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Preparation and Solid State Structures of Tetra(amino)silane Organolithium Compounds Containing a Li_8 Core Forming a Johnson Solid J26 and a Li_4 Core

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Tris(dimethylamino)silyl substituted aniline HNPh{Si(NMe_2)$_3$} (**1**) was prepared in high yield by metathesis reaction of lithium anilide with tris(dimethylamino)chlorosilane. **1** reacts with 1 equiv of *n*-butyl lithium at elevated temperatures to yield the corresponding lithium salt [LiNPh{Si(NMe_2)$_3$}] (**2**). Treatment of **1** with 2 equiv of *n*-butyl lithium leads to dilithiated compounds [$Li_2N(C_6H_4)$\{Si(NMe_2)$_3$\}]$_4$ (**3a**) or [$Li_2(THF)_2N(C_6H_4)$\{Si(NMe_2)$_3$\}]$_2$ (**3b**) depending on the solvent used for crystallization, the former being crystallized in heptane, the latter in tetrahydrofuran (THF). Single crystal analyses of **3a** and **3b** confirm the occurrence of two lithium atoms per ligand, where the anilino nitrogen atom and one ortho carbon atom of the phenyl group are deprotonated. In both cases organolithium compounds with polynuclear lithium cores are formed. The molecular structure of **3a** represents the first example of an organolithium compound consisting of a Li_8 core that forms a polyhedron in which two trigonal prisms share one square face and are twisted by 90°. Such a polyhedron is known in mathematics as the Johnson solid J26 or as Gyrobifastigium and is rare in chemistry. The coordinating carbon atoms are situated above the other square faces with three close contacts and one slightly longer contact to four lithium atoms. Furthermore, the central four lithium atoms form an Li_4N_4 square with almost linear N−Li−N bonds, a rare structural situation. The molecular structure of **3b** shows each lithium atom to be additionally coordinated by a molecule of THF compared to that of **3a**. Thus, a dimeric structure is found with a Li_4 core that forms a planar parallelogram. The carbon atoms are found in close contact to a triangular Li_3 face on each side of the Li_4 plane.

Introduction

There is an increasing interest in compounds of silicon that are bound to a maximum number of nitrogen atoms because of their potential use as single source precursors for the chemical preparation of nitride silicates.[1−10] These silicon amides offer the possibility to obtain the inorganic materials at lower temperatures by sol−gel techniques. Nitrogen has a significant influence on the properties leading to a dramatic increase of hardness and thermal stability compared to oxide-based materials, the majority of materials prepared by sol−gel techniques. The first report of the use of a tetraamido silane, $(Me_2N)_3SiNH_2$, as a sol−gel precursor was published in 1999 leading to silicon nitride materials exhibiting mesoporous structures with high surface area and narrow pore size distribution.[11,12] The high lability of the $(Me_2N)_3Si$ group seems to be essential for a controlled reaction.[8,13−16]

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For this reason, there is an active interest in new silicon amido compounds of the type $(Me_2N)_3SiNHR$ that are useful single source precursors, where the various R groups influence the properties of the inorganic material. Furthermore, corresponding lithium salts of the type $(Me_2N)_3SiNRLi$ represent convenient reagents for the introduction of additional metal centers into the final material.

Although a plethora of lithium amido chemistry is known in the literature,[17−22] only a limited number of compounds of the type $(Me_2N)_3SiNR_2$ and lithium derivatives thereof have been structurally characterized. The first crystal structure of such a ternary amido silicon unit, the bulky disilazane $[(Me_2N)_3Si]NHSiMe_3$, was reported in 1993.[9] $[(Me_2N)_3SiNHLi]_4$ was prepared by lithiation of $(Me_2N)_3SiNH_2$, and its crystal structure was found displaying an unusual ladder-type structure consisting of seven four-membered rings.[10] Chivers and co-workers reported a series of lithium derivatives of homoleptic polyimido anions containing p-block element centers including the first preparation of the tetrasilicate $[(Et_2O)Li]_4[Si\{N(naph)\}_4]$.[23−25] Jansen and co-workers used $(Me_2N)_2Si(NLiR)_2$ ($R = CMe_3, SiMe_3$)[26] as single source precursors for subsequent conversion with transition metals.[27−29]

Here, we report the preparation of a silyl compound bound to four nitrogen atoms, tris(dimethylamido)anilinosilane (**1**), and its reactivity toward lithiation. Meeting carefully the stoichiometric requirements, we find that **1** can be converted into its monolithium salt lithium tris(dimethylamino)anilidosilane (**2**) or into its dilithium salt, dilithium tris(dimethylamino)anilidosilane (**3**). Depending on the solvent used for crystallization two different X-ray crystal structures $[Li_2N(C_6H_4)\{Si(NMe_2)_3\}]_4$ (**3a**) and $[Li_2(THF)_2N(C_6H_4)\{Si(NMe_2)_3\}]_2$ (**3b**) were determined exhibiting Li_8 and Li_4 core structures, respectively.

