalline solid started to precipitate. The product crystallized at –40 °C (yield: 4.2 g = 78%). Anal. Calcd for $C_{19}H_{49}N_3Si_3$: C, 56.51; H, 12.23; N, 10.40. Found: C, 56.39; H, 12.41; N, 10.28. $^1H$-NMR ($C_6D_6$, 295 K): $\delta = -1.25$ (s, $\mathit{H}C\{Si(CH_3)_2NH\text{-}t\text{-}Bu\}_3$), 0.37 (s, $Si(C\mathit{H}_3)_2$), 1.22 (s, $NC(C\mathit{H}_3)_3$). $\{^1H\}^{13}C$-NMR ($C_6D_6$, 295 K): $\delta = 4.5$ ($H\mathit{C}\{Si(CH_3)_2\text{-}NH\text{-}t\text{-}Bu\}_3\}$, 7.3 ($Si(\mathit{C}H_3)_2$), 34.1 ($NC(\mathit{C}H_3)_3$), 50.1 ($\mathit{C}(CH_3)_3$). $^{29}Si$-NMR ($C_6D_6$, 295 K): $\delta = -2.3$. IR ($CCl_4$): 3290 (br), 2940 (s), 2882 (w), 1538 (w), 1460 (w), 1376 (m), 1352 (m), 1245 (msh), 1240 (s), 1215 (s), 1023 (m), 1011 (s), 1002 (s) $cm^{-1}$.

**Reaction of 4 with *tert*-Butylamine.** Reaction of **4** with *tert*-butylamine under analogous reaction conditions yielded a pale yellow oil which slowly solidified and was identified as $C_6H_5C\{Si(CH_3)_2NH\text{-}t\text{-}Bu\}_2\{Si(CH_3)_2\text{-}Br\}$ **7**. Anal. Calcd for $C_{21}H_{40}N_2BrSi_3$; C, 52.04; H, 8.32; N, 5.78. Found: C, 51.92; H, 8.38; N, 5.88. $^1H$-NMR ($C_6D_6$, 295 K): $\delta = 0.22$, 0.62, 0.68 (s, $Si(C\mathit{H}_3)_2$), 1.26 (s, $C(C\mathit{H}_3)_3$), 6.80 – 7.26 (m, $C_6\mathit{H}_5$). The product was subsequently stirred in 30 mL of *tert*-butylamine for 20 h, then the excess amine was evaporated, and the residue was extracted with 50 mL of diethyl ether. The solution was concentrated to 10 mL and stored at –60 °C. Colorless needles of $C_6H_5\{(CH_3)_2SiNH\text{-}t\text{-}Bu\}\{[(CH_3)_2\text{-}Si]_2N\text{-}t\text{-}Bu\}$ (**8**) crystallized at this temperature (59% yield). Anal. Calcd for $C_{21}H_{42}N_2Si_3$: C, 62.00; H, 10.41; N, 6.89. Found: C, 62.38; H, 10.52; N, 6.61. $^1H$-NMR ($CDCl_3$, 295 K): $\delta = -0.40$, 0.19, 0.66 (s, $Si(C\mathit{H}_3)_2$), 1.19, 1.21 (s, $C(C\mathit{H}_3)_3$), 6.72–7.21 (m, s, $C_6\mathit{H}_5$). $\{^1H\}^{13}C$-NMR ($CDCl_3$, 295 K): $\delta = 2.6, 4.5, 6.0$ ($Si(\mathit{C}H_3)_2$), 33.9, 34.0 ($C(\mathit{C}H_3)_3$), 50.1, 51.6 ($\mathit{C}(CH_3)_3$), 122.7, 127.1, 132.9, 142.0 ($\mathit{C}_6H_5$). $^{29}Si$-NMR ($CDCl_3$, 295 K): $\delta = -4.5$ ($\mathit{Si}\text{–}NH\text{-}t\text{-}Bu$), 6.8 ($\mathit{Si}\text{–}N\text{–}\mathit{Si}$). IR ($CCl_4$): 3395 (br), 3056 (w), 3042 (w), 3004 (w) 2948 (s), 2885 (w), 1595 (w), 1481 (w), 1476 (w), 1375 (m), 1352 (m), 1246 (vs), 1224 (m), 1214 (m), 1190 (s), 1079 (s), 1026 (m), 1008 (m).

**$HC\{(CH_3)_2SiN(Li)\text{-}t\text{-}Bu\}_3$ (9).** A 3-mL aliquot of a 2.5 M *n*-BuLi/hexane solution were added to a solution of 1 g (2.48 mmol) of **5** in 30 mL of pentane, which was cooled to –50 °C. The reaction mixture was then slowly warmed to room temperature and subsequently refluxed for 15 min. The clear colorless solution was concentrated to ca 10 mL and stored at –20 °C to yield **9** as colorless crystals. Yield: 0.83 g (79%). Anal. Calcd for $C_{19}H_{46}N_3Si_3Li_3$: C, 54.12; H, 11.00; N, 9.97. Found: C, 54.10; H, 10.92; N, 9.83. $^1H$-NMR ($C_6D_6$, 295 K): $\delta = -1.14$ (s, $\mathit{H}CSi_3$), 0.43 (s, $(C\mathit{H}_3)_2Si$), 1.08 (s, $(C\mathit{H}_3)_3C$). $\{^1H\}^{13}C$-NMR ($C_6D_6$, 295 K): $\delta = 11.1$ ($(\mathit{C}H_3)_2Si$), 14.2 ($H\mathit{C}Si_3$), 37.2 ($(\mathit{C}H_3)_3C$), 52.1 ($(CH_3)_3\mathit{C}$). $^{29}Si$-NMR (toluene-$d_8$, 295 K): $\delta = -4.1$ (m). $^7Li$-NMR ($C_6D_6$, 295 K): $\delta = 0.19$.

**$HC\{(CH_3)_2SiN(Li)\text{-}t\text{-}Bu\}_3\cdot 2THF$ (11).** A solution of 2.5 M *n*-BuLi/hexane (2.5 mL) was slowly added to a solution of **5** (0.758 g = 1.88 mmol) in 35 mL of THF, which was cooled to –70 °C. The reaction mixture was warmed to room temperature and subsequently stirred at 50 °C for 30 min. The clear, light yellow solution was concentrated to ca. 10 mL and layered with 10 mL of pentane. Within a few hours large clear colorless crystals of $HC\{(CH_3)_2SiN(Li)\text{-}t\text{-}Bu\}_3\cdot 2THF$ formed. Yield: 0.87 g (81%). Anal. Calcd for $C_{27}H_{62}N_3O_2Si_3Li_3$: C, 57.31, H, 11.04, N, 7.43. Found: C, 56.98; H, 10.87; N, 7.53. $^1H$-NMR (toluene-$d_8$, 295 K): $\delta = -1.05$ (s, $\mathit{H}CSi_3$), 0.51 (s, $(C\mathit{H}_3)_2Si$), 1.29 (m, $[C\mathit{H}_2\text{–}CH_2]_2O$), 1.32 (s, $(C\mathit{H}_3)_3C$), 3.55 (m, $[CH_2\text{–}C\mathit{H}_2]_2O$). $\{^1H\}^{13}C$-NMR (toluene-$d_8$, 295 K): $\delta = 11.7$ ($(\mathit{C}H_3)_2Si$), 12.6 ($H\mathit{C}Si_3$), 25.4 ($[\mathit{C}H_2\text{–}CH_2]_2O$), 37.5 ($(\mathit{C}H_3)_3C$), 52.3 ($\mathit{C}(CH_3)_3$), 68.5 ($[CH_2\text{-}\mathit{C}H_2]_2O$). $^{29}Si$-NMR ($[D_8]$-Toluene, 295 K): $\delta = -9.2$. $^7Li$-NMR (toluene-$d_8$): 295 K, $\delta = 4.82$; 180 K, $\delta = 4.36$ (exchange broadened).

