A Monolithiated and Its Related 1,3-Dilithiated Benzylsilane: Syntheses and Crystal Structures

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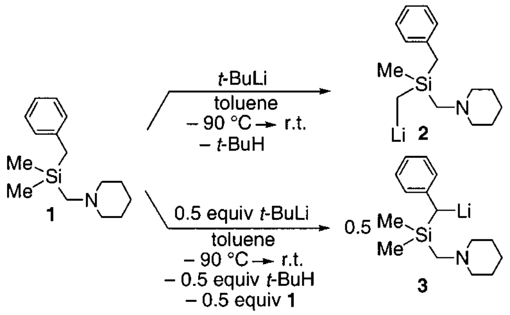
*Summary: The monolithiated (aminomethyl)benzylsilane $Me_2Si[CHLi(C_6H_5)](CH_2NC_5H_{10})$ (**3**) and the corresponding 1,3-dilithiated compound $Me_2Si[CHLi(o\text{-}C_6H_4Li)](CH_2NC_5H_{10})$ (**4**) ($CH_2NC_5H_{10}$ = piperidinomethyl), metalated at the benzyl position and at the ortho position of the phenyl ring, were obtained by successive deprotonation of $Me_2Si[CH_2(C_6H_5)](CH_2NC_5H_{10})$ (**1**). Monolithiated **3**, an internally coordinated cyclic tetramer, and 1,3-dilithiated **4**, an internally coordinated cyclic hexamer, were structurally characterized by single-crystal X-ray diffraction methods.*

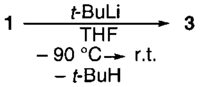
Introduction

Due to their difunctionality, 1,3-dilithiated alkyls are important synthetic building blocks, especially for the synthesis of cyclic systems.[1,2] To date, only a few compounds with a 1,3-dilithiated benzyl substituent, as in silane **4** (Scheme 3), are known.[3,4a,5,6] All of these dilithio compounds were synthesized in the presence of external donor molecules, such as TMEDA (tetramethylethylenediamine) or THF. Furthermore, in only two cases[3,4a] were both lithium atoms introduced by deprotonation. In the other cases, at least one of the two lithium atoms was introduced by halide−lithium exchange[6] or tin−lithium exchange.[5] For the most part, these 1,3-dilithiated species have been characterized indirectly by trapping reactions, while only one was investigated in the solid state by single-crystal X-ray diffraction: Bis[(*o*-lithiophenyl)lithiomethyl]methylphosphine was crystallized as a dimer in the presence of TMEDA by Müller and co-workers.[6] In contrast to this structure, molecular structures **3** and **4** do not contain any external donor molecules. On one hand, this allows a systematic comparison of the two structures, as we are interested in controlling reactivity, aggregation behavior, and the structure-determining principles of lithiated silanes by sidearm-donation of their own donor functions. On the other hand, 1,3-dilithiated alkyls are the object of theoretical studies,[2,4] which were mostly performed without external coordinating additives but nevertheless were compared with the known solid state structures.

Scheme 1



Scheme 2



Results and Discussion

When (aminomethyl)benzylsilane **1** was treated with 1 equiv of *tert*-butyllithium in *n*-pentane or toluene at −90 °C, surprisingly, one of the methyl groups was lithiated selectively (Scheme 1), yielding the benzyl(lithiomethyl)silane **2**, which forms a tetramer in the solid state.[7] Selective metalation of the benzyl position occurs only when the same reaction is carried out in a polar donor solvent, such as THF. But (lithiophenylmethyl)silane **3** is formed as THF adduct (Scheme 2), which precludes further deprotonation and crystallization in the absence of THF. Therefore, we carried out the synthesis of **3** in toluene at −90 °C, but using only 0.5 equiv of *tert*-butyllithium (Scheme 1). The starting silane very likely coordinates to *tert*-butyllithium through its nitrogen donor site, which directs the deprotonation to the benzyl position. However, compound **3** does not

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(7) Synthesis of tetra[benzyl(lithiomethyl)methyl(piperidinomethyl)silane] (**2**): In a Schlenk flask, a solution of 550 mg (2.22 mmol) of **1** in toluene (4 mL) was cooled to −90 °C and 1.31 mL of *t*-BuLi (in *n*-pentane, $c = 1.7\ \text{mol}\cdot\text{L}^{-1}$) (2.22 mmol) was added. After warming to room temperature, the solvent was removed in vacuo, and the residual yellow oil was dissolved in a mixture of toluene and *n*-pentane. After 3 days at −30 °C, colorless crystals of **2** were isolated, washed with *n*-pentane, and dried in vacuo.