Experimental Section

All manipulations were carried out under argon using standard Schlenk techniques or an argon glovebox. All used solvents were purified via a solvent purification system and additionally passed over aluminum oxide. Celite and aluminum oxide were purchased from commercial sources and dried in vacuo at 300 °C.

All ^1H and ^{13}C NMR spectra were recorded at 360 MHz using a Bruker AMX 360 spectrometer. All ^7Li NMR spectra were recorded at 117 MHz using a Varian Mercury Plus spectrometer at the Institute of Inorganic Chemistry at the University of Technology in Graz. Chemical shift values are given in ppm, which have been referenced to external standards (Me_4Si for ^1H and ^{13}C NMR and LiCl in D_2O for ^7Li NMR). All deuterated solvents were purchased from Deuterio GmbH and first passed over aluminum oxide and dried over molecular sieves. Elemental analyses were carried out using a Heraeus Vari Elementar automatic analyzer at the Institute of Inorganic Chemistry at the University of Technology in Graz. Mass spectra have been measured on an Agilent 5973 MSD-Direct Probe mass spectrometer using the EI ionization technique.

The starting materials *n*-butyl lithium (1.6 M in hexane), tris(dimethylamino)chlorosilane, and aniline were purchased from commercial sources.

Synthesis of $HNPh\{Si(NMe_2)_3\}$ (1). To a solution of aniline (1.8 mL, 20.4 mmol) in a mixture of pentane and tetrahydrofuran (THF, 45:5, 50 mL) was added *n*-BuLi (12.7 mL, 1.6 M in hexane, 20.4 mmol). A white precipitate was immediately formed. After the mixture was stirred for an additional 30 min, the precipitate was separated from the solvent, washed with pentane, and redissolved in a mixture of pentane and THF (4:1, 50 mL). Tris(dimethylamino)chlorosilane (4.1 mL, 20.4 mmol) was added, and the reaction mixture was heated under stirring at 50 °C for 3 h. After cooling to room temperature, the stirring was continued overnight. The suspension was filtered to remove LiCl, and the solvents were evaporated. The crude product was purified by vacuum distillation (90 °C at 1 mbar) giving **1** as a yellow clear oil (4.3 g, 84%). Anal. Calcd for $C_{12}H_{24}N_4Si$: C, 57.10; H, 9.58; N, 22.19. Found: C, 57.30; H, 9.40, N, 22.64%. ^1H NMR, (benzene-*d*$_6$): δ 2.47 (s, 18H, $N(CH_3)_2$), 3.29 (s, 1H, N*H*), 6.71 (d, 2H, Ar), 6.76 (t, 1H, Ar), 7.17 (t, 2H, Ar). ^{13}C NMR (benzene-*d*$_6$): δ 37.8 ($N(CH_3)_2$), 116.9, 118,1, 129.4, 147.6. MS (EI): *m/z* (%) 252 (100) [M^+], 208 (90) [$M^+ - NMe_2$].

Synthesis of $[LiNPh\{Si(NMe_2)_3\}]$ (2). To a solution of **1** (1.70 g, 6.7 mmol) in 40 mL of heptane was added *n*-BuLi (4.2 mL, 1.6 M in hexane, 6.7 mmol) via syringe. The colorless solution was stirred at 80 °C for 5 h. After cooling the reaction mixture to ambient temperature, the formed white precipitate was filtered and washed with pentane and dried in vacuo yielding 1.61 g (93%) of **2**. Anal. Calcd for $C_{12}H_{23}N_4LiSi$: C, 55,79; H, 8.97; N, 21.68. Found: C, 55.55; H, 8.85, N, 21.84%. ^1H NMR (benzene-*d*$_6$): δ 2.89 (s, 18H, NMe_2), 6.37 (t, 1H, Ar), 6.71 (d, 2H, Ar), 7.06 (t, 2H, Ar).