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[13] Heble, L. S.; Nadkarni, D. R.; Wheeler, T. S. *J. Chem. Soc.* **1938**, 1322.

**Table I.** Crystal Data and Experimental Details for **9** and **11**

| | 9 | 11 |
|---|---|---|
| empirical formula | $C_{19}H_{46}Li_3N_3Si_3$ | $C_{27}H_{62}Li_3O_2Si_3N_3$ |
| fw | 421.67 | 565.89 |
| cryst syst | monoclinic | monoclinic |
| cell params | | |
| $a$ (Å) | 17.379(6) | 11.783(4) |
| $b$ (Å) | 8.483(3) | 19.026(6) |
| $c$ (Å) | 18.801(3) | 16.761(5) |
| $V$ (Å$^3$) | 1053.2 | 1063.5 |
| $\beta$ (deg) | 91.39(3) | 104.34(8) |
| $Z$ | 4 | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 1.011 | 1.032 |
| space group | $P2_1/c$ | $P2_1/n$ |
| $F$(000) | 928 | 1246 |
| $\mu$(Cu K$\alpha$) (cm$^{-1}$)$^a$ | 16.28 | 13.79 |
| 2$\theta$(max) (deg) | 115.9 | 110.0 |
| no. of observns with $I > 3.00\sigma(I)^b$ | 1452 | 2731 |
| no. of variables$^c$ | 254 | 343 |
| residuals: $R$; $R_w$ | 0.053; 0.056 | 0.058; 0.067 |
| goodness of fit | 1.79 | 2.22 |
| largest peak in final diff map (e Å$^{-3}$) | 0.21 | 0.19 |

[a] An empirical absorption correction, using the program DIFABS (Walker, N.; Stuart, D. *Acta. Crystallogr. A* **1983**, *39*, 158) was applied for both crystals. The data were corrected for Lorentz and polarization effects. [b] The intensities of the representative reflections were measured every 60 minutes of X-ray exposure time. They remained constant throughout the data collection indicating in both cases crystal and electronic stability (no decay correction was applied). [c] Neutral atom scattering factors were taken from: Cromer, D. T.; Waber, J. T. *International Tables of X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A. Anomalous dispersion effects were included in the final $F_{calc}$ (Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781).

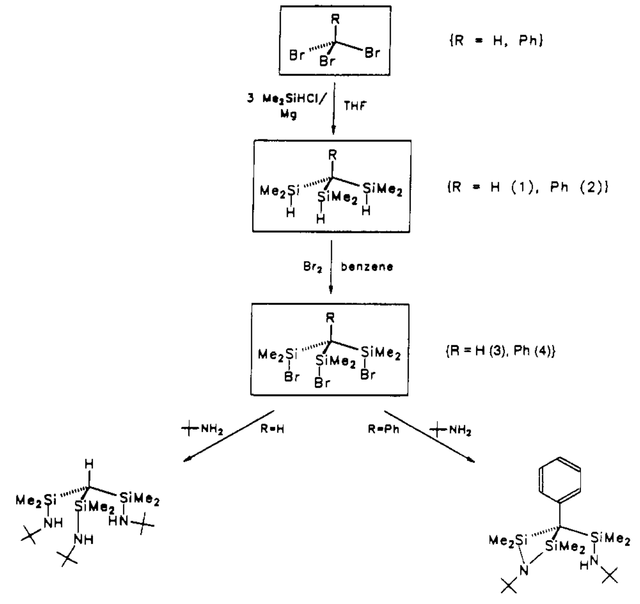
**X-ray Crystallographic Study of 9 and 10.** The clear, colorless crystals of **9** had a long prismatic habit while those of **11** were obtained as almost square colorless blocks. An irregularly shaped fragment of a crystal of **9** with the approximate dimensions of 0.200 × 0.250 × 0.120 mm was mounted under argon in a Lindemann capillary. A regularly shaped crystal of **11** with the approximate dimensions 0.350 × 0.350 × 0.500 mm was mounted in a similar way. The X-ray diffraction data were collected using an Enraf Nonius CAD4A diffractometer with graphite monochromated Cu K$\alpha$ radiation. Unit cell parameters were determined by a least-squares analysis of 25 automatically centered reflections in the range $30° < 2\theta < 36°$. Data were collected at 23 ± 1 °C using the $\omega/2\theta$ scan technique with full details presented in Table I.

The data analysis and refinement was carried out with the programs of the TEXAN software package. Both structures were solved by using direct methods and refined with anisotropic thermal parameters assigned to all non-hydrogen atoms. The positions of the hydrogen atoms in both structures were located in electron density difference maps and were included in the final full-matrix refinement.

## Results and Discussion

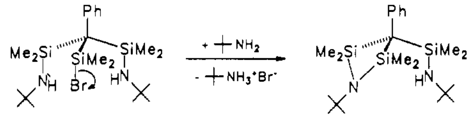
**Synthesis and Characterization of Amino-Functionalized Trisilylmethanes.** The central building block which links the amino functions, the trisilylmethane unit, may be synthesized by reductive coupling of a $\{CBr_3\}$ group with a suitable chlorosilane, such as $(CH_3)_2SiHCl$. The synthesis of silanes of the general type $RC\{(CH_3)_2SiH\}_3$ is achieved by the (slightly modified) method originally described by Merker and Scott for the buildup of polysilylated $C_1$ units.[14,15] The starting material for the parent compound $HC\{(CH_3)_2SiH\}_3$ (**1**) is $HCBr_3$ while its phenyl-substituted analogue $C_6H_5C\{(CH_3)_2SiH\}_3$ (**2**) may be synthesized from readily available $\alpha,\alpha,\alpha$-tribromotoluene (Scheme I). **1** was probably first generated by Merker and Scott as a byproduct of their synthesis of $C\{(CH_3)_2SiH\}_4$ but was not characterized at the time; the synthesis of **2** nicely demonstrates the general applicability of the chosen method.