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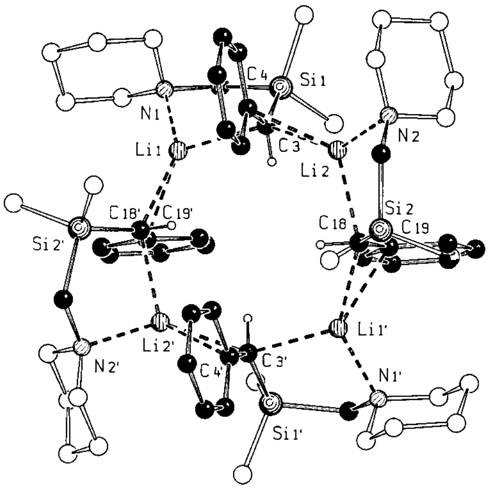
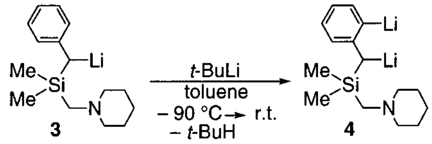


Figure 1. Molecular structure and numbering scheme of tetrameric molecule **3** in the crystal (Schakal plot).[16] Selected bond distances (Å) and angles (deg): Si(1)−C(1) = 1.859(3), Si(1)−C(2) = 1.874(3), Si(1)−C(3) = 1.821(3), Si(1)−C(10) = 1.907(3), Si(2)−C(16) = 1.879(3), Si(2)−C(17) = 1.868(3), Si(2)−C(18) = 1.824(3), Si(2)−C(25) = 1.911(3), C(3)−C(4) = 1.453(4), C(4)−C(5) = 1.427(4), C(5)−C(6) = 1.381(4), C(6)−C(7) = 1.379(5), C(7)−C(8) = 1.385(4), C(8)−C(9) = 1.376(4), C(9)−C(4) = 1.410(4), C(18)−C(19) = 1.444(4), C(19)−C(20) = 1.427(4), C(20)−C(21) = 1.376(4), C(21)−C(22) = 1.374(4), C(22)−C(23) = 1.386(4), C(23)−C(24) = 1.380(4), C(24)−C(19) = 1.416(4), C(3)−Li(1) = 2.352(5), C(3)−Li(2) = 2.273(5), C(18)′−Li(1) = 2.236(5), C(18)−Li(2) = 2.345(5), C(4)−Li(2) = 2.416(5), C(19)−Li(1)′ = 2.415(5), N(1)−Li(1) = N(2)−Li(2) = 2.064(5), C(18)′−Li(1)−C(3) = 121.3(2), C(3)−Li(2)−C(18) = 121.7(2), Li(1)−C(3)−Li(2) = 143.9(2), Li(1)−C(18)′−Li(2)′ = 143.1(2), Si(2)−C(18)−C(19)−C(20) = 2.3(4), Si(1)−C(3)−C(4)−C(5) = 1.3(4), Si(1)−C(3)−C(4)−C(9) = 2.1(2).

Scheme 3



form an adduct with **1**. Instead it crystallizes as an internally coordinated tetramer (Figure 1). Thus, unreacted **1** is recovered.[8] After recovery of unconverted **1**, (lithiophenylmethyl)silane **3** could be further deprotonated at the *ortho* position of the phenyl substituent in toluene at −90 °C using *tert*-butyllithium. The 1,3-dilithiated title compound **4** was formed selectively (Scheme 3). In the solid state, **4** forms an internally coordinated hexamer (Figure 2).[9]