Synthesis of $[Li_2N(C_6H_4)\{Si(NMe_2)_3\}]_4$ (3a). To a solution of **1** (0.18 g, 0.7 mmol) in heptane (30 mL) was added *n*-BuLi (0.9 mL, 1.6 in hexane, 1.4 mmol). The reaction mixture was heated under stirring at 70 °C for 5 h and subsequently cooled to room temperature. After 2 weeks colorless crystals of **3a** were formed that were filtered off and dried in vacuo (0.14 g, 77%). Anal. Calcd for $C_{12}H_{22}N_4Li_2Si \cdot 0.15C_7H_{16}$: C, 56.11; H, 8.80; N, 20.06. Found: C, 56.29; H, 8.71, N, 20.86%. ^1H NMR (benzene-*d*$_6$): δ 2.27 (s, 18H, NMe_2), 6.97 (m, 2H, Ar), 7.25 (dd, 1H, Ar), 8.04 (d, 1H,

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Ar). ^{13}C NMR (benzene-d_6): δ 39.5, 121.3, 130.7, 142.9, 165.3, 182.5. ^7Li NMR (toluene-d_8, 0.09 mol/L, rt): δ 2.46. ^7Li NMR (toluene-d_8, 0.09 mol/L, −90 °C): δ 2.22, 2.47.

Synthesis of [$Li_2(THF)_2N(C_6H_4)\{Si(NMe_2)_3\}]_2$ (3b). To a solution of **1** (0.22 g, 0.9 mmol) in heptane (30 mL) was added *n*-BuLi (1.1 mL, 1.6 in hexane, 1.7 mmol). The reaction mixture was heated under stirring at 70 °C for 7 h and subsequently cooled to room temperature resulting in a white suspension. All volatiles were removed under reduced pressure. The white residue was dissolved in 3 mL of hot THF, and compound **3b** crystallized at −20 °C after a few days as colorless plates that were filtered and dried in vacuo (0.10 g, 43%). The dried compound gave identical spectroscopic data to **3a**.

X-ray Structure Determinations. All the measurements were performed using graphite-monochromatized Mo Kα radiation (α = 0.71073 Å) at 95 K using a Bruker Smart Apex diffractometer. The structures were solved by direct methods (SHELXS-97)[30] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).[31] All non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the phenyl ring were put at the external bisector of the C−C−C angle at a C−H distance of 0.95 Å, and a common isotropic displacement parameter was refined.

Diffraction Data for 3a. The heptane molecules are disordered over four orientations and were refined with site occupation factors of 0.25 and with one isotropic displacement parameter for the C atoms. The C−C bonds in this solvent molecule were restrained to 1.54 Å. The H atoms of the heptane molecules were included at calculated positions with their isotropic displacement parameters fixed to 1.2 (CH_3 groups 1.3) times U_{eq} of the C atom to which they are bonded. The C−H distances were fixed to 0.98 and 0.99 Å for the primary and secondary hydrogen atoms, respectively. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with tetrahedral angles, enabling rotation around the X-C bond, and C−H distances of 0.98 Å.

Diffraction Data for 3b. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with tetrahedral angles, enabling rotation around the N−C bond, and C−H distances of 0.98 Å. The H atoms of the CH_2 groups of the THF molecules were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with approximately tetrahedral angles and C−H distances of 0.99 Å.

Results and Discussion

Preparation of Tris(dimethylamino)anilinosilane (1). Reaction of tris(dimethylamino)chlorosilane with 1 equiv of lithium anilide at 50 °C for 3 h gave, after workup, a yellow clear oil of tris(dimethylamino)anilinosilane HNPh{$Si(NMe_2)_3$} (**1**) in high yield (eq 1). Product **1** was characterized by ^1H and ^{13}C NMR spectroscopy, where the protons of the three dimethyl amino groups give rise of a singlet resonance at 2.47 and 37.8 ppm, respectively. The resonance for the NH proton in the ^1H spectrum is found at 3.29 ppm. Elemental analysis and electron impact mass spectrometry confirm the composition.

1

(1)

Anilino compounds with a tris(dimethylamino) substituent are rare. Only one other example has previously been reported in 1997 by Schmidbaur and co-workers, where the aniline is substituted by two fluoro substituents leading to 2,4-difluoroanilinotris(dimethylamino)silane.[32−34] No further reactivity of this amine was investigated, and no structural information was reported.