**Scheme I.** Synthetic Route to **5** and **8**



5 8

**Scheme II.** Intramolecular Bromide Displacement Generating **8**



7 8

**1** and **2** are obtained in moderate yields by reaction of $(CH_3)_2SiHCl$ with $HCBr_3$ and $C_6H_5CBr_3$, respectively, in the presence of magnesium metal. Bromination of the silane in dry benzene[16] gives the bromosilanes $HC\{(CH_3)_2SiBr\}_3$ (**3**) and $C_6H_5C\{(CH_3)_2SiBr\}_3$ (**4**) which are highly moisture sensitive solids. Aminolysis of **3** with *tert*-butylamine yields the corresponding tris(aminosilyl)methane $HC\{(CH_3)_2SiNH\text{-}t\text{-}Bu\}_3$ (**5**) as a colorless crystalline solid. The amine is thermally stable at ambient temperature but decomposes when heated above 70 °C, liberating $t$-$BuNH_2$. The influence of the N-bonded alkyl group on the stability of the amine is highlighted by the elusiveness of $HC\{(CH_3)_2SiNHCH_3\}_3$ (**6**), the methyl-substituted analogue of **5**. Its extreme thermal lability has thus far prohibited its isolation and purification by vacuum distillation.

The factors which are responsible for the stability of **5** in comparison to **6** remain obscure. However the reaction of the phenyl-substituted **4** with $t$-$BuNH_2$ demonstrates the influence that steric overcrowding by the peripheral hydrocarbon moieties may have on the course of the aminolysis. The conversion initially proceeds to the disubstituted compound $C_6H_5C\{(CH_3)_2SiNH\text{-}t\text{-}Bu\}_2\{(CH_3)_2SiBr\}$ (**7**), and complete substitution of the bromide is only achieved by prolonged stirring in the presence of a large excess of the amine. However, the remaining bromide is not displaced by an external nucleophilic attack of a third *tert*-butylamine molecule but through intramolecular substitution by one of the silyl-bonded secondary amino groups. This leads exclusively to a compound which has been characterized on the basis of its analytical and spectroscopic data as $C_6H_5C\{(CH_3)_2SiNH\text{-}t\text{-}Bu\}\{[(CH_3)_2Si]_2N\text{-}t\text{-}Bu\}$ (**8**) (Scheme II).

**Synthesis and Structure of $HC\{(CH_3)_2SiN(Li)\text{-}t\text{-}Bu\}_3$ (9).** Reaction of **5** with 3 molar equiv of $n$-butyllithium in hydrocarbon

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(14) Merker, R. L.; Scott, M. J. *J. Org. Chem.* **1964**, *29*, 953.

(15) Work on trisilylmethane itself has been reported by: (a) Amberger, E.; Boeters, H. D. *Chem. Ber.* **1964**, *97*, 1999. (b) Morrison, J. A.; Bellama, J. M. *J. Organomet. Chem.* **1975**, *92*, 163. (c) Schmidbaur, H.; Ebenhöch, J. *Z. Naturforsch. B* **1986**, *41*, 1527. (d) Schmidbaur, H.; Dörzbach, C. *Ibid.* **1987**, *42*, 1088. (e) Schmidbaur, H.; Hager, R. *Ibid.* **1988**, *43*, 571. (f) Hager, R.; Steigelmann, O.; Müller, G.; Schmidbaur, H. *Chem. Ber.* **1989**, *122*, 2115.

(16) Whitmarsh, C. K.; Interrante, L. V. *J. Organomet. Chem.* **1991**, *418*, 69.

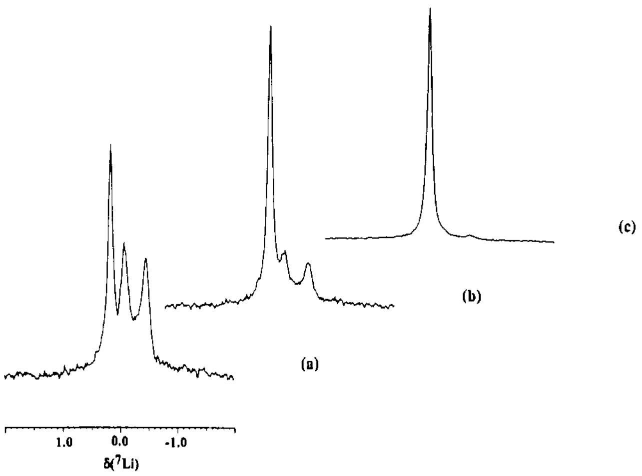
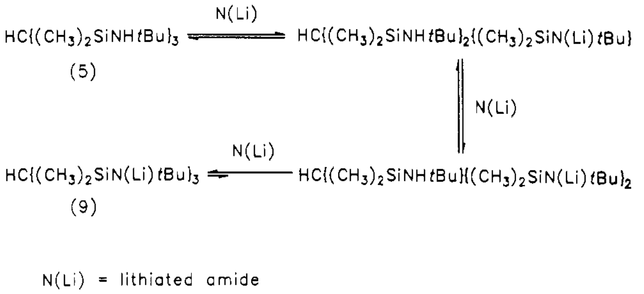


**Figure 1.** $^7$Li-NMR spectra recorded after successive addition of *n*-BuLi to a solution of **5** in $C_6D_6$: (a) 12%, (b) 33%, and (c) 100% of the required amount of *n*-BuLi (the ordinate scales of the three spectra are different).

**Scheme III.** Proposed Metal-Exchange Equilibria of Partially Lithiated **5**



solvents yielded the trilithium salt **9**. The $^1$H-, $^{13}$C-, $^{29}$Si-, and $^7$Li-NMR spectra of **9** recorded in $C_6D_6$ and toluene-$d_8$ display a resonance pattern which is consistent with a 3-fold symmetry of the compound. The same spectra recorded at 180 K (toluene-$d_8$) show no sign of exchange broadening and therefore suggest that the observed effective symmetry probably corresponds to the actual molecular symmetry in solution.

If the titration of the amine dissolved in $C_6D_6$ (295 K) with the lithiating agent is monitored by $^1$H- and $^7$Li-NMR spectroscopy, the immediate formation of **9** ($\delta(^7\mathrm{Li}) = 0.18$; external reference 1 M LiI/$H_2O$) can be observed even at the early stages of the addition of *n*-butyllithium. It has proved impossible to isolate (or even to detect greater amounts of) the corresponding mono- and dilithium salts. Only at the beginning of the addition of the lithiating reagent did the $^7$Li-NMR spectrum indicate the presence of two additional species ($\delta = -0.08$ and $-0.46$) the resonances of which diminish in intensity relative to that attributed to the trilithium salt on further metalation (Figure 1). A possible explanation for this behaviour may be the kinetic inertness of **9** to Li-exchange reactions which is a consequence of the shielding of the $(LiN)_3$ core by the ligand periphery (vide infra) as well as an inherent thermal stability of the triamide. The mono- and dilithiated species may not adopt a similarly compact structural arrangement and therefore participate in Li-exchange reactions (Scheme III).