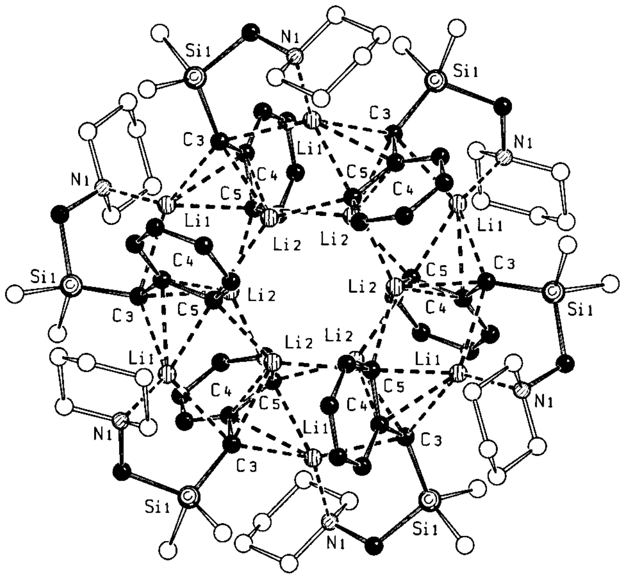


Figure 2. Molecular structure and numbering scheme of hexameric molecule **4** (molecule A) in the crystal (Schakal plot).[16] Selected bond distances (Å) and angles (deg): Si(1)−C(1) = 1.866(4), Si(1)−C(2) = 1.865(4), Si(1)−C(3) = 1.824(2), Si(1)−C(10) = 1.905(3), C(3)−C(4) = 1.450(3), C(4)−C(5) = 1.463(3), C(5)−C(6) = 1.405(3), C(6)−C(7) = 1.402(4), C(7)−C(8) = 1.384(4), C(8)−C(9) = 1.364(4), C(9)−C(4) = 1.426(3), C(3)−Li(1) = 2.495(5), C(3)−Li(2) = 2.376(4), C(4)−Li(2) = 2.499(4), C(5)−Li(2) = 2.253(5), C(3)−Li(1)′ = 2.472(5), C(4)−Li(1)′ = 2.381(5), C(5)−Li(1)′ = 2.238(5), C(5)−Li(2)′ = 2.222(4), C(5)−Li(2)″ = 2.549(4), Li(1)−Li(2) = 2.700(6), N(1)−Li(1) = 2.087(5), C(3)−Li(1)−C(3)′ = 127.8(2), Li(1)−C(3)−Li(1)′ = 142.2(2), Si(1)−C(3)−C(4)−C(5) = 11.0(2), Si(1)−C(3)−C(4)−C(9) = 11.0(3).

Monolithiated compound **3** crystallized from toluene.[10,11] In the asymmetric unit are found two crystallographically independent silane molecules, building up the cyclic tetramer **3** with C_2- and pseudo-S_4 symmetry. Each lithium center participates in the formation of four contacts (Figure 1): Li(1) intramolecularly to N(1) and C(3) and intermolecularly to C(18)′ and C(19)′; Li(2) intramolecularly to N(2) and C(18) and intermolecularly to C(3) and C(4). With the exception of C(4) and C(19)′, which merely complete the coordination spheres of the lithium centers, this results in the formation of a central eight-membered ring of alternating lithium and carbon centers with characteristic distances and angles (see Figure 1, caption). As a result of the stabilizing effect of the silicon centers, the bonds between the metalated carbon center and the α-silicon centers are shortened (compared to standard literature values[12]): C(3)−Si(1) = 1.821(3) and C(18)−Si(2) = 1.824(3) Å. The C−C bond

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(8) Synthesis of tetra[(lithiophenylmethyl)dimethyl(piperidinomethyl)silane] (**3**): In a Schlenk flask, a solution of 550 mg (2.22 mmol) of **1** in toluene (4 mL) was cooled to −90 °C and 654 *μ*L of *t*-BuLi (in *n*-pentane, $c = 1.7$ mol·L^{-1}) (1.11 mmol) was added. After warming and 5 days at room temperature, colorless crystals of **3** were isolated, washed with *n*-pentane, and dried in vacuo. Unreacted **1** was recovered by concentration of the washing solution.