Lithiation of Tris(dimethylamino)anilinosilane (1). Treatment of **1** with 1 or 2 equiv of *n*-butyl lithium afforded the monolithium compound [$LiNPh\{Si(NMe_2)_3\}$] (**2**), and the dilithium compounds [$Li_2N(C_6H_4)\{Si(NMe_2)_3\}]_4$ (**3a**) and [$Li_2(THF)_2N(C_6H_4)\{Si(NMe_2)_3\}]_2$ (**3b**), respectively (Scheme 1). Thus, reaction of **1** with 1 equiv of *n*-butyl lithium in a mixture of heptane and hexane at elevated temperatures (80 °C) for 5 h afforded the monolithium compound [$LiNPh\{Si(NMe_2)_3\}$] (**2**), which can be isolated as a white powder in high yield. It can be stored at room temperature in the glovebox for several months, but exposure to ambient atmosphere leads to immediate decomposition. Characterization by ^1H spectroscopy confirms the lithiation, since the resonance for the proton at nitrogen is absent in the spectrum of **2**.

The analogous addition of *n*-butyl lithium to **1** but employing 2 equiv led to the dilithiated compound [$Li_2N(C_6H_4)\{Si(NMe_2)_3\}]_4$ (**3a**). Usual workup and crystallization in hydrocarbon solvents gave light yellow crystals of **3a**. They proved to be even more air and moisture sensitive which made their handling challenging. Strict exclusion of oxygen and water is extremely important. The structure of **3a** was investigated in solid state, as well as in solution. An X-ray diffraction analysis of a suitable single crystal revealed a tetrameric structure (vide infra). Characterization by ^1H and ^{13}C NMR spectroscopy points to a compound with the general formula [$Li_2N(C_6H_4)\{Si(NMe_2)_3\}$]. Thus, the ^1H spectrum of **3a** in benzene-d_6 shows a singlet at 2.27 ppm for the NMe_2 groups and resonances for four protons in the aromatic region between 6.94−8.05 ppm. Again, a signal for an NH proton is absent. A ^7Li NMR spectrum in toluene-d_8 at room temperature shows only one resonance at 2.46 ppm. Stepwise cooling of the sample to −90 °C leads to splitting into two signals of equal intensities at 2.47 and 2.22 ppm as depicted in Figure 1.

This is consistent with the two chemically different surroundings of the lithium atoms in the molecule. Presumably, the broader resonance found at 2.22 ppm belongs to

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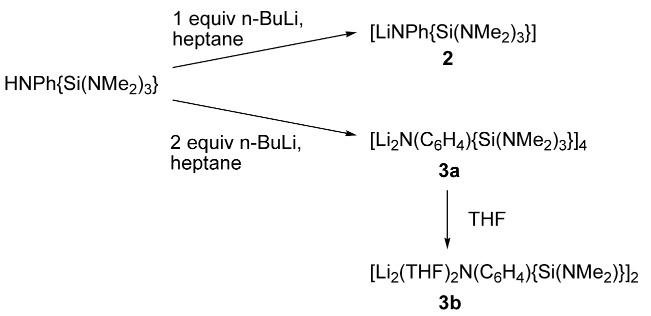
Scheme 1



the Li atom at nitrogen where either unresolved coupling or interference of the quadrupole nitrogen nucleus leads to the observed broadening. These two signals point to the formation of only one species in solution but do not allow a determination of the degree of aggregation.

Crystallization of the dilithiated material at −20 °C in the coordinating solvent THF led to the formation of another type of colorless crystals suitable for X-ray diffraction analysis that proved to be another dilithiated species but of dimeric nature with an additional molecule of THF coordinated to each lithium atom $[Li_2(THF)_2N(C_6H_4)\{Si(NMe_2)_3\}]_2$ (**3b**). The observed dilithiations in **3a** and **3b** represent C−H bond activations in the ortho position of the aniline phenyl groups and are interesting in the context of undesirable contamination of carbon in silicon nitride materials. Thus, when using aniline derivatives as potential single source precursors in combination with electrophilic metal centers, the stoichiometric requirements must be strictly met.

Crystals Structures of 3a and 3b. The crystal structures of both compounds **3a** and **3b** were determined by X-ray diffraction analyses. Crystallographic data and refinements are given in Table 1, and selected bond lengths and angles can be found in Table 2. Crystals of **3a** were obtained by slow crystallization in heptane at room temperature, whereas those of **3b** were obtained by slow crystallization in THF at −20 °C. CCDC 696812 (**3a**) and CCDC 696811 (**3b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