The trilithium salt **9** may be isolated as a colorless crystalline solid from its pentane solutions. A single-crystal X-ray structure analysis has established the high molecular symmetry of the trilithium salt which was inferred from the spectral patterns found for solutions of the compound. The molecular structure of **9** and a plot of the unit cell are depicted in Figure 2, the principal bond distances and interbond angles are listed in Table II, and the positional coordinates are given in Table III.

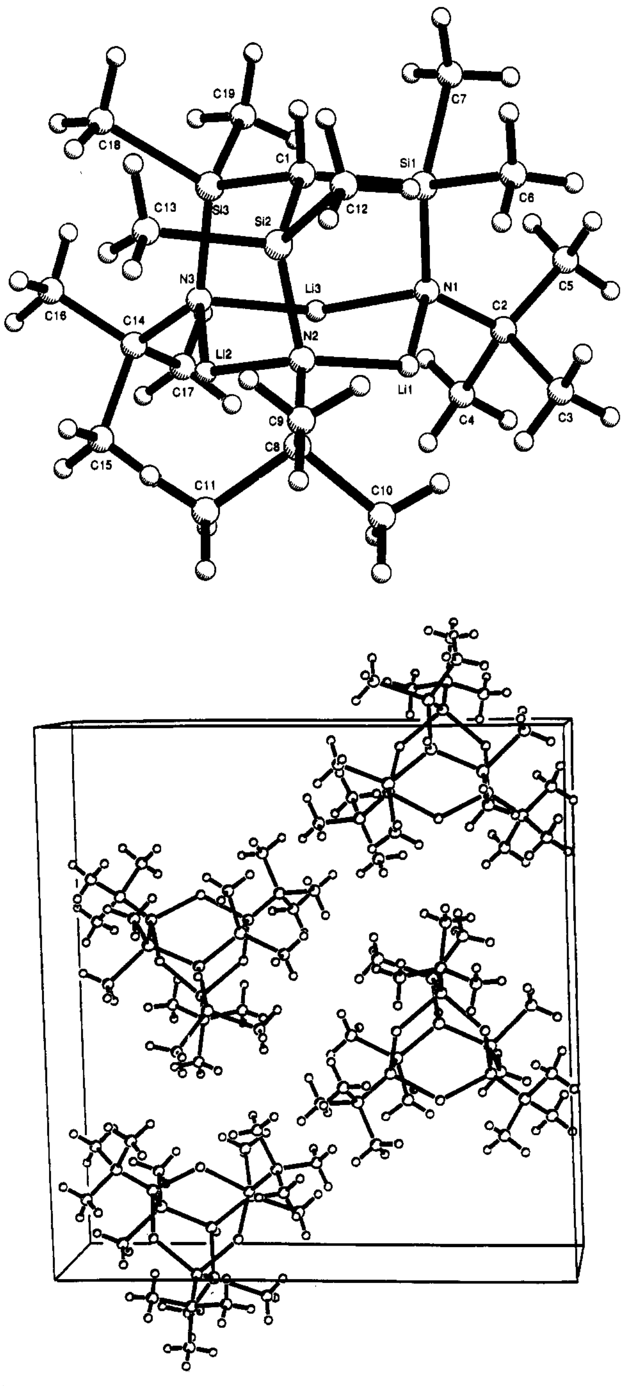


**Figure 2.** Top: (a) Molecular structure of HC{$(CH_3)_2$SiN(Li)-*t*-Bu}$_3$ (**9**). Bottom: (b) Packing of **9** in the unit cell showing the monomeric structure of the molecule.

Its structural center piece is an adamantane-related cage comprising, respectively, three Li,N, and Si atoms as well as the carbon atom at the apex of the trisilylmethane unit. Close "inorganic" analogues are the cage structures of, for example, $P_4O_6$ and $P_4O_{10}$. The molecule as packed in the crystal is slightly distorted from its idealized $C_{3v}$ symmetry. Whereas the neopentane-derived trilithium triamides referred to above were found to be dimeric aggregates,[11] **9** crystallizes as a monomer as is shown in Figure 2b. The cyclic $(LiN)_3$ unit is effectively shielded by *tert*-butyl groups on the N atoms, and we attribute the fact that dimerization does not occur to this situation, leaving the Li atoms two-coordinate. The details of the structure are best appreciated by comparison with those of $[\{(CH_3)_3Si\}_2N(Li)]_3$ (**10**) which also contains a cyclic $(LiN)_3$ unit.[17] **10** is one example of a number of trimeric aggregates of nonsolvated monofunctional amides.[4,8,18] In these structures a planar $(RR'NLi)_3$-ring (R,R'

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(17) (a) Mootz, D.; Zinnius, A.; Böttcher, B. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 378. (b) Rogers, R. D.; Atwood, J. L.; Grüning, R. *J. Organomet. Chem.* **1978**, *157*, 229.