(9) Synthesis of hexa{[(*o*-lithiophenyl)lithiomethyl]dimethyl(piperidinomethyl)silane} (**4**): In a Schlenk flask, a solution of **3** in toluene (3 mL) was cooled to −90 °C and 654 *μ*L of *t*-BuLi (in *n*-pentane, $c = 1.7$ mol·L^{-1}) (1.11 mmol) was added. After warming and 2 days at room temperature, the solution had turned darker and orange-colored needles of **4** were isolated.

(10) Crystallographic data for **3** (colorless crystals from toluene, 0.30 × 0.30 × 0.20 mm^3): $C_{60}H_{96}Li_4N_4Si_4$, $M = 1013.53$ g·mol^{-1}, orthorhombic, space group *Pnna* (no. 52), $a = 16.429(8)$ Å, $b = 19.319(4)$ Å, $c = 19.972(5)$ Å, $U = 6339.0(36)$ Å^3, $Z = 4$, $D_c = 1.062$ Mg/m^3, type of radiation Mo Kα, $\lambda = 0.71073$ Å, $\mu = 0.131$ mm^{-1}. Measurements: Stoe IPDS diffractometer, $T = 173$ K. The structure was solved using direct and Fourier methods; 47 950 reflections measured with θ in the range 2.61−25°, 5579 unique reflections; 3479 with $I > 2\sigma(I)$; refinement by full-matrix least-squares methods (based on F_o^2, SHELXL-93); anisotropic thermal parameters for all non-H atoms in the final cycles; the H atoms were refined on a riding model in their ideal geometric positions, except H(3) and H(18), which were refined isotropically; $R = 0.0601$ $[I > 2\sigma(I)]$, $wR(F_o^2) = 0.1549$ (all data). SHELXS-86 and SHELXL-93 computer programs were used.

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of the benzyl substituent is influenced by the metalation of C(3) [and C(18)] as well. While the single bond to the *ipso* carbon center is shortened, the aromatic C−C bonds between the *ipso* and *ortho* carbon centers are elongated (compared to standard literature values[12]). Two comparable crystal structures of a benzylsodium compound and a mixed benzylsodium−lithium compound with the motif of an eight-membered ring of alternating metal and carbon atoms have been reported, both containing externally coordinating TMEDA molecules: $(NaCH_2C_6H_5\cdot TMEDA)_4$ by Schleyer and co-workers[13] and $[Li_{1.67}Na_{2.33}(CH_2C_6H_5)_4\cdot 4TMEDA]$ by Mulvey and co-workers.[14]

The lithiated benzylic carbon center is almost planar. This is expressed by two least-squares planes. The first plane that includes C(3), C(4), Si(1), and H(3) shows an rms deviation of only 0.002 Å. The largest deviation from the plane is 0.003(8) Å for C(3). The second plane that includes C(18), C(19), Si(2), and H(18) shows an rms deviation of 0.007 Å. The largest deviation from this plane is 0.013(8) Å for C(18). This is underlined by the average Si−C−C−C torsion angles around the C(3)−C(4) and C(18)−C(19) bonds, which are 1.8(4)° and 2.3(4)°, respectively.

Dilithiated compound **4** crystallized from toluene.[15,11] Two crystallographically independent silane molecules were detected in the asymmetric unit, each building up one cyclic hexamer of **4** (due to the similarity of the structural parameters, only the molecular structure of molecule A in the crystal is shown and discussed). Deriving the molecular structure of hexameric **4** from that of tetrameric **3**, the hydrogen atoms in *ortho* positions, which are pointing into the center of the ring, are replaced by lithium atoms. These *ortho* lithium centers formally create a six-membered lithium ring in dilithiated hexameric **4**. Just as in monolithiated tetrameric **3**, the metalated benzylic carbon centers are part of a larger "concentric" carbon−lithium ring that is 12-membered in **4**. Two C−Li distances of C(3)−Li(1) = 2.495(5) and C(3)′−Li(1) = 2.472(5) Å can be found in this ring. As can be seen in the detailed drawing (Figure 3), each silane unit is in contact with five lithium centers, although only Li(1) and Li(2) must be formally associated with the particular silane unit shown. The fragment Li(1)−C(3)−Li(1)′ is part of the 12-membered ring [while the centers Li(2), Li(2)′, and Li(2)″ belong to the central six-membered ring]. The benzylic carbon center C(3) has three, the *ipso* carbon center C(4) two, and the *ortho* carbon center C(5) four lithium contacts. The structural result is an η^3-coordination situation, in which Li(1)′ and Li(2) are bridging the C(3)−C(4)−C(5) unit from both sides of the plane, and an η^1-coordination of Li(2)′ and Li(2)″ by C(5).