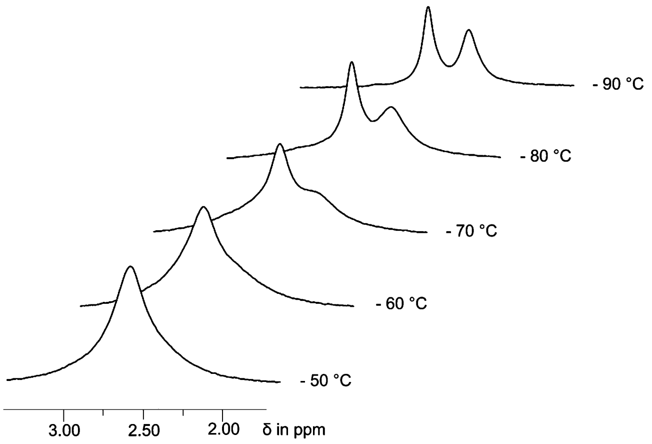


Figure 1. Variable temperature ^7Li NMR spectrum of $[Li_2N(C_6H_4)\{Si(NMe_2)_3\}]_4$ (**3a**) in toluene-d_8.

Table 1. Crystal Data and Structure Refinement for Compounds **3a** and **3b**

complex	**3a**	**3b**
empirical formula	$C_{48}H_{88}Li_8N_{16}Si_4 \cdot C_7H_{16}$	$C_{40}H_{76}Li_4N_8O_4Si_2$
Fw	1157.42	817.03
crystal description	yellow octahedron	colorless plate
crystal size	0.22 × 0.20 × 0.16 mm	0.40 × 0.40 × 0.10 mm
crystal system	tetragonal	orthorhombic
space group	$P4_22_12$	*Pbca*
a [Å]	12.999(2)	14.524(9)
b [Å]		21.881(10)
c [Å]	20.068(3)	15.076(8)
$\alpha = \beta = \gamma$ [deg]	90	90
V [Å^3]	3391.0(9)	4791(4)
Z	2	4
μ [mm^{-1}]	0.134	0.119
calculated density [mg/m^3]	1.134	1.133
θ range/deg	2.56 to 26.00	2.69 to 26.00
no. observed data collected	4994	5306
no. indep. reflns. (R_{int})	3327 [0.0221]	4681 [0.0664]
data/parameters/restraints	3327/208/12	4681/283/0
goodness-of-fit on F^2	1.056	1.029
R1,[a] wR2[b] ($I > 2\sigma(I)$)	0.0387, 0.0876	0.0792, 0.1777
R1,[a] wR2[b] (all data)	0.0461, 0.0916	0.1247, 0.2060
largest diff. peak and hole [e/Å^3]	0.310 and −0.232	0.304 and −0.365

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds **3a** and **3b**

Compound **3a**			
Li1−N1	2.180(4)	N1−Li1−N3	77.07(12)
Li1−N3	2.135(4)	Li1−N1−Li2	72.33(12)
Li2−N1	1.9580(16),	Li2−N1−Li3	89.4(2)
Li3−N1	2.0733(16),	N1−Li3−N1′	179.2(3)
Li1−C12′	2.243(4)	N1−Li2−N1″	177.5(3)
Li1−C12″	2.248(4)	C11−Li3−C12	37.36(7)
Li2−C11	2.4305(19)	Li1′−C12-Li1″	73.27(14)
Li2−C12	2.423(3)	Li1′−C12-Li2	108.50(16)
Li3−C11	2.235(2)	Li1′−C12-Li3	67.36(11)
Li3−C12	2.234(2)	Li1−N1−C11	143.81(15)
Li1−Li2	2.449(4)	Li2−N1−C11	90.49(11)
Li1−Li3	2.483(4)	Li3−N1−C11	76.99(11)
Li1−Li1″	2.6794(45)		
Li2−Li3	2.8363(47)		
Si1−N1	1.7027(17)		
Si1−N2	1.7122(18)		
Si1−N3	1.7814(17)		
Si1−N4	1.7213(19)		
Compound **3b**			
Li1−N1	2.001(7)	Li1−N1−Li2	76.3(3)
Li2−N1	2.010(7)	Li1−C2−Li1′	69.67(24)
Li1−C2	2.184(7)	Li1−C2−Li2′	78.0(3)
Li1−C2′	2.297(7)	C1−N1−Li1	87.45(25)
Li2−C2′	2.202(7)	C1−N1−Li2	123.8(27)
Li1−C1	2.398(7)	N1−Li1−Li2′	121.88(31)
Li1−O5	1.923(7)	N1−Li1−O5	126.5(4)
Li2−O6	1.950(7)	N1−Li2−O6	133.9(4)
Li1−Li2	2.478(9)	C2−Li1−O5	127.9(3)
Li1−Li1′	2.5611(87)		
Li1−Li2′	2.7601(89		
Si1−N1	1.669(3)		
Si1−N2	1.723(3)		
Si1−N3	1.725(3)		
Si1−N4	1.761(3)		