**Table II.** Principal Bond Distances (Å) and Interbond Angles (deg) of **9**

| | | | |
|---|---|---|---|
| Si1–N1 | 1.699(6) | N2–C8 | 1.456(9) |
| Si1–C1 | 1.899(7) | N2–Li1 | 1.93(2) |
| Si1–C6 | 1.897(8) | N2–Li2 | 1.95(2) |
| Si1–C7 | 1.888(8) | N3–C14 | 1.475(9) |
| Si2–N2 | 1.689(6) | N3–Li2 | 1.89(2) |
| Si2–C1 | 1.913(7) | N3–Li3 | 1.93(2) |
| Si2–C12 | 1.853(8) | C2–C3 | 1.54(1) |
| Si2–C13 | 1.891(8) | C2–C4 | 1.54(1) |
| Si3–N3 | 1.685(6) | C2–C5 | 1.51(1) |
| Si3–C1 | 1.889(7) | C8–C9 | 1.52(1) |
| Si3–C18 | 1.883(8) | C8–C10 | 1.50(1) |
| Si3–C19 | 1.894(9) | C8–C11 | 1.53(1) |
| N1–C2 | 1.461(8) | C14–C15 | 1.51(1) |
| N1–Li1 | 1.93(2) | C14–C16 | 1.48(1) |
| N1–Li3 | 1.89(1) | C14–C17 | 1.49(1) |
| N1–Si1–C1 | 105.2(3) | Si3–N3–C14 | 128.0(6) |
| N1–Si1–C6 | 112.2(4) | Si3–N3–Li2 | 110.6(5) |
| N1–Si1–C7 | 118.2(3) | C14–N3–Li2 | 110.3(7) |
| C1–Si1–C6 | 110.7(3) | C14–N3–Li3 | 106.5(6) |
| C1–Si1–C7 | 109.6(4) | Li2–N3–Li3 | 99.8(7) |
| C6–Si1–C7 | 100.9(4) | Si1–C1–Si2 | 115.2(3) |
| N2–Si2–C1 | 106.0(3) | Si1–C1–Si3 | 115.6(3) |
| N2–Si2–C12 | 118.1(4) | Si2–C1–Si3 | 115.0(3) |
| N2–Si2–C13 | 112.1(4) | N1–C2–C3 | 111.3(7) |
| C1–Si2–C12 | 110.0(3) | N1–C2–C4 | 108.0(6) |
| C1–Si2–C13 | 109.6(4) | N1–C2–C5 | 115.7(7) |
| C12–Si2–C13 | 100.8(4) | C3–C2–C4 | 106.5(7) |
| N3–Si3–C1 | 106.0(3) | C3–C2–C5 | 108.3(7) |
| N3–Si3–C18 | 118.3(4) | C4–C2–C5 | 106.6(7) |
| N3–Si3–C19 | 111.8(4) | N2–C8–C9 | 116.7(7) |
| C1–Si3–C18 | 110.7(3) | N2–C8–C10 | 109.8(7) |
| C1–Si3–C19 | 109.6(3) | N2–C8–C11 | 110.1(7) |
| C18–Si3–C19 | 100.3(4) | C9–C8–C10 | 107.7(8) |
| Si1–N1–C2 | 127.0(5) | C9–C8–C11 | 107.1(8) |
| Si1–N1–Li1 | 96.3(5) | C10–C8–C11 | 104.8(8) |
| Si1–N1–Li3 | 111.0(5) | N3–C14–C15 | 109.0(7) |
| C2–N1–Li1 | 105.8(6) | N3–C14–C16 | 114.4(8) |
| C2–N1–Li3 | 111.0(6) | N3–C14–C17 | 112.5(8) |
| Li1–N1–Li3 | 101.0(7) | C15–C14–C16 | 104.2(9) |
| Si2–N2–C8 | 127.8(5) | C15–C14–C17 | 106(1) |
| Si2–N2–Li1 | 110.3(5) | C16–C14–C17 | 110.1(9) |
| Si2–N2–Li2 | 96.5(6) | N1–Li1–N2 | 124.7(8) |
| C8–N2–Li1 | 110.6(7) | N2–Li2–N3 | 125.7(8) |
| C8–N2–Li2 | 108.9(7) | N1–Li3–N3 | 123.6(8) |
| Li1–N2–Li2 | 97.2(7) | | |

= alkyl, aryl, silyl) is shielded by the R and R′ groups which project above and below the $(LiN)_3$ ring and thus inhibit the stacking of these units (Scheme IV).

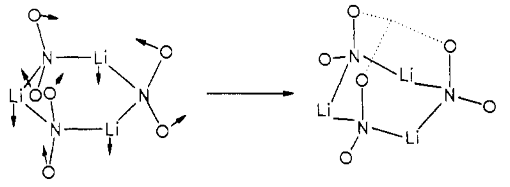
In **9** the three R groups on one side of the plane are drawn towards each other and "stitched" together by the trisilylmethane carbon atom. The lone pairs on the amido N atoms are moved out of the plane and, consequently, the $(LiN)_3$ ring adopts a puckered conformation with torsion angles Li–N–Li′–N′ lying in the range 53–56°. The Li–N distances in **9** ($d_{av}$(Li–N) = 1.92 Å) are significantly shorter than those found in **10** ($d_{av}$(Li–N) = 2.00 Å) but well within the range found in other ring structures ($[\{PhCH_2\}_2NLi]_3$, $d_{av}$(Li–N) = 1.95 Å;[8] $[\{(CH_3)_3Ge\}_2NLi]_3$, $d_{av}$(Li–N) = 1.92 Å).[18] The Li–N–Li angles vary between 97.2 and 101.0° (**10**: 90.4–94.1°) and the corresponding N–Li–N angles lie between 123 and 125° (**10**: 144.0–150°).

The 2-fold coordination of the lithium atoms in organolithium compounds is frequently associated with close intramolecular "agostic" Li···H–C contacts[9a] which, for example, in $[\{PhCH_2\}_2NLi]_3$ are thought to influence the structural arrangement of the benzyl groups.[8] The distances between some of the hydrogen atoms on the methyl groups in **9** are as short as 2.35 Å (shortest $d$(CH···Li) in $[\{PhCH_2\}_2NLi]_3$, 2.32 Å). There are, however, no appreciable structural implications of this situation, and we therefore regard these CH···Li contacts to be of little significance for the overall structure of **9**.

**Table III.** Positional Coordinates of **9**

| atom | *x* | *y* | *z* |
|---|---|---|---|
| Si1 | 0.1579(1) | 0.2081(3) | 0.0858(1) |
| Si2 | 0.2636(1) | 0.3184(3) | –0.0433(1) |
| Si3 | 0.3413(1) | 0.2230(3) | 0.1070(1) |
| N1 | 0.1543(3) | 0.3847(6) | 0.1282(3) |
| N2 | 0.2416(3) | 0.5070(7) | –0.0232(3) |
| N3 | 0.3476(3) | 0.4163(7) | 0.1268(3) |
| C1 | 0.2560(4) | 0.2024(8) | 0.0435(3) |
| C2 | 0.0905(5) | 0.447(1) | 0.1686(5) |
| C3 | 0.0368(5) | 0.550(1) | 0.1215(5) |
| C4 | 0.1242(5) | 0.557(1) | 0.2270(5) |
| C5 | 0.0420(5) | 0.326(1) | 0.2060(5) |
| C6 | 0.0783(4) | 0.186(1) | 0.0158(4) |
| C7 | 0.1437(5) | 0.023(1) | 0.1399(5) |
| C8 | 0.2370(5) | 0.641(1) | –0.0713(4) |
| C9 | 0.2283(7) | 0.605(1) | –0.1504(5) |
| C10 | 0.1709(6) | 0.746(1) | –0.0516(5) |
| C11 | 0.3085(6) | 0.745(1) | –0.0616(6) |
| C12 | 0.2068(5) | 0.220(1) | –0.1151(4) |
| C13 | 0.3642(5) | 0.299(1) | –0.0783(5) |
| C14 | 0.4049(5) | 0.496(1) | 0.1736(5) |
| C15 | 0.4257(6) | 0.652(1) | 0.1410(6) |
| C16 | 0.4793(6) | 0.412(1) | 0.1812(6) |
| C17 | 0.3742(7) | 0.533(2) | 0.2451(6) |
| C18 | 0.4284(5) | 0.122(1) | 0.0705(5) |
| C19 | 0.3254(5) | 0.099(1) | 0.1890(4) |
| Li1 | 0.1594(9) | 0.513(2) | 0.0437(8) |
| Li2 | 0.326(1) | 0.540(2) | 0.0449(8) |
| Li(3) | 0.2500(8) | 0.433(2) | 0.1733(8) |