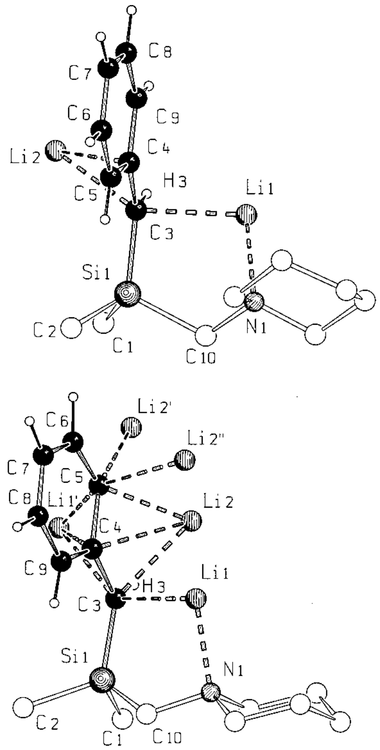

Figure 3. Detailed drawings of particular silane units of **3** and **4** in the crystal (Schakal plots),[16] both having lithium contacts to further silane units in both the tetramer and hexamer.

Comparing the hexamer with the tetramer, the distance Li(1)−C(3) = 2.495(5) Å between the benzylic carbon center and the intramolecularly coordinated lithium center is 0.22 Å longer in the hexamer, while the distance N(1)−Li(1) = 2.087(5) Å remains almost identical. The η^3-bridging *ortho* lithium center Li(2) forms three lithium carbon contacts: C(3)−Li(2) = 2.376(4), C(4)−Li(2) = 2.499(4), and C(5)−Li(2) = 2.253(5) Å. The distance Si(1)−C(3) = 1.824(2) Å is identical to that in tetrameric **3**.

The benzylic carbon center C(3) is less planarized than that in the monolithiated tetramer, deviating by 0.082(8) Å from a least-squares plane including C(3), C(4), Si(1), and H(3) with an rms deviation of 0.048 Å. This is underlined by the average Si−C−C−C torsion angle around the C(3)−C(4) bond of 11.0(4)°. Furthermore, the lengths of three aromatic C−C bonds differ from those in tetrameric **3**. Due to the metalation of C(5), the distances C(4)−C(5), C(5)−C(6), and C(6)−C(7) are slightly longer in dilithiated hexameric **4**.

It is of great interest now to investigate if the sidearm donation of other (aminomethyl)silanes allows dilithiation by deprotonation in nonpolar solvents. The synthetic potential of the difunctional title compound **4** with an easily removable activating silyl group is being examined.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Crystallographic data for **4** (orange crystals from toluene, 0.60 × 0.20 × 0.20 mm^3): $C_{90}H_{138}Li_{12}N_6Si_6$, $M = 1555.88$ g·mol^{-1}, trigonal, space group $R\bar{3}$ (no. 148), $a = 26.801(3)$ Å, $c = 22.361(2)$ Å, $U = 13910.0(28)$ Å^3, $Z = 6$, $D_c = 1.114$ Mg/m^3, type of radiation: Mo Kα, $\lambda = 0.71073$ Å, $\mu = 0.135$ mm^{-1}. Measurements: Stoe IPDS diffractometer, $T = 173$ K. The structure was solved using direct and Fourier methods; 33 756 reflections measured with θ in the range 2.49−25°, 5428 unique reflections; 3641 with $I > 2\sigma(I)$; refinement by full-matrix least-squares methods (based on F_o^2, SHELXL-93); anisotropic thermal parameters for all non-H atoms in the final cycles; the H atoms were refined on a riding model in their ideal geometric positions, except H(3), H(6), H(7), H(8), H(9), H(18), H(21), H(22), H(23), and H(24), which were refined isotropically; $R = 0.0609$ $[I > 2\sigma(I)]$, $wR(F_o^2) = 0.1696$ (all data). SHELXS-86 and SHELXL-93 computer programs were used.

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