The X-ray structure of compound **3a** confirms the presence of two lithium atoms versus one $[N(C_6H_4)\{Si(NMe_2)_3\}]^{2-}$ dianion. The lithium atoms replace one hydrogen atom at nitrogen and one at the ortho position of the phenyl ring so that lithium nitrogen, as well as lithium carbon, bonds can be found in the structure. Four of those units form a tetramer consisting of an octanuclear core of eight lithium atoms (Figure 2). An Oak Ridge Thermal-Ellipsoid Plot (ORTEP)

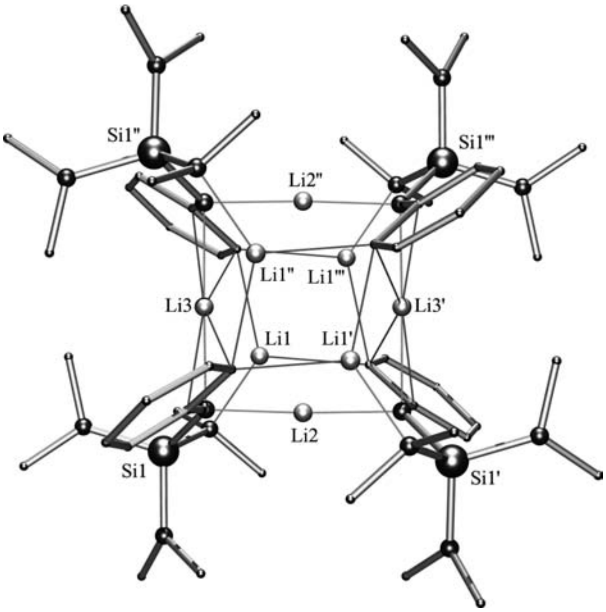


Figure 2. Molecular structure of tetrameric $[Li_2N(C_6H_4)\{Si(NMe_2)_3\}]_4$ (**3a**). The H atoms are omitted for clarity reasons. Symmetry transformations used to generate equivalent atoms: ′ (1 − *x*, 1 − *y*, *z*), ″ (*y*, *x*, 1 − *z*); ‴ (1 − *y*, 1 − *x*, 1 − *z*).

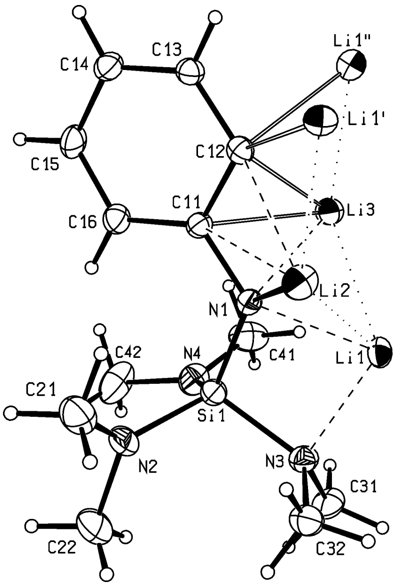


Figure 3. ORTEP plot with the numbering scheme of the asymmetric unit in $[Li_2N(C_6H_4)\{Si(NMe_2)_3\}]_4$ (**3a**) with two equivalent atoms of Li1 added to show all close contacts to lithium atoms. Li1 is at a general position, and Li2 and Li3 are located at 2-fold rotational axes. Symmetry transformations used to generate symmetry-equivalent atoms of Li1: ′ (1 − *x*, 1 − *y*, *z*); ″ (*y*, *x*, 1 − *z*).

plot of one of the ligands showing all close contacts of lithium atoms is shown in Figure 3. The lithium atom Li1 is situated in the plane which is formed by the phenyl ring, N1, Si1, and N3, and it is coordinated in a bidentate fashion by N1 and N3 (Li1−N1 2.180(4) Å and Li1−N3 2.135(4) Å). The lithium atoms Li2 and Li3 are found above and below this ligand plane with relatively short contacts to N1 (Li2−N1 1.9580(16) Å and L3−N1 2.0733(16) Å). Interestingly, Li3 is symmetrically in close contact to two carbon atoms of the phenyl ring (Li3−C12 2.234(2) Å and Li3−C11 2.235(1) Å) leading to an olefinic η^2-type coordination toward the Li3 atom. Close contacts are also found between C12 and Li1′ and Li1″ (C12−Li1′ 2.243(4) Å and C12−Li1″ 2.248(4) Å) which leads to three close and one slightly longer Li−C contacts for the deprotonated carbon atom C12 (see Figure 3).