**Scheme IV.** Structural Relationship Between $[\{(CH_3)_3Si\}_2N(Li)]_3$ (**10**) and $HC\{(CH_3)_2SiN(Li)\text{-}t\text{-}Bu\}_3$ Where Silyl and *tert*-Butyl Units Are Schematically Drawn as Circles



10 9

**Synthesis and Structure of $HC\{(CH_3)_2SiN(Li)\text{-}t\text{-}Bu\}_3\cdot 2THF$ (11).** The structural relationship between **9** and $[\{(CH_3)_3Si\}_2N(Li)]_3$ (**10**) has been discussed in the previous section. If $\{(CH_3)_3Si\}_2NH$ is lithiated in donor solvents such as $Et_2O$ or THF, the solvated species is $[\{(CH_3)_3Si\}_2NLi(S)]_2$ (S = $Et_2O$ or THF); i.e., the trimeric structure of **10** is broken up to give the dimeric structure of its solvate.[19] This behavior has been attributed to the wider coordination arc for the attachment of the donor molecule in the dimeric than in a trimeric structure.[4,9a] Since the trisilylmethane backbone in **5** prohibits a similar structural rearrangement and reduction of the degree of aggregation, it was of interest to study the structural implications of its metalation in the presence of a donor solvent.

If the lithiation of **5** is performed in THF instead of hydrocarbon solvents and the clear pale yellow solution obtained is carefully layered with pentane, the THF solvate of the trilithium salt is obtained in large colorless crystals. The signal patterns in the $^1H$-, $^{13}C$-, $^{29}Si$-, and $^7Li$-NMR spectra recorded at ambient temperature are similar to those of **9**, albeit shifted and including a set of resonances due to coordinated THF, and thus suggested a 3-fold symmetry of the molecule. However, the analytical data are only compatible with the formulation of this compound as $HC\{(CH_3)_2SiN(Li)\text{-}t\text{-}Bu\}_3\cdot 2THF$ (**11**), i.e. the bis-THF adduct. Since this formula is inconsistent with an overall 3-fold symmetry

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(18) Rannenberg, M.; Hausen, H.-D.; Weidlein, J. *J. Organomet. Chem.* **1989**, *320*, C27.

(19) (a) Lappert, M. F.; Slade, M. J.; Singh, A.; Atwood, J. L.; Poogers, R. D.; Shakir, R. *J. Am. Chem. Soc.* **1983**, *105*, 302. (b) Engelhardt, L. M.; May, A. S.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 1671. (c) Engelhardt, L. M.; Jolly, B. S.; Junk, P. C.; Raston, C. L.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1986**, *39*, 1337.

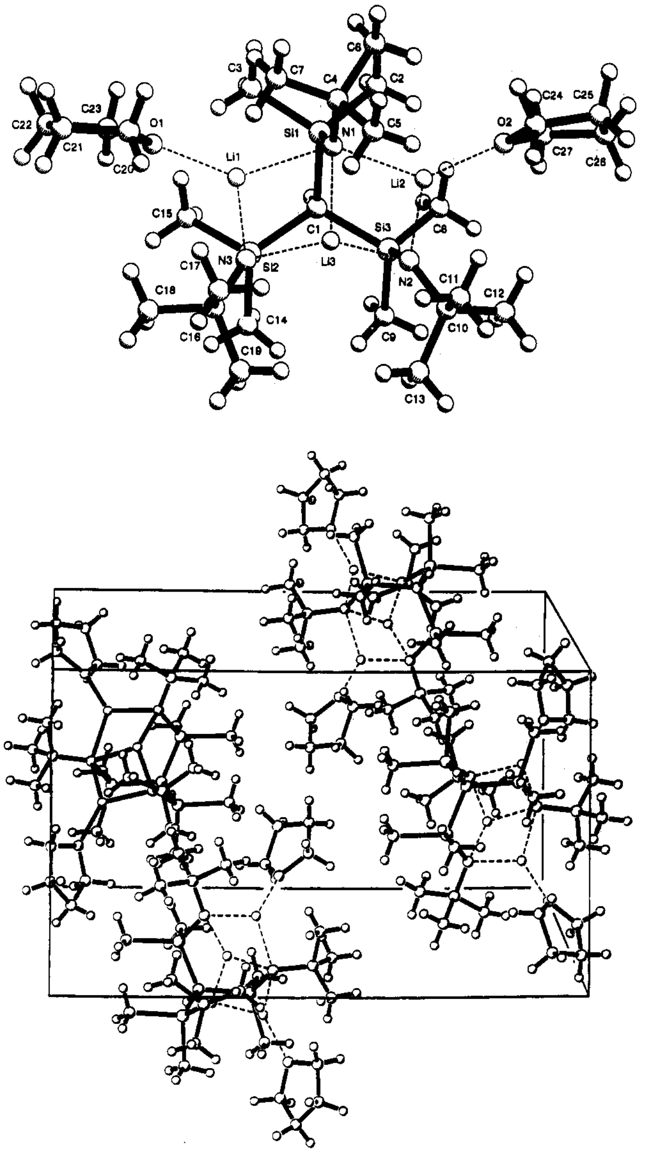

**Figure 3.** Top: (a) Molecular structure of **11**. Bottom: (b) Packing of **11** in the unit cell of the crystal.

of the molecule as deduced from the NMR spectra at room temperature, the system must be dynamic and the resonance patterns observed those representing the regime of fast chemical exchange. Indeed, cooling a solution of **11** in toluene-$d_8$ to 180 °C leads to a considerable exchange broadening of the signals in the $^1$H- and $^7$Li-NMR spectra. Unfortunately, the exchange processes were not frozen out under these conditions, and the molecular structure could thus not be established by NMR spectroscopy.

The structural implications of this somewhat unexpected formulation of **11** therefore had to be elucidated by a single-crystal X-ray structure analysis of the compound. Its molecular structure in the crystal and a plot of the unit cell are depicted in Figure 3, while the principal bond distances and interbond angles as well as the positional coordinates are listed in Tables IV and V. The molecule has idealized $C_s$ point symmetry which is slightly distorted in the solid, the virtual mirror plane being spanned by C1, Si1, N1, and Li3. The three nitrogen centers of the triamide adopt a tripodal arrangement and lie at the corners of an almost regular triangle similar to the arrangement in **9**. Two THF-solvated lithium atoms, Li1 and Li2, bridge two edges of this triangle (N1–N3 and N1–N2, respectively) but are drawn away from its center, while the third Li atom which bridges the N2–N3 edge leans over to form an additional contact with N1 ($d$(Li3–N1) = 2.07 Å) thus generating an unprecedented $(LiN)_3$ array (Scheme V). The structure of **11** may thus be viewed as centering on the "concave" (N2–Li3–N3) angle [138.7(6)°], whereas the environments of Li1 and Li2 (and all Li of **9**) are "convex". The *tert*-butyl group attached to N1 retains the radial orientation observed in the structure of **9** whereas those on N2 and N3 turn away from the coordinated THF molecules, thus closing the gap for a potential third THF-molecule coordinating to Li3.

**Table IV.** Principal Bond Distances (Å) and Interbond Angles (deg) of **11**

| | | | |
|---|---|---|---|
| Si1–N1 | 1.700(4) | N1–C4 | 1.479(7) |
| Si1–C1 | 1.898(6) | N1–Li1 | 2.28(1) |
| Si1–C2 | 1.889(7) | N1–Li2 | 2.17(1) |
| Si1–C3 | 1.901(7) | N1–Li3 | 2.07(1) |
| Si2–N3 | 1.687(5) | N2–C10 | 1.462(7) |
| Si2–C1 | 1.916(6) | N2–Li2 | 1.98(1) |
| Si2–C14 | 1.904(8) | N2–Li3 | 2.00(1) |
| Si2–C15 | 1.883(7) | N3–C16 | 1.463(8) |
| Si3–N2 | 1.692(5) | N3–Li1 | 1.96(1) |
| Si3–C1 | 1.923(6) | N3–Li3 | 1.98(1) |
| Si3–C8 | 1.881(7) | C4–C5 | 1.54(1) |
| Si3–C9 | 1.898(7) | C4–C6 | 1.525(9) |
| O1–C20 | 1.42(1) | C4–C7 | 1.53(1) |
| O1–C23 | 1.399(9) | C10–C11 | 1.53(1) |
| O1–Li1 | 2.06(1) | C10–C12 | 1.532(9) |
| O2–C24 | 1.420(8) | C10–C13 | 1.53(1) |
| O2–C27 | 1.429(8) | C16–C17 | 1.52(1) |
| O2–Li2 | 2.00(1) | C16–C18 | 1.52(1) |
| | | C16–C19 | 1.50(1) |
| N1–Si1–C1 | 106.8(2) | Si3–N2–Li2 | 107.4(4) |
| N1–Si1–C2 | 115.0(3) | Si3–N2–Li3 | 97.1(4) |
| N1–Si1–C3 | 113.0(3) | C10–N2–Li2 | 114.6(5) |
| C1–Si1–C2 | 109.6(3) | C10–N2–Li3 | 122.0(5) |
| C1–Si1–C3 | 110.6(3) | Li2–N2–Li3 | 77.6(5) |
| C2–Si1–C3 | 101.8(4) | Si2–N3–C16 | 127.6(4) |
| N3–Si2–C1 | 105.9(2) | Si2–N3–Li1 | 108.5(4) |
| N3–Si2–C14 | 116.6(3) | Si2–N3–Li3 | 96.3(4) |
| N3–Si2–C15 | 116.1(3) | C16–N3–Li1 | 112.6(5) |
| C1–Si2–C14 | 112.9(3) | C16–N3–Li3 | 121.1(5) |
| C1–Si2–C15 | 107.9(3) | Li1–N3–Li3 | 80.6(5) |
| C14–Si2–C15 | 97.2(4) | Si1–C1–Si2 | 114.8(3) |
| N2–Si3–C1 | 106.1(2) | Si1–C1–Si3 | 113.6(3) |
| N2–Si3–C8 | 115.5(3) | Si2–C1–Si3 | 115.5(3) |
| N2–Si3–C9 | 117.7(3) | N1–C4–C5 | 107.8(5) |
| C1–Si3–C8 | 108.4(3) | N1–C4–C6 | 114.0(6) |
| C1–Si3–C9 | 112.1(3) | N1–C4–C7 | 112.8(6) |
| C8–Si3–C9 | 96.8(4) | C5–C4–C6 | 104.6(7) |
| Si1–N1–C4 | 127.7(4) | C5–C4–C7 | 108.0(7) |
| Si1–N1–Li1 | 92.1(3) | C6–C4–C7 | 109.1(7) |
| Si1–N1–Li2 | 98.4(4) | N2–C10–C11 | 108.4(5) |
| Si1–N1–Li3 | 97.3(3) | N2–C10–C12 | 111.8(5) |
| C4–N1–Li1 | 99.9(4) | N2–C10–C13 | 113.4(6) |
| C4–N1–Li2 | 101.5(5) | C11–C10–C12 | 109.4(6) |
| C4–N1–Li3 | 134.9(5) | C11–C10–C13 | 106.7(6) |
| Li1–N1–Li2 | 142.8(4) | C12–C10–C13 | 106.9(6) |
| Li1–N1–Li3 | 71.5(4) | N3–C16–C17 | 107.9(6) |
| Li2–N1–Li3 | 71.7(4) | N3–C16–C18 | 111.4(7) |
| Si3–N2–C10 | 126.9(4) | N3–C16–C19 | 114.0(6) |
| C17–C16–C18 | 108.5(7) | O2–Li2–N1 | 135.0(6) |
| C17–C16–C19 | 107.2(7) | O2–Li2–N2 | 124.4(6) |
| C18–C16–C19 | 107.6(7) | N1–Li2–N2 | 100.4(5) |
| O1–Li1–N1 | 140.8(6) | N1–Li3–N2 | 103.1(5) |
| O1–Li1–N3 | 121.0(6) | N1–Li3–N3 | 104.5(5) |
| N1–Li1–N3 | 97.9(5) | N2–Li3–N3 | 138.7(6) |

This arrangement generates a four-coordinate environment for N2 and N3 while N1 is bonded to all three lithium atoms and thus displays a remarkable 5-fold coordination reminiscent of that found previously by us[11] and others[20] in dimeric di- and trilithium amides and, more frequently, in oligomeric iminolithium aggregates.[21] The bonding within the $(LiN)_3$ framework is to be viewed as primarily ionic in nature,[9a] and it is in this light that the hypercoordinate nitrogen should be seen.

The Li–N distances found in this structure vary widely but basically fall into two categories, those lying in the range 1.96–2.07 Å, which are comparable to those normally found in