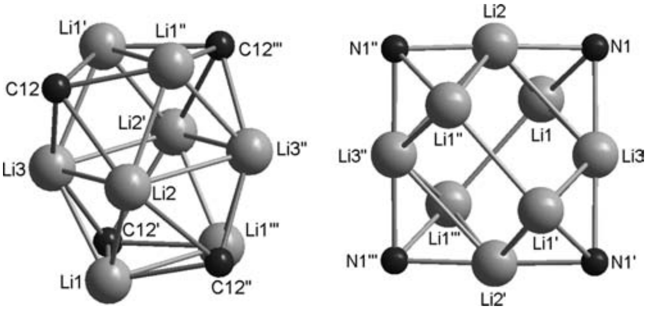


Figure 4. Left: central octanuclear Li_8C_4 core in **3a**. Right: view of the Li_8N_4 core in **3a** showing the Li_4N_4 square.

The eight lithium atoms form a polyhedron in which two trigonal prisms share one square face and are twisted by 90°. Such a polyhedron is known in mathematics as the Johnson solid J26 or by the name Gyrobifastidium. Lithium−lithium contacts range between 2.449(4) and 2.483(4) Å. The four ortho-C atoms of the phenyl groups are located above the square faces of the Li_8 polyhedron with the mentioned short Li−C bond lengths. The central Li_8C_4 core in shown in Figure 4. Furthermore, the four N1 atoms and two lithium atoms (Li2 and Li3) form an almost perfect square with linear N−Li−N bonds (N1−Li2−N1 177.5(3)° and N1−Li3−N1 179.2(3)°) and orthogonal Li−N−Li bonds (89.4(4)°, Figure 4).

The structural situation found in **3a** is unprecedented in organolithium chemistry. In general, organolithium compounds consisting of eight lithium atoms are extremely rare. To the best of our knowledge only two other organolithium compounds exhibiting eight lithium atoms were reported, but both form completely different polyhedrons.[35,36] Equally rare in any octanuclear lithium compound is the polyhedron found in **3a**. Only two other structures with this topology have been published, none of them contain lithium carbon bonds.[29,37] Both, the structure of $[Si(NLiCH_3)_2(N(CH_3)_2)]_4$[29] and that of $[Li_2(THF)_{0.5}\{(C_R,C_R/C_S,C_S)\text{-}2\text{-}P(2,4,6\text{-}i\mathrm{Pr}_3C_6H_2)\text{-}1\text{-}O\text{-}cyclo\text{-}C_6H_{10}\}]_4$[37] consist of a similar octanuclear core of the type Li_8N_8 and $Li_8O_4P_4$, respectively. Furthermore, a literature search for compounds containing eight-membered Li_4N_4 squares with linear N−Li−N bonds as found in **3a** gave only a very limited amount of hits[38−40] demonstrating the unusual structural situation in **3a**.

The X-ray diffraction analysis of suitable crystals of compound **3b** also confirms the presence of two lithium

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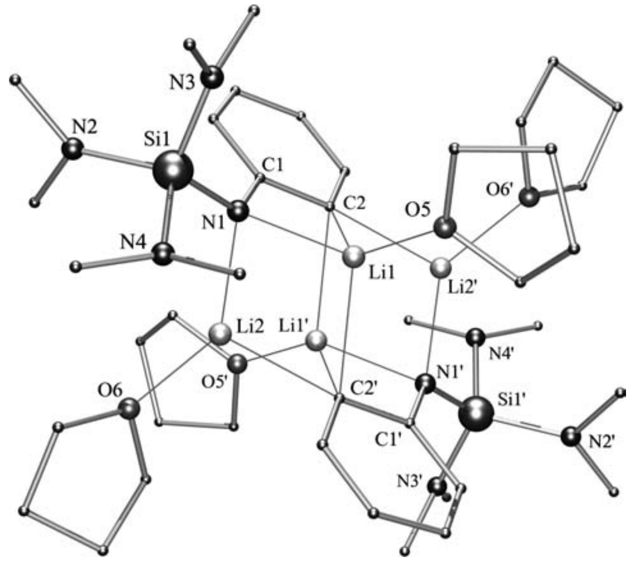