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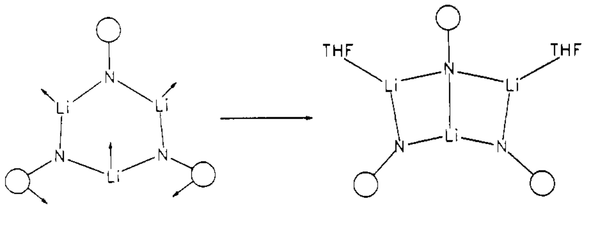
**Table V.** Positional Coordinates of **11**

| atom | *x* | *y* | *z* |
|---|---|---|---|
| Si1 | 0.6104(2) | 0.1201(1) | 0.8434(1) |
| Si2 | 0.6408(2) | 0.2496(1) | 0.7274(1) |
| Si(3) | 0.4457(2) | 0.2550(1) | 0.8343(1) |
| O1 | 0.7418(4) | 0.0548(3) | 0.6233(3) |
| O2 | 0.2469(4) | 0.0645(2) | 0.8645(3) |
| N1 | 0.5102(4) | 0.0789(2) | 0.7673(3) |
| N2 | 0.3402(4) | 0.2095(2) | 0.7674(3) |
| N3 | 0.5686(4) | 0.1988(2) | 0.6487(3) |
| C1 | 0.5926(5) | 0.2180(3) | 0.8224(4) |
| C2 | 0.5971(7) | 0.1009(4) | 0.9513(4) |
| C3 | 0.7668(6) | 0.0915(4) | 0.8492(5) |
| C4 | 0.4912(6) | 0.0024(3) | 0.7550(4) |
| C5 | 0.3657(8) | −0.0087(4) | 0.7013(5) |
| C6 | 0.4945(9) | −0.0382(4) | 0.8340(5) |
| C7 | 0.576(1) | −0.0315(4) | 0.7110(7) |
| C8 | 0.4427(6) | 0.2480(5) | 0.9457(4) |
| C9 | 0.4406(7) | 0.3545(4) | 0.8278(5) |
| C10 | 0.2210(6) | 0.2331(4) | 0.7295(4) |
| C11 | 0.1537(6) | 0.1721(5) | 0.6804(5) |
| C12 | 0.1574(6) | 0.2575(4) | 0.7940(5) |
| C13 | 0.2157(7) | 0.2938(4) | 0.6692(5) |
| C14 | 0.6260(8) | 0.3486(4) | 0.7117(5) |
| C15 | 0.8055(6) | 0.2454(5) | 0.7520(5) |
| C16 | 0.5429(7) | 0.2146(4) | 0.5606(5) |
| C17 | 0.4861(8) | 0.1497(5) | 0.5139(4) |
| C18 | 0.6536(9) | 0.2314(5) | 0.5338(5) |
| C19 | 0.4595(8) | 0.2748(5) | 0.5346(5) |
| C20 | 0.726(1) | 0.0008(6) | 0.5633(7) |
| C21 | 0.827(1) | 0.0015(6) | 0.5272(6) |
| C22 | 0.9175(8) | 0.0423(6) | 0.5805(6) |
| C(23) | 0.8619(8) | 0.0692(6) | 0.6459(6) |
| C24 | 0.1667(9) | 0.0081(5) | 0.8410(6) |
| C25 | 0.0904(8) | 0.0047(5) | 0.8996(6) |
| C26 | 0.118(1) | 0.0638(6) | 0.9519(6) |
| C27 | 0.2362(8) | 0.0880(4) | 0.9432(5) |
| Li1 | 0.6167(9) | 0.1006(6) | 0.6732(6) |
| Li2 | 0.353(1) | 0.1103(6) | 0.8035(7) |
| Li3 | 0.443(1) | 0.1681(5) | 0.7010(6) |

**Scheme V.** Ring–Ladder Interconversion on Solvation of **9** with Two THF Molecules Generating **11** (View along an Axis Perpendicular to the $Li_3N_3$ Unit) Where *tert*-Butyl Groups Are Schematically Represented by Circles



9

11

nonsolvated and solvated Li–amides,[3-9] and two long distances, Li1–N1 and Li2–N1 (2.28 and 2.17 Å, respectively). The latter may be an indirect consequence of the steric repulsion between the two Li-bonded THF molecules and the *tert*-butyl group on N1 which draws the Li atoms away from N1. Another manifestation of this situation is the increase of the Li–O(THF) distances (*d*(Li1–O1) = 2.06(1) Å and *d*(Li2–O2) = 2.00(1) Å) in comparison to those found in $[\{(CH_3)_2Si\}_2NLi(THF)]_2$ (*d*(Li–O) = 1.88 Å),[19c] $[\{Ph_3Si\}_2NLi(THF)_2]$ (*d*(Li–O) = 1.95 Å),[21] and $[\{Ph_2(CH_3)Si\}_2NLi(THF)_2]$ (*d*(Li–O) = 1.91 Å).[22]

The rearrangement of the $(LiN)_3$ unit which accompanies the solvation of **9** (yielding **11**) may be viewed as a conversion of a ring to a ladder array. The relationship between rings and ladders in lithium amides and the structural preferences for various solvated and nonsolvated species have been theoretically studied for the idealized system $(LiNH_2)_4(H_2O)_m$ ($m$ = 0, 2, 4).[9a,23] Here, ladder structures are favored if solvation of the outer lithium atoms is assumed, while ring structures are energetically more favorable in nonsolvated compounds. Snaith et al. have reported the crystal structures of $\{[H_2C(CH_2)_3NLi]_3 \cdot PMDETA\}_2$ and $\{[H_2C(CH_2)_3NLi]_2 \cdot TMEDA\}_2$ (PMDETA = pentamethyldiethylenetriamine, TMEDA = tetramethylethylenediamine) which contain tetrametric (i.e. "four-runged") LiN ladders solvated by the polydentate tertiary amine ligands at both ends.[23,24] While the theoretical considerations mentioned above may play a decisive role in the aggregation of these species, we believe that the conversion of **9** to **11** is primarily a consequence of the steric demand of the components of the system, along with the presence of a structural framework which limits the degrees of freedom of the nitrogen centers. It should be pointed out that N-ligand-containing ladder arrays of the kind described by Snaith and us find their counterparts in transition metal chemistry.[25,26] A notable example is $[(R_2TaN)_5(NH_3)]$ in which the Lewis base $NH_3$ also coordinates to an end metal of the ladder.[26]

Steric shielding of the $(LiN)_3$-unit by the bulky *tert*-butyl moieties is probably the reason for the apparent instability of the tris-THF solvate, which we would expect to have an overall 3-fold molecular symmetry. Attempts to generate the species by evaporation of a solution of **11** in THF yield materials the analytical data of which are consistent with the presence of a mixture of **11** and the tris-THF solvate. We have thus far not been able to adequately characterize the latter.

## Conclusions

The aim of this study was the synthesis of trifunctional lithium amides containing a trisilylmethane backbone which may adopt a tripodal geometry and the study of the structural implications this amino-functionalized framework has for both the corresponding nonsolvated and solvated amidolithium compounds. The latter was of particular interest since solvated monofunctional amides normally exhibit a lower degree of aggregation than the nonsolvated species, a situation which was precluded in the systems studied here. Indeed, the coordination of THF molecules to two of the Li atoms in **11** leads essentially to a mere rearrangement of the $(LiN)_3$ core giving a thus far unique structural array for such a system. With the synthesis and characterization of these species, a new type of tridentate amido ligand is now available for the synthesis of, particularly, early transition metal complexes. Such work is currently underway.

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**Supplementary Material Available:** Tables of positional and thermal parameters, interatomic distances and angles, and torsion angles for **9** and **11** (25 pages). Ordering information is given on any current masthead page.

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