Figure 5. Molecular structure of dimeric $[Li_2(THF)_2\{N[Si(NMe_2)_3(C_6H_4)]\}]_2$ (**3b**). The H atoms are omitted for clarity reasons. Symmetry transformation used to generate equivalent atoms: ′ (1 − *x*, 1 − *y*, 1 − *z*).

atoms versus one $[N(C_6H_4)\{Si(NMe_2)_3\}]^{2-}$ dianion; however, in contrast to **3a** two additional THF molecules are coordinated to each lithium atom with similar distances (Li1−O5 1.92(4) Å, Li2−O6 1.95(1) Å). Here, only two of those units aggregate to a dimer in which the four lithium atoms form a parallelogram. The molecule is lying around a center of symmetry, so that the four lithium atoms are coplanar. A view of the dimeric molecule is shown in Figure 5. The Li−Li distances within the four-membered ring are 2.4778(84) and 2.7601(89) Å. The two nitrogen and four lithium atoms form a six membered ring in chair conformation (Figure 5). This topology is rare as only three such structures were deposited in the Cambridge Crystallographic Data Centre (CCDC), and these represent unusual dilithiated carbon dianions.[41−43]

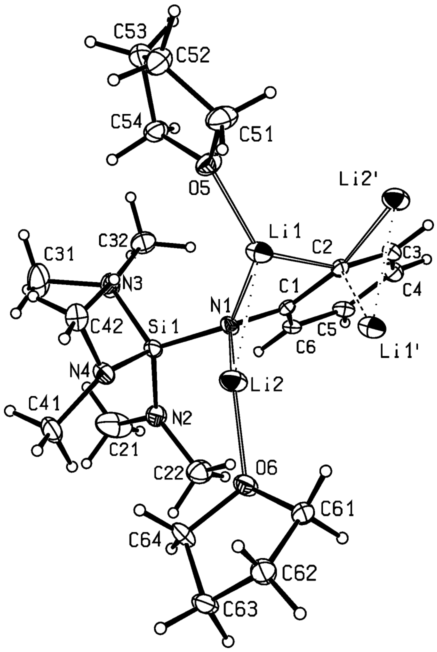

Figure 6. ORTEP plot with the numbering scheme of one of the two ligands in $[Li_2(THF)_2N(C_6H_4)\{Si(NMe_2)_3\}]_2$ (**3b**) showing all close contacts to the four lithium atoms.

An ORTEP plot of one of the ligands showing all close contacts of the four Li atoms is shown in Figure 6. In contrast to **3a**, no olefinic η^2-interaction of a lithium atom is found in the structure. Thus, in **3b** the distance to C1 (C1−Li1 2.398(7) Å) is distinctly larger than that to C2 (C2−Li1 2.184(7) Å). Similar to **3a**, the deprotonated carbon atom (C2) in **3b** is involved in close contacts to three lithium atoms (C2−Li1 2.184(7) Å, C2−Li1′ 2.297(7) Å and C2−Li2′ 2.202(7)), which is slightly shorter than reported distances.[41−43] The bonding of one carbon atom to a triangular face of three lithium atoms is interesting as this is also found in the tetrahedral structure of methyl lithium reported earlier by Weiss and Lucken[44] and by Hope and Power.[45] The coordination of the THF molecules to the Li atoms lead to slightly longer Li−N1 bond lengths in **3b** in comparison to **3a** (Li−N1 2.001(7) Å in **3b** vs 1.9580(16) Å in **3a**) and to shorter SiN1 bond lengths (Si−N1 1.669(3) Å in **3b** vs. 1.7027(17) Å in **3a**).

Conclusion

This article reports an easy access to a molecular precursor for the potential use in silicon nitride materials syntheses. Thus, tris(dimethylamino)anilinosilane can be prepared in high yield. Its bulkiness is evident by the fact that lithiation even with the highly efficient reagent *n*-butyl lithium requires refluxing conditions leading to the expected lithium anilide **2**. Furthermore, we could demonstrate that the stoichiometry must be strictly kept. The addition of more than 1 equiv of *n*-butyl lithium leads to the dilithiated species **3a** or **3b** depending on the solvent. The observed dilithiations represent C−H bond activations in the ortho position of the aniline phenyl groups forming the lithium carbon bonds. This type of reactivity could explain the, in some cases, found undesirable carbon contaminations in the final materials. From a structural point of view, **3a** and **3b** are very interesting. Both exhibit rare topologies, and that of **3a** is unprecedented in organolithium chemistry.